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DERWISH (G. A. W.)

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1959.
INVESTIGATIONS OF SOME PHYSICAL PROPERTIES OF
ORGANOTIN COMPOUNDS

A Thesis Submitted to the University of London for the Degree of
Doctor of Philosophy

By
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March 1959
The absorption spectra of ten organotin compounds were measured in the infrared region 2.5-15.3 μ(4000-650 cm⁻¹) and in the ultraviolet region 200-400 μ. The compounds used were: the homologous series PhₙSnCl₄-n (n=1,2,3, and 4), tetrabenzyltin, tribenzyltin chloride, tetra-µ-tolyltin, tetrakis-2-chlorophenyltin, triethyltin phenoxide and N:triethyltin phthalimide. The results have been analysed and discussed in detail and a tentative assignment of many of the normal vibrational frequencies carried out. Some of the vibrational fine structures of the electronic absorption bands has been tentatively assigned. The spectral measurements were carried out on samples in the liquid or the solid state and in solutions.

The effect of the tin atom on the normal vibrational frequencies of the phenyl, benzyl and ethyl groups seems to be negligible and most of the normal frequencies fall within the range expected for hydrocarbons. Certain variations in some of the normal frequencies of the homologous series PhₙSnCl₄-n are correlated to the number of chlorine atoms attached to tin. No interaction between phenyl, benzyl or ethyl groups attached to the same tin atom was observed. Evidence from both vibrational and electronic absorption spectra of the phenylin compounds confirms the formation of d-p bond between the -electronic cloud of the benzene nucleus and the empty outermost d-orbital of tin; and that the electronegativity of tin increases in the phenyl compounds in the following order:

\[
\text{Ph}_4\text{Sn} < \text{Ph}_2\text{SnCl} < \text{Ph}_2\text{SnCl}_2 < \text{PhSnCl}_3
\]

The following electronic configuration may participate appreciably in determining the electronic structure of the phenylin compounds:

\[
\begin{align*}
\text{Sn} = & \begin{array}{c}
\text{Cl}^- \\
\end{array} \\
\end{align*}
\]

An equation derived from the electrostatic theory for the effect of the interaction between the substituent and the ortho-hydrogens of nonosubstituted benzenes on the \( \delta \cdot \cdot \cdot \cdot \) vibrations was developed which leads to the calculation of group dipole moments which are in good agreement with the accepted values from other methods.

Tetraphenylin and tetrabenzyltin were prepared by an improved method and a new method for the preparation of tetra-µ-tolyltin is described.
PREFACE

The work described in this Thesis was carried out in the laboratories of the Chemistry Department of Battersea College of Technology under the supervision of the late Dr. F.R. Goss and Dr. J.E. Salmon and the direction of Dr. V.S. Griffiths.

The writer wishes to express his most sincere appreciation and thanks for the constant help and encouragement received from Dr. V.S. Griffiths during the course of this work. Sincere thanks are due to Dr. Joan A. Reid for her kind help and advice especially on the preparation of organotin compounds. Grateful thanks are also due to the staff of the Chemistry Department for their most valuable help and advice.
Abstract
Preface
Contents

General Introduction

Part One: A Review of the Physical Chemistry of Organotin Compounds

I.1. Introduction
I.2. The Atomic Properties of the Elements of Group IVB
I.3. Physical Properties of Organotin Compounds
I.4. Organotin Compounds of Quadrivalent tin
I.5. Organotin Compounds of Bivalent tin

Part Two:

II.1. Preparations of Organotin Compounds
II.2. Absorption Spectroscopic Measurements

Part Three: The Infrared Absorption Spectra of Organotin Compounds

III.1. Theoretical Introduction
III.2. The Infrared Absorption Spectra of Phenyltin Compounds
III.3. The Infrared Absorption Spectra of Benzyltin Compounds
III.4. The Infrared Absorption Spectra of Tetra-p-tolyltin and Tetrakis-p-chlorophenyltin
III.5. The Infrared Absorption Spectra of Triethyltin Phenoxide and N-Triethyltin Phthalimide


Part Four: The Ultraviolet Absorption Spectra of Organotin Compounds

IV.1. General Introduction

IV.2. The Ultraviolet Absorption Spectra of Phenyltin Compounds

IV.3. The Ultraviolet Absorption Spectra of Benzyltin Compounds

IV.4. The Ultraviolet Absorption Spectra of Tetra-\(p\)-tolyltin and Tetrakis-\(p\)-chlorophenyltin

IV.5. The Ultraviolet Absorption Spectra of Triethyltin Phenoxide and N-Triethyltin Phthalimide

IV.6. General Discussion on the Ultraviolet Absorption Spectra of Organotin Compounds
The chemistry of the carbon-metal bond conveniently involves the
three main branches of chemistry. The study of organometallic compounds
provides a wide field for the investigation of the nature of the chemical
linkage, especially the transition from the ionic bond to the covalent
bond. The transition from the metallic to the non-metallic properties of
the elements is reflected, in most cases, in their organic derivatives.
Tin exists in two allotropic modifications, a non-metallic form, grey tin,
stable at ordinary temperature and a metallic form, white tin, stable at
elevated temperatures. The former has the diamond structure while the
latter possesses a more close-packed metallic structure. This fact is
reflected in the chemistry of the tin compounds, for example, tin is
capable of forming both salt-like (inorganic) compounds and covalent
(organic) compounds of remarkable stability. This applies not only to
quadrivalent tin but also, to a lesser extent, to bivalent tin.

The most powerful tools, so far developed, for the study of the nature
of chemical linkages are the physical methods and in particular those
methods which are capable of picturing the molecule as a whole (e.g.
X-ray crystallography, electron diffraction etc.) and those which picture
the nuclear and electronic notions of the molecule (e.g. absorption
spectroscopy etc.). It was therefore planned to use absorption spectroscopy
in the study of the carbon-tin bonds and the halogen-tin bonds in
organotin compounds containing both linkages. The following compounds
were chosen for that purpose: the homologous series Ph₄SnCl₄-n (where
n = 1, 2, 3, and 4), tetrabenzyltin, tribenzyltin chloride, tetra-p-tolyltin,
tetraakis-p-chlorophenyltin, triethyltin phenoxide and N-triethyltin
phthalide.

The work to be described in this thesis falls into four parts, each
part being complete within itself. For the proper understanding of the
problems of organotin compounds and for the logical presentation of the
results of the present work an introductory survey of the physical chemistry
of organotin compounds is given in Part One, covering the developments in
the field for the last three decades or so.

Part Two gives an outline of the preparations of organotin compounds and techniques and instruments for the spectral measurements. An improved method for the preparation of tetraphenylytin and tetrabenzyltin are described, together with a new method for the preparation of tetm-p-tolyltin.

Part Three and Part Four of the thesis present the results of the infrared and ultraviolet absorption spectroscopic measurements together with detailed analysis of the spectra and discussion of the results.
PART ONE

A REVIEW OF THE PHYSICAL CHEMISTRY

OF ORGANOTIN COMPOUNDS
I.1. INTRODUCTION

IN view of the absence of any treatise on the physical chemistry of the carbon-metal bond as exemplified in the wide field of organometallic compounds, it was necessary for the proper understanding of the problem in hand to review the existing literature on the physico-chemical properties of organotin compounds and their place among the analogous compounds of the elements of Group IVB of the Periodic Table. In this respect the recent reviews (71,98,125) on the organometallic compounds of silicon, germanium, and lead have proved of great value.

Although a comprehensive survey of the literature for the period 1930-1957 was carried out, references to earlier work have only been included when they proved relevant to the discussion. The more recent publications have been included whenever possible. Krause and von Grosse in their book (122) on the organometallic compounds have adequately covered the field of organotin compounds up to 1935. More recent reviews (35, 111, 144, 145) on the subject have concentrated upon the preparative aspects and upon the tabulation of melting and boiling points. Consequently in this review no effort will be made to give a comprehensive list of these properties.
I.2. THE ATOMIC PROPERTIES OF THE ELEMENTS OF GROUP IVB

The physical constants of the elements C, Si, Ge, Sn, and Pb are given in Table 1.

To interpret the variations in the physical and chemical properties of the elements of Group IV, the electronic configuration of the atoms have to be examined. From Table 2 the following points arise:

1. The outer electronic configuration in all the atoms of Group IVB elements is $\text{ns}^2 \text{np}^2$ which indicates that the expected valency state will be the normal valency of carbon i.e. 4; but in all the atoms of the B Sub-Group including silicon, there are empty d-orbitals which are within the outermost orbits. Therefore, while carbon is unable to expand its covalency beyond four, the other elements of the Group can easily expand their covalency by making use of the empty d-orbitals.

It is of interest to note that the atoms of the elements of the A Sub-Group can actually use their d-orbital electrons for bond formation and thus acquire their transitional properties.

2. The increase in the nuclear charge in descending the Group far exceeds the increase in the size of the atom as indicated by comparing covalent radii differences with nuclear charges differences as set out in Table 3.

The relatively high nuclear charge, especially in lead, tends to deactivate the $\text{ns}^2$ electrons and produce what is generally known as the "inert pair effect". This effect, which is at its maximum in lead,
### Table 1

**Physical Constants of the Elements of Group IV**

<table>
<thead>
<tr>
<th>Property</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number (a)</td>
<td>6</td>
<td>14</td>
<td>32</td>
<td>50</td>
<td>82</td>
</tr>
<tr>
<td>Outer electron configuration (a)</td>
<td>2s 2p</td>
<td>3s 3p</td>
<td>4s 4p</td>
<td>5s 5p</td>
<td>6s 6p</td>
</tr>
<tr>
<td>Mass number of stable isotopes (a)</td>
<td>12, 13</td>
<td>28, 29, 30</td>
<td>70, 72, 73, 74, 76</td>
<td>112, 114, 115, 116, 117, 118, 119, 120, 122, 124</td>
<td>204, 206, 207, 208</td>
</tr>
<tr>
<td>Atomic weight (b)</td>
<td>12.01 165</td>
<td>28.0874</td>
<td>72.629</td>
<td>118.752</td>
<td>207.225</td>
</tr>
<tr>
<td>Density of solid at 20 °C, g/cm³ (a)</td>
<td>3.51 *</td>
<td>2.33 **</td>
<td>5.30 **</td>
<td>7.31 **</td>
<td>11.34 **</td>
</tr>
<tr>
<td>Atomic volume of solid, cm³ (a)</td>
<td>3.42</td>
<td>12.04</td>
<td>13.55</td>
<td>16.23</td>
<td>18.27</td>
</tr>
<tr>
<td>Melting point °C (a)</td>
<td>ca 3570</td>
<td>1414</td>
<td>958.5</td>
<td>231.8</td>
<td>327.5</td>
</tr>
<tr>
<td>Boiling point °C (a)</td>
<td>3470 subl</td>
<td>2355</td>
<td>2362</td>
<td>1755</td>
<td></td>
</tr>
</tbody>
</table>

(a) Taken from T. Moeller (161)  
(b) Taken from A. H. Wapstra (249)

* diamond,  † graphite,  ‡ diamond structure,  § metallic structure,  
# white tin (diamond structure),  ● gray tin (metallic structure)
### TABLE 2

**ELECTRONIC CONFIGURATION OF THE ELEMENTS OF GROUP IV**

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Zr</td>
<td>40</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Hf</td>
<td>72</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

(a) Taken from L. Pauling (174)

### TABLE 3

**ATOMIC RADII AND NUCLEAR CHARGES OF THE ELEMENTS OF GROUP IV**

<table>
<thead>
<tr>
<th>Element</th>
<th>Nuclear charge Z</th>
<th>ΔZ</th>
<th>Atomic radius x A</th>
<th>Δr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6</td>
<td>8</td>
<td>0.77</td>
<td>0.40</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>18</td>
<td>1.17</td>
<td>0.05</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>18</td>
<td>1.22</td>
<td>0.18</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>32</td>
<td>1.40</td>
<td>0.06</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td></td>
<td>1.46</td>
<td></td>
</tr>
</tbody>
</table>

(a) Taken from L. Pauling (174)
also operates, but to a lesser degree, in tin. The ground state of lead is, therefore, a $^3$P-state derived from the $s^2p^2$ configuration(125) which gives rise to the bivalency of lead and to its pronounced metallic character. In carbon the stable ground state is a $^5$S-state derived from the $sp^3$ configuration which gives rise to the stable quadrivalent carbon. While silicon and germanium resemble carbon, tin resembles lead, and it is with tin that a stable bivalent ion of Group IVB is obtained. However, it has been shown that bivalent silicon and germanium ions do exist, but these are strong reducing agents. Spectroscopic data(88) on the monohydrides of the Group show that there is a remarkable difference in the electronic configuration of lead compared with the rest of the Group. In covalent compounds, such as the tetraalkyls and aryls, the elements of the B Sub-Group are usually quadrivalent; but in addition there are a number of biocvalent tin and lead alkyls and aryls but they are very unstable and tend to polymerize (see later). The bivalency is therefore preferred in ionic compounds of lead and tin which might indicate that the inert pair effect is much more effective in the ion than in the corresponding neutral atom.

The quadrivalent state of the elements of Group IVB involves a tetrahedral $sp^3$ configuration(174). The tetrahedral arrangement has been supported by electron diffraction measurements(17-20,141) on the tetramethyls and tetrahalides of Si, Ge, Sn and Pb. Further support for this arrangement comes from the observation of optical activity in certain compounds of some of these elements in which the elements concerned is the centre of asymmetry(33,166,177-8,204)(see later).
The bivalent state of lead and tin involves p electrons and therefore a bond angle of less than 180° is expected. Lister and Sutton (142) from electron diffraction studies have found that the bond angle in stannous and plumbous halides is certainly less than 180° and probably 95° which indicates an angular structure.

The increase in the size of the atoms of the elements of Group IVB (as can be seen from comparison of their covalent radii given in Table 4) on descending the Group produces the following effects in the tin and lead organic compounds as compared with the rest of the Group:

1. Reduced steric hinderance permits the attachment of rather larger groups to the central atom and increases the ease of approach of attacking reagents.

2. There is an increased tendency to expand the covalency on descending the group. While carbon can not expand its covalency beyond four, silicon and germanium can form hexavalent compounds. Tin, e.g. in the oxalato complexes (9,189), and lead can expand their covalency up to eight and their coordination compounds are the most stable in the Group. For fuller discussion on the complex compounds of silicon, germanium, tin and lead see reference (212).

3. The reduced nuclear field at the outermost electronic orbit gives rise to a high polarizability which favours the formation of ions and of highly polar covalent bonds in which the tin, or lead, atom forms the positive end of the dipole.

4. The overlap of p-orbitals which is necessary for multiple bonds formation in the carbon family, is hindered by the increased size
### TABLE 4

**ATOM DIMENSIONS OF THE ELEMENTS OF GROUP IV**

<table>
<thead>
<tr>
<th>Dimension A</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metallic radii (a):</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v=4</td>
<td>0.771</td>
<td>1.173</td>
<td>1.223</td>
<td>1.399</td>
<td>-</td>
</tr>
<tr>
<td>v=2.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.412</td>
<td>1.538</td>
</tr>
<tr>
<td><strong>Covalent radii (b):</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>single bond</td>
<td>0.77</td>
<td>1.17</td>
<td>1.22</td>
<td>1.40</td>
<td>-</td>
</tr>
<tr>
<td>double bond</td>
<td>0.66</td>
<td>1.07</td>
<td>1.12</td>
<td>1.30</td>
<td>-</td>
</tr>
<tr>
<td>triple bond</td>
<td>0.60</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Tetrahedral covalent radii,sp³ (b):</strong></td>
<td>0.77</td>
<td>1.17</td>
<td>1.22</td>
<td>1.40</td>
<td>1.46</td>
</tr>
<tr>
<td><strong>Octahedral covalent radii,sp³d² (b):</strong></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.45</td>
<td>1.50</td>
</tr>
<tr>
<td><strong>Ionic radii (c):</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M^+$</td>
<td>0.15</td>
<td>0.41</td>
<td>0.53</td>
<td>0.71</td>
<td>0.84</td>
</tr>
<tr>
<td>$M^2$</td>
<td>-</td>
<td>-</td>
<td>0.93 (d)</td>
<td>1.17 (a)</td>
<td>1.32</td>
</tr>
<tr>
<td>$M^{-2}$</td>
<td>2.60</td>
<td>2.71</td>
<td>2.72</td>
<td>2.94</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) From L. Pauling (175)
(b) From L. Pauling (174)
(c) From T. Moeller (161)
(d) From K. B. Yatimirskii (260)
of the atom. But as mentioned earlier, the presence of empty d-orbitals enhances the formation of d-p-bonds \((40)\) with atoms or groups of high p-electron content.

Although there is no general agreement on the values of electronegativities especially for the elements of Group IV, estimates can be made of their relative electronegativities. The metallic properties of tin and lead can not be doubted and hence they should occupy a rather low position in the electronegativity scale of this Group, but the position of silicon and germanium must be considered uncertain in view of the disagreement of published data.

Table 5 gives values of electronegativities of the carbon family according to different workers, who differ not only in their approach to the subject but also in their treatment of the results. The values given in the Table are reduced to the Pauling scale of electronegativities.

The question of the electronegativities of silicon and germanium is obviously of interest if any real understanding of the trends of the chemical and physical properties of the Group is to be achieved.

Pritchard and Skinner (180) doubt the basic concept of Sanderson's electronegativity \((192-9)\), but they accept Gordy's values \((77)\) derived from electric potential at the covalent boundary, and, indeed, they recalculate his values using Slater's effective nuclear charge \((216)\). Examination of the latter shows that germanium is more electronegative than silicon. However, Gordy's third scale of electronegativity \((79, 185)\) which is based on the quadrupole coupling \((eQq)\) shows also that
germanium is more electronegative than silicon (201a, 211a). Allred and Rochow (1a, 1b) have calculated the electronegativities of the elements carbon, silicon, germanium, tin and lead from nuclear magnetic resonance, from nuclear quadrupole resonance, from thermochemical data, from electrostatic attraction and from work function data. Their values which are given in Table 5a indicate uniformly that germanium is more electronegative than silicon.

There is also a certain amount of chemical evidence, e.g. from hydrolysis and from reduction studies etc., in support of the rather high electronegativity of germanium compared with that of silicon (188, 194, 258).

This peculiarity of germanium leads to the situation where the electronegativity of tin and of lead will be comparable with that of silicon. However, the importance of electronegativities must not be overemphasized in considering trends of chemical behaviour in view of the many other complex factors, some of which has already been mentioned.

It is to be expected that the electronegativities of an atom will vary with the valency state, and, indeed, it has been shown that the bond dissociation energy in a compound decreases with increasing valency of the bonded atoms; as in the case of tin and lead (79a):  

<table>
<thead>
<tr>
<th></th>
<th>Sn(II)</th>
<th>Pb(II)</th>
<th>Sn(IV)</th>
<th>Pb(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.65</td>
<td>1.6</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>


### TABLE 5

**ELECTRONEGATIVITIES OF FEW ELEMENTS**

<table>
<thead>
<tr>
<th></th>
<th>Pauling's thermo-chemical values (a)</th>
<th>Gordy's force constant values (a)</th>
<th>Gordy's values derived from electric potential at covalent boundary (a)</th>
<th>Ditto recalculated with Slater effective nuclear charge (a)</th>
<th>Mullikan's values from electron affinity &amp; ionization potential (a)</th>
<th>Sanderson's values from stability constant (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.1</td>
<td>2.13</td>
<td>2.17</td>
<td>-</td>
<td>2.28</td>
<td>2.31</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
<td>2.55</td>
<td>2.52</td>
<td>2.51</td>
<td>2.63</td>
<td>2.47</td>
</tr>
<tr>
<td>Si</td>
<td>1.8</td>
<td>1.8</td>
<td>1.82</td>
<td>1.84</td>
<td>2.44</td>
<td>1.74</td>
</tr>
<tr>
<td>Ge</td>
<td>1.7</td>
<td>1.7</td>
<td>1.77</td>
<td>1.87</td>
<td>-</td>
<td>2.31</td>
</tr>
<tr>
<td>Sn IV</td>
<td>1.7</td>
<td>1.7</td>
<td>1.61</td>
<td>1.74</td>
<td>-</td>
<td>2.02</td>
</tr>
<tr>
<td>Pb IV</td>
<td>-</td>
<td>1.5</td>
<td>1.56</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N</td>
<td>3.0</td>
<td>3.0</td>
<td>3.01</td>
<td>3.02</td>
<td>2.33</td>
<td>2.93</td>
</tr>
<tr>
<td>O</td>
<td>3.5</td>
<td>3.45</td>
<td>3.47</td>
<td>3.48</td>
<td>3.17</td>
<td>3.46</td>
</tr>
<tr>
<td>F</td>
<td>4.0</td>
<td>3.95</td>
<td>3.94</td>
<td>4.00</td>
<td>3.91</td>
<td>3.92</td>
</tr>
<tr>
<td>Cl</td>
<td>3.0</td>
<td>2.97</td>
<td>3.00</td>
<td>2.98</td>
<td>3.00</td>
<td>3.28</td>
</tr>
<tr>
<td>Br</td>
<td>2.8</td>
<td>2.75</td>
<td>2.68</td>
<td>2.73</td>
<td>2.76</td>
<td>2.96</td>
</tr>
<tr>
<td>I</td>
<td>2.5</td>
<td>2.45</td>
<td>2.36</td>
<td>2.50</td>
<td>2.56</td>
<td>2.50</td>
</tr>
</tbody>
</table>

(a) From H.O. Pritchard and H.A. Skinner (180)

(b) From R.T. Sanderson (199)

See the above two references for details of the derivation of electronegativities.
# TABLE 5A

**ELECTRONEGATIVITIES OF THE ELEMENTS OF GROUP IV**

<table>
<thead>
<tr>
<th>Method</th>
<th>Electronegativity of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Nuclear magnetic resonance and</td>
<td>2.60</td>
</tr>
<tr>
<td>nuclear quadrupole resonance</td>
<td></td>
</tr>
<tr>
<td>Thermochemical:</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>2.60</td>
</tr>
<tr>
<td>(b)</td>
<td>2.65</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>2.50</td>
</tr>
<tr>
<td>Work function</td>
<td>-</td>
</tr>
</tbody>
</table>

*From A.L. Allred and E.G. Rochow (1b)*

Recalculation of Pauling's electronegativities using more accurate thermal data:

(a) recalculated from bond energy data

(b) recalculated from heats of formation data.
1.3. PHYSICAL PROPERTIES OF ORGANOTIN COMPOUNDS

A. BOILING POINTS, MELTING POINTS AND DENSITIES

English and Nicholls (56) have found that Egloff's empirical equation (54), relating the boiling point (T°K) of an aliphatic hydrocarbon to the number of central atoms (n), viz.

\[ T = a \ln(n+b) + k \] \[ (1) \]

where \( a \) and \( b \) are constants for all hydrocarbons except for those with widely differing structures, while \( k \) varied with structure (32,54), applies equally well to mono-\( n \)-alkyl silanes, poly-\( n \)-alkyl silanes, \( \alpha,\beta \)-disilyl alkanes, germanes and mono-\( n \)-alkyl germanes.

English (57) extended equation (1) to stannane and plumbane by extrapolating the empirical constants \( a \) and \( b \) with respect to the atomic weights. Further, since the above equation gives rather a high boiling point for the first member of the series, where \( n=1 \), English modified the equation to:

\[ T = a \ln(n+b) + k - 18/ n^\infty \] \[ (2) \]

which has the advantage of keeping \( k \) constant for all the members of the same series.

Table 6 gives the observed boiling points and those calculated from equations (1) and (2) for the compounds of the type \( MH_4 \) (where \( M = C, Si, Ge, Sn \) or \( Pb \)). Values of \( a \) and \( b \) for different series of compounds are given in Table 7.

English (57) found that for "normal" compounds e.g. dimethyl stannane,
### TABLE 6

**COMPARISON OF OBSERVED AND CALCULATED BOILING POINTS (°K.) FOR MH₄ COMPOUNDS**

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Boiling point calculated from equation (1)</th>
<th>Boiling point calculated from equation (2)</th>
<th>observed boiling point</th>
<th>Δ T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>129.6</td>
<td>111.6</td>
<td>111.6</td>
<td>0</td>
</tr>
<tr>
<td>SiH₄</td>
<td>176.0</td>
<td>161.6</td>
<td>161.6</td>
<td>+0.6</td>
</tr>
<tr>
<td>GeH₄</td>
<td>202.1</td>
<td>184.1</td>
<td>183.0</td>
<td>-1.1</td>
</tr>
<tr>
<td>SnH₄</td>
<td>240</td>
<td>222</td>
<td>221</td>
<td>-1</td>
</tr>
<tr>
<td>PbH₄</td>
<td>278</td>
<td>260</td>
<td>260</td>
<td>0</td>
</tr>
</tbody>
</table>

* Taken from W. D. English (57)
TABLE 7

CONSTANTS OF EQUATION (2) (a)

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-alkanes</td>
<td>323.7</td>
<td>4.4</td>
</tr>
<tr>
<td>silanes</td>
<td>395.8</td>
<td>3.5</td>
</tr>
<tr>
<td>germane</td>
<td>446.1</td>
<td>3.0</td>
</tr>
<tr>
<td>stannane</td>
<td>482.0</td>
<td>2.9</td>
</tr>
<tr>
<td>plumbane</td>
<td>520.6</td>
<td>2.8</td>
</tr>
<tr>
<td>monoalkyl silanes (terminal Si)</td>
<td>321.1</td>
<td>5.2</td>
</tr>
<tr>
<td>polyalkyl silanes (internal Si)</td>
<td>322.0</td>
<td>5.0</td>
</tr>
<tr>
<td>α,ω-disilyl alkanes (two terminal Si)</td>
<td>342.2</td>
<td>5.1</td>
</tr>
<tr>
<td>monoalkyl germanes (terminal Ge)</td>
<td>303.4</td>
<td>7.0</td>
</tr>
<tr>
<td>polyalkyl stannanes (internal Sn)</td>
<td>324.7</td>
<td>6.3</td>
</tr>
</tbody>
</table>

(a) From W.D. English (57)
\[ k = -416.3, \text{ while for a compound with an "iso-structure", e.g. trimethyl stannane and dimethylethyl stannane, } k = -424.5. \text{ Table 8 gives observed and calculated boiling points for some stannane derivatives.} \]

The following relationship has been suggested (100) between the boiling point \( T^0K \), under 10 mm of Hg pressure, of alkyltin compounds containing only straight chains and the molecular weight \( M \):

\[
T_{10\text{mm}} = 22.566 M^{\frac{1}{2}} \quad \text{.................(3)}
\]

However this equation does not give good results for the methyl compounds.

It has been found that the molecular volume at 20\(^\circ\)C \( V_{20} \) of alkyltin compounds is related to the number of carbon atoms \( n \) in the molecule by the following equations (100):

- for tetraalkyltin \( V_{20} = 64.35 + 16.550 \)  \text{.....(4)}
- for trialkyltin bromide \( V_{20} = 75.87 + 16.550 \)  \text{.....(5)}

which hold both for compounds with straight or branched carbon chains.

A relationship between the density at 20\(^\circ\)C \( D_{20} \) of tin tetraalkyls with straight carbon chains, the boiling point \( T_{10\text{mm}} \) and the number of carbon atoms \( n \) in the molecule may be obtained by combining equations (3) and (4) to give:

\[
D_{20} = (T_{10\text{mm}})^{2} / 509.4 \ (64.35 + 16.550) \quad \text{.................(6)}
\]

It has been found with the limit of pressure used in the preparation of organotin compounds, that: \[ \log p = A - B/T, \] where \( T \) is the boiling point in \(^\circ\)K under any pressure \( p \) mm of Hg and \( A \) and \( B \) are constants.

For tetra-\( n \)-propyltin the corresponding equation was found (100) to be:
TABLE 8
BOILING POINTS OF ALKYLSTANNANES

\[ T = 324.7 \ln(n+6.3) + k - \frac{18}{n} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( k )</th>
<th>( n )</th>
<th>B.pt.°K observed</th>
<th>B.pt.°K calcd.</th>
<th>( \Delta T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl stannane</td>
<td>(-416.3)</td>
<td>2</td>
<td>273(a)</td>
<td>271</td>
<td>+2</td>
</tr>
<tr>
<td>Dimethyl stannane (b)</td>
<td>(-416.3)</td>
<td>3</td>
<td>308</td>
<td>308</td>
<td>0</td>
</tr>
<tr>
<td>Trimethyl stannane (b)</td>
<td>(-424.5)</td>
<td>4</td>
<td>332</td>
<td>331</td>
<td>+1</td>
</tr>
<tr>
<td>Dimethylethyl stannane (b)</td>
<td>(-424.5)</td>
<td>5</td>
<td>363</td>
<td>363</td>
<td>0</td>
</tr>
</tbody>
</table>

(a) From A.E. Finholt, A.C. Bond, K.E. Wilzbach and H.I. Schlesinger (61)

(b) From W.D. English (57)

TABLE 9
COMPARISON OF BOILING POINTS OF METHYL AND ETHYL DERIVATIVES OF C, Si, Ge, Sn & Pb

<table>
<thead>
<tr>
<th>Element</th>
<th>((\text{CH}_3)_4\text{M})</th>
<th>((\text{C}_2\text{H}_5)_4\text{M})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>(-16.63^\circ\text{C})</td>
<td>(-33.03^\circ\text{C})</td>
</tr>
<tr>
<td>Si</td>
<td>(-99.04)</td>
<td>(-83.8)</td>
</tr>
<tr>
<td>Ge</td>
<td>(-88)</td>
<td>(-92.7)</td>
</tr>
<tr>
<td>Sn</td>
<td>(-54.9)</td>
<td>(-131.01)</td>
</tr>
<tr>
<td>Pb</td>
<td>(-30.2)</td>
<td>(-130.22)</td>
</tr>
</tbody>
</table>
If the ratio of the boiling points of two similar compounds with the same central atom is assumed to be constant at any one pressure the boiling point of a compound under another pressure can be calculated by making use of equations (3) and (7).

The melting points of tin tetraalkyls and tetraaryls follow similar lines as those of analogous compounds of carbon, silicon, germanium and lead, viz. increase in melting point as the molecular weight increases. However, the methyl derivatives, \((\text{CH}_3)_4\text{M}\), have higher melting points than the ethyl derivatives, except in the case of silicon compounds (98, 100, 125, 144-5, 224-6) as can be seen from Table 9.

No regularities can be expected in the melting points since they depend so much on the crystal structure of the solid phase. The aryl compounds are solid at room temperature while the alkyls of corresponding number of carbon atoms are liquids. Also, derivatives containing branched carbon chains or chains with multiple bonds have lower melting points and boiling points than those of the straight chain isomers (98, 100, 125, 144-5).

It is interesting to note the effect of the position of substituents in the phenyl groups attached to tin on the melting points. A few examples are given in Table 10 where the meta-compounds show the lowest and the para-compounds the highest melting points.

In the compounds of the general formula \(\text{R}_3\text{SnAn}\) (where An is an anionic group e.g. halide or hydroxide, and \(\text{R}\) is an alkyl group) the melting point decreases as the number of carbon atoms in the \(\text{R}\) group increases.
### TABLE 10

**Melting Points of Substituted Phenyl Derivatives**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetra-0-tolyl</td>
<td>175.6</td>
<td>158.9</td>
<td>201.2</td>
</tr>
<tr>
<td>tetra-m-tolyl</td>
<td>146.1, 150.1</td>
<td>128.5</td>
<td>122.1, 123</td>
</tr>
<tr>
<td>tetra-p-tolyl</td>
<td>224, 227</td>
<td>230</td>
<td>240</td>
</tr>
<tr>
<td>tetra-m-xylyl</td>
<td>-</td>
<td>219.5</td>
<td>-</td>
</tr>
<tr>
<td>tetra-p-xylyl</td>
<td>-</td>
<td>272-3</td>
<td>-</td>
</tr>
</tbody>
</table>

### TABLE 11

**Parachors of Group IV Hydrides**

<table>
<thead>
<tr>
<th>Compd</th>
<th>T_D K(a)</th>
<th>P_cald(a)</th>
<th>P(H)</th>
<th>Atomic Parachors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lewis</td>
</tr>
<tr>
<td>CH_4</td>
<td>111.7</td>
<td>73.2</td>
<td>68.4</td>
<td>4.8</td>
</tr>
<tr>
<td>SiH_4</td>
<td>161.0</td>
<td>97.1</td>
<td>68.4</td>
<td>28.7</td>
</tr>
<tr>
<td>GeH_4</td>
<td>184.5</td>
<td>108.5</td>
<td>68.4</td>
<td>40.1</td>
</tr>
<tr>
<td>SnH_4</td>
<td>221.0</td>
<td>126.3</td>
<td>68.4</td>
<td>57.9</td>
</tr>
<tr>
<td>PbH_4</td>
<td>256.5</td>
<td>143.4</td>
<td>68.4</td>
<td>75.0</td>
</tr>
</tbody>
</table>

(a) From D.T. Lewis (133)

* These values were used by Lewis to evaluate the constants of equation (8).
E. MOLECULAR VOLUME

In this section the following properties will be discussed:

1) Parachors: Lewis (132-3) has evolved a set of equations whereby the parachors \( P \) of a set of structurally similar compounds containing the same number of atoms can be calculated from their critical temperatures \( T_c \) or boiling points \( T_b \):

\[
P = \frac{(T_c + \alpha_c)}{K_c} = \frac{(T_b + \alpha_b)}{K_b} \quad \ldots (8)
\]

Similar equations have also been suggested for the parachors of the members of homologous series:

\[
P = e^{\frac{(T_c + \alpha_c)}{K_c}} = e^{\frac{(T_b + \alpha_b)}{K_b}} \quad \ldots (9)
\]

In both sets of equations the compounds are required to be non-associated liquids and the critical temperatures equations were found to give more accurate results than the boiling points equations in the case of the hydrocarbons.

Lewis (133) found that these equations apply remarkably well to the silanes and was able to calculate the parachors of the hydrides of the elements of Group IV as well as the atomic parachors of these elements. Considering the values of atomic parachors of carbon and tin which he used to evaluate the constants of equation (8) these were in good agreement with those given by other workers (12, 230) as can be seen from Table 11.

It is interesting to compare the variations in parachors with different valencies of tin (36). Assuming a constant parachor for chlorine (54.6) as given by Bayliss (12), the atomic parachors of Sn(IV) and
Sn(II) are evaluated from the molecular parachors of their chlorides.

The following values are obtained:

<table>
<thead>
<tr>
<th></th>
<th>$P_{\text{obsd}}$</th>
<th>bond $P$</th>
<th>At.$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl$_2$(36)</td>
<td>183.8</td>
<td>91.9</td>
<td>73.6</td>
</tr>
<tr>
<td>SnCl$_4$(230)</td>
<td>272.8</td>
<td>68.2</td>
<td>54.4</td>
</tr>
</tbody>
</table>

Since bond parachors are related to bond polarizibility, the Sn(II)-Cl bond is more ionic than the Sn(IV)-Cl bond (36). This conclusion is supported by electronegativity data and bond dissociation energy data.

(2) **Viscosity:** Hugel (90) has measured the viscosity at 20°C of a number of alkyltin and alkyllead compounds. He found that, contrary to expectation, the viscosity coefficients for mono-, di- and tetrapropyl stannane were nearly equal when measured under conditions such that there were the same number of tin atoms per unit volume. It was found that whilst the corresponding tin and lead tetraalkyls have very nearly equal molecular volumes but different molecular weights, their viscosities were only slightly different under similar conditions (90,134).

The self-diffusion coefficient of tetramethyltin which is related theoretically to its viscosity have been measured between 10-30°C and found to be $2.29 \times 10^{-5}$ cm$^2$ sec$^{-1}$ at 20°C. The activation energy of self-diffusion for the same compound was found to be 1.87 Kcal. (8a).

(3) **Refractions:** West and Rochow (256) analysed the data on the refraction of 93 organotin compounds and the tetrahalides and found a system of bond refractions for tin. They based their analysis on the fundamental values for C-H and C-C bonds refractions of Denbigh viz. 1.69 and 1.25 respectively. Vogel evaluated a new set of bond refractions for C-H
## TABLE 12

**BOND REFRACTIONS OF ORGANOTIN COMPOUNDS**

<table>
<thead>
<tr>
<th>bond</th>
<th>West and Rochow</th>
<th>Vogel, Crosswell, and Leicester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-C prim.</td>
<td>4.09</td>
<td>4.16</td>
</tr>
<tr>
<td>Sn-C sec.</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>Sn-C ter*</td>
<td>(4.52, 4.87, 4.89)</td>
<td>-</td>
</tr>
<tr>
<td>Sn-C ar.</td>
<td>3.54</td>
<td>3.78</td>
</tr>
<tr>
<td>Sn-Cl</td>
<td>8.81</td>
<td>8.91</td>
</tr>
<tr>
<td>Sn-Br</td>
<td>12.02</td>
<td>12.00</td>
</tr>
<tr>
<td>Sn-I</td>
<td>17.95</td>
<td>17.92</td>
</tr>
<tr>
<td>Sn-Sn</td>
<td>10.96</td>
<td>10.77</td>
</tr>
<tr>
<td>Sn-O</td>
<td>3.84</td>
<td>3.84</td>
</tr>
</tbody>
</table>

* From R. West, M. H. Webster and G. Wilkinson (257)
and C-C bonds which were supported later by Vickery and Denbigh.

Vogel, Cresswell and Leicester (246) re-examined the data of West and Rochow and produced a revised system for the tin compounds calculated on the basic values of 1.676 for the C-H bond refraction and 1.296 for the C-C bond refraction. They also produced systems for silicon, germanium and lead organic compounds (246). Table 12 gives the bond refractions for organotin compounds as given by the two groups of investigators.

Vogel, Cresswell and Leicester (246) argued against having more than one bond refraction for the Sn-C bond on the grounds that among the twelve compounds considered by West and Rochow (256) to contain secondary carbon atoms, only two contained secondary carbon atoms directly attached to tin. However, they failed to produce any convincing argument in favour of overlooking the case of a tertiary carbon atom attached to tin, for in the three compounds studied by West, Webster and Wilkinson (257) viz. dimethyl-di-t-butylditin, dimethyl-di-t-amyltin and di-n-butyl-di-t-butylditin the values are considerably higher than 4.16, being respectively: 4.87, 4.52, and 4.89. West, Webster and Wilkinson suggested that the reason for this marked exaltation is the replacement of an α-hydrogen atom by the more negative methyl group which increases the polarity of the metal-carbon bond. In the case of analogous compounds of silicon no such exaltation has been observed (257).

Table 13 gives the atomic refractions \([r]_D\) for tin which were derived from the Lorenz-Lorentz molecular refractions \([R_L]_D(100)\).
TABLE 13
MOLECULAR REFRACTION AND ATOMIC REFRACTION FOR ORGANOTIN COMPOUNDS

<table>
<thead>
<tr>
<th>compound</th>
<th>$[R_L^D]$</th>
<th>$[r_L^D]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetramethyltin(a)</td>
<td>36.43</td>
<td>-</td>
</tr>
<tr>
<td>tetraethyltin(b)</td>
<td>54.90</td>
<td>13.56</td>
</tr>
<tr>
<td>tetra-n-propyltin(b)</td>
<td>73.95</td>
<td>14.13</td>
</tr>
<tr>
<td>tetra-n-butyltin(b)</td>
<td>92.07</td>
<td>13.78</td>
</tr>
<tr>
<td>tetra-n-amyltin(b)</td>
<td>110.64</td>
<td>13.88</td>
</tr>
<tr>
<td>tetra-n-hexyltin(b)</td>
<td>128.78</td>
<td>13.55</td>
</tr>
<tr>
<td>tetra-n-heptyltin(b)</td>
<td>147.40</td>
<td>13.70</td>
</tr>
<tr>
<td>tetra-n-octyltin(b)</td>
<td>165.66</td>
<td>13.48</td>
</tr>
</tbody>
</table>

(a) From A. I. Vogel, W. T. Cresswell and J. Leicester (246)
(b) From W. J. Jones, D. P. Evans, T. Gulwell and D. C. Griffiths (100)
FIG. 1

14.0

13.8

13.6

1 2 4 6 8

No. OF CARBON ATOMS

[r]

L D
It is interesting to note the periodic variations in $[r]_D$ for tin in ascending the series from ethyl to octyl. When the tin atom is attached to an "odd number" carbon chain $[r]_D$ is greater than when the tin atom is attached to an "even number" carbon chain, as illustrated in Figure 1.

C. BOND PROPERTIES

Bond properties have been fully discussed by Pauling (194), Baughan (11) and Cottrell (39). The energy of a bond, $B_{X-Y}$, in a molecule $XY_n$ is defined (11, 39, 174) as:

$$B_{X-Y} = \frac{1}{n} \cdot Q_f(XY_n)$$  \hspace{1cm} (11)

where $Q_f(XY_n)$ is the heat of formation at 0°C and zero pressure of the gas $XY_n$ from its elements in the gaseous state.

The evaluation of $Q_f$ requires a knowledge of the heat of atomization of the combining elements and of the heat of vaporization of the resulting compound from their normal states. The complexity of the thermal measurements makes the results inaccurate.

Pauling utilized the following empirical equation to calculate bond energies. He found that $B_{X-Y}$ is related to the energies of the bonds $X-X$ and $Y-Y$:

$$B_{X-Y} = \frac{1}{2} \cdot \left( B_{X-X} + B_{Y-Y} \right) + R_{XY}$$  \hspace{1cm} (12)

and the term $R_{XY}$ which is called "the ionic-covalent resonance energy" is due to the polarity of the $X-Y$ bond. It can be seen that Pauling's equation is independent of the heat of atomization of the elements.
Further, Pauling pointed out that the geometric mean of $B_{X-X}$ and $B_{Y-Y}$ is a better approximation than the arithmetic mean, but the former will require the absolute values of the bond energy. The term $B_{XY}$ in equation (12) has been found to be related to the electronegativity difference $\Delta X$ of the two bonded atoms X and Y.

Another method involving the use of thermal data depends on measurements of equilibrium-constant at high temperatures. This method can be associated, with great advantages, with mass spectroscopy experiments where electron bombardment produces both ionization and bond fission. Considering a molecule $XY_n$, the last stage in the dissociation process is: $XY \rightarrow X + Y - D$ Kcal.

where D is the dissociation energy of the diatomic molecule into atoms in their ground states. Applying Hess's law, one gets:

$$\sum_{i} n_i D_i = nB_{X-Y} \quad \text{(13)}$$

Molecular spectroscopy can be used to evaluate bond energies. This method gives values for the force constants and interatomic distances. Although there are considerable difficulties in applying this method, especially to complicated molecules, one can obtain very satisfactory results by combining it with other methods, such as X-ray and electron diffractions, or even with thermal data.

Chemical kinetics and photolytic methods have also been used for polyatomic molecules, assuming that the activation energy for radical recombination is zero, and therefore the activation energy of the dissociation process is equal to the heat of reaction.
Heat of atomization of the elements of the carbon family are given in Table 14. It is important to point out that spectroscopic investigations (50, 55, 243-4) on the monoxides, and especially on SiO, SnO and PbO show that they dissociate according to the scheme:

\[ \text{MO (E-state)} \rightarrow \text{M (P2)} + \text{O (P)} \]

which gives a rather high heat of vaporization of the elements. If carbon monoxide dissociates according to the same scheme then the high heat of atomization of carbon (170 Kcal/gm atom), which is preferred by Gaydon (65), can be explained. However, Herzberg (85) prefers the much lower value of 125 Kcal/gm atom.

Now, in the case of tin, there are two well known allotropes, grey tin, stable at ordinary temperature, and white tin, stable at high temperature. The former has the diamond structure (22), but the latter has a metallic structure. The value of the heat of atomization refers to the normal state of the element, in this case to grey tin:

\[ \text{Sn (grey)} \rightarrow \text{Sn (g)} \]. The situation with regard to tin, as reviewed by Cottrell (39), is far from satisfactory and values have been reported ranging from 55 to 73.4 Kcal/gm atom for the latent heat of vaporization of tin. Even recent values differ widely; e.g. Baughan (11) gives the value of 62.4±2 from consideration of the Third Law of Thermodynamics, whilst Brewer and Porter (16) give 70±2 Kcal/gm atom obtained by the Kunsden method. The latter authors suggested that the lower values for the heat of vaporization, corresponding to higher values for the vapour pressure, are due to contamination of tin by oxygen. There is, however, the question of the nature of tin vapour. Recent researches (86, 113).
205, 206) indicate the presence of various polyatomic species in very small quantities which should be taken into account in the calculation of the heat of vaporization of the element.

The energy of a bond X-Y varies with the valency state of the bonded atoms. Thus the bond energies as well as other bond properties such as bond refraction, bond parachors, bond dipole etc. for bivalent tin are different from those for quadrivalent tin (11). The Sn(II)-hal bond is stronger and therefore more polar than the Sn(IV)-hal bond. Table 15 provides for comparison bond energies, bond dissociation energies and bond lengths involving quadrivalent and bivalent tin.

The bond dissociation energy (D) is defined as the difference in energy between the molecule XY_n and the fragments XY_{n-1}+X. For diatomic molecule the bond dissociation energy is equal to the bond energy (B), but not for the polyatomic molecules. The bond dissociation energies for similar bonds are not necessarily equal, as they depend not only on the bond concerned but also on the remainder of the molecule, thus the bond dissociation energy for X-Y bond in XY_n is different from that in XY_{n-1} and so on.

Bond lengths or interatomic distances (l) have been shown (174) to be linearly related to the bond dissociation energies in a number of related compounds. Barrow (10) has illustrated graphically the case of the oxides, sulphides, selenides and tellurides of the elements of Group IV.

Bond energies (B), bond dissociation energies (D), force constants (k) and bond lengths (l) are given in Table 16 for a number of carbon, silicon, germanium, tin and lead bonds to other elements.
TABLE 14
HEAT OF VAPORIZATION OF THE ELEMENTS OF GROUP IV

<table>
<thead>
<tr>
<th>element</th>
<th>Baughan's $\Delta H^0$</th>
<th>Cottrell's $\Delta H^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td>-</td>
<td>138</td>
</tr>
<tr>
<td>silicon</td>
<td>89.2 ±3</td>
<td>89</td>
</tr>
<tr>
<td>germanium</td>
<td>88.8 ±4</td>
<td>89</td>
</tr>
<tr>
<td>tin (a)</td>
<td>62.4 ±2</td>
<td>70</td>
</tr>
<tr>
<td>lead</td>
<td>-</td>
<td>46</td>
</tr>
</tbody>
</table>

(a) A.W. Searcy and R.D. Freeman (206) give the following value for the heat of vaporization of tin, $\Delta H^0_{25} = 71.9 ±2$.

TABLE 15
COMPARISON OF BOND PROPERTIES OF BIVALENT AND QUADRIVALENT TIN

<table>
<thead>
<tr>
<th>bond</th>
<th>bond energy (a)</th>
<th>bond dissociation energy (b)</th>
<th>bond length (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(IV)-Cl</td>
<td>74</td>
<td>76.7</td>
<td>2.30 Å</td>
</tr>
<tr>
<td>Sn(II)-Cl</td>
<td>89</td>
<td>91.3</td>
<td>2.42 Å</td>
</tr>
<tr>
<td>Sn(IV)-Br</td>
<td>62</td>
<td>64.4</td>
<td>2.44 Å</td>
</tr>
<tr>
<td>Sn(II)-Br</td>
<td>76</td>
<td>77.6</td>
<td>2.55 Å</td>
</tr>
<tr>
<td>Sn(IV)-I</td>
<td>-</td>
<td>-</td>
<td>2.64 Å</td>
</tr>
<tr>
<td>Sn(II)-I</td>
<td>63</td>
<td>-</td>
<td>2.73 Å</td>
</tr>
</tbody>
</table>

(a) From H.O. Pritchard and H.A. Skinner (180)
(b) From E.C. Baughan (11)
<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HCN</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>NO</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>Se</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>Te</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>Cl</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>Br</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td>1.08</td>
<td>1.54</td>
<td>1.47</td>
<td>-</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.36</td>
<td>1.761</td>
<td>1.942</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>O</td>
<td>N</td>
<td>O</td>
<td>S</td>
<td>Se</td>
<td>Te</td>
<td>F</td>
<td>Cl</td>
<td>Br</td>
<td>I</td>
</tr>
<tr>
<td>-----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
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<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>-</td>
<td>94</td>
<td>75</td>
<td>109</td>
<td>81</td>
<td>-</td>
<td>74</td>
<td>71</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>42</td>
<td>-</td>
<td>4.46</td>
<td>2.96</td>
<td>2.58</td>
<td>2.08</td>
<td>-</td>
<td>2.59</td>
<td>1.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>kr</td>
<td>1.34</td>
<td>-</td>
<td>1.93</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lk</td>
<td>1.85</td>
<td>2.29*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) These values are taken from T.L.Cottrell (39), unless otherwise specified.

(*) From M.L.Delwaulle (47)

(**) From L.P.Lindeman and M.K.Wilson (138)

(*) From L.Pauling (174)

(*) From L.O.Brockway and H.O.Jenkins (20)

(*) From E.C.Baughan (11)

(*) From S.S.Mitra (159)

(*) From R.W.Kilb and L.Pierce (106b)

(*) In $MX_4$ compounds

(**) In $MX$ compounds
I.4. ORGANOTIN COMPOUNDS OF QUADRIVALENT TIN

A. SYMMETRICAL AND UNSYMMETRICAL TIN COMPOUNDS

The tetrahedral arrangement of four equivalent single covalent bonds round the tin atom in its quadrivalent state has been demonstrated by electron diffraction work on tetramethyltin (20).

A number of symmetrical tetraaryltin compounds including tetraphenyltin, tetra-$\alpha$-tolyltin, tetrakis-$p$-ethoxyphenyltin and tetrakis-$p$-methoxyphenyltin, have been studied by X-ray crystallographic methods (68, 92-3, 263-4). It has been found that the crystal symmetry decreased with the increasing size of the aryl group. Frevel, Rima and Anderson (64) have tabulated the X-ray crystallographic data on a number of organotin compounds. The isomorphous crystallization of tetraphenyl derivatives of silicon, tin and lead have been studied (167).

Supporting evidence for the tetrahedral arrangement of groups around the tin atom is forthcoming from the fact that Pope and Peachey (177-8) obtained methylethylpropyltin iodide optically active. From an aqueous solution of methylethylpropyltin (+)-camphorsulphonate only one of the two possible isomers could be isolated; this on treatment with potassium iodide solution gave (+)-methylethylpropyltin iodide. Under no conditions could the other diastereoisomeride be obtained; on heating an aqueous solution of the (+)-methylethylpropyltin (+)-camphorsulphonate the rotation changed to that indicating the presence of the two isomers.
but evaporation of this solution to dryness gave the original diasteroisomeride. Schwarz and Lewinsohn (204) succeeded in obtaining (+)-methylethylphenylgermanium bromide by the method used by Pope and Peachey for the tin compounds. However, Naumov and Manulkin (166) following the method of Pope and Peachey but using the salt of (-)-camphorsulphonate could not obtain (-)-methylethylpropyltin iodide. Moreover, Ziegler and Wenz (265) were unable to obtain an optically active tin compound by this method. The experimental details given by Pope and Peachey are brief and it is probable that both the isolation of (+)-methylethylpropyltin (+)-camphorsulphonate and its successful conversion into the optically active iodide are very dependent upon experimental conditions. If, as is suggested by Turner and Harris (240) a second order asymmetric transformation is involved during the separation of the camphorsulphonate then the rate of crystallization would be critical in determining whether one diasteroisomeride separated or a mixture of the two. Also, the conditions of the conversion of the camphorsulphonate into the iodide are no doubt important especially since Pope and Peachey found that the rotation of the iodide obtained from the (+)-bromocamphorsulphonate was very variable and indeed in some cases the inactive iodide was obtained. If as Sidgewick (212) suggested retention of optical activity during the conversion is dependent upon the formation of the hydrated cation \(\text{MeEtPrSnHgO}_2\) experimental conditions will no doubt determine the extent of the racemization of this cation. Even, if this is not the case, the experimental conditions used in the conversion of the camphorsulphonate
into the iodide might determine the mechanism of the reaction and thus the degree of optical activity of the product (91).

As has already been mentioned, a similar situation exists in the germanium compounds. In the case of quadrivalent lead the following compound has been prepared by Austin, 1933, (125) but no one succeeded yet in separating any of its isomers:

$$\text{C}_6\text{H}_5\text{Pb-C}_6\text{H}_4\text{OCH(CH}_3\text{)(CH}_2\text{)CH}_3$$

However, in the case of silicon, Challenger and Kipping, 1910, (33) resolved the following compound into d- and l- isomers:

$$\text{n-C}_5\text{H}_7\text{Si-CH}_2\text{C}_6\text{H}_5$$

Malatesta and Pizzotti (148) have measured the dipole moments of few unsymmetrical tin and lead organic compounds and found that these dipole moments approximate to the dipole moments of the analogous carbon compounds rather than to the silicon compounds (146-9), as can be seen from Table 17. This was explained (148) on the ground that resonance of the following type may take place in the silicon compounds:

$$\text{Si}$$

while such resonance may be insignificant in the tin and lead compounds. However, recent work (see later) does not justify such explanation (35,41).

Magnetic susceptibility measurements (101-3) of several symmetrical alkyl derivatives of tin and lead (from C_1 to C_6) show that if constant
values are assumed for the alkyl groups, the magnetic susceptibility of the metal decreases with the increase in the number of carbon atoms in the alkyl chain. This may be due to the compression of the metallic atom (c.f. atomic refraction).

Studies on the parachors (101-2) of a series of symmetrical alkyl derivatives of tin and lead showed that the parachors decrease with increase in the number of carbon atoms in the alkyl chain; and that the parachors for the compounds with odd number of carbon atoms in the alkyl chain are higher than the values for the adjacent compounds with even number of carbon atoms (c.f. atomic refraction). Similar behaviour is observed if the magnetic susceptibilities are plotted against the number of carbon atoms in the radical. Magneto-optical studies (247) of n-alkyl stannanes revealed similar trends in the values of the molar magnetic rotations.

The infrared and Raman spectra of tetramethyltin have been investigated by a number of workers (53, 106a, 140, 172, 213, 250, 252a, 262). It is interesting to find that every one of those workers produced different set of results and argued in favour of it attributing to the impurity of the compounds used by the others their different values. It is of interest to compare some of the fundamental frequencies of \( \text{M(CH}_3\text{)}_4 \) compounds of Group IV elements. Figure 2 illustrates the variation in the skeletal deformation frequencies, and the skeletal stretching frequencies.

Fassel and his coworkers (122a, 157) have studied the effect of the metallic atom M on the vibrational frequencies of the phenyl group in the compounds \( \text{Ph}_4\text{M} \). They found that the frequency of the C-H out-of-plane
**TABLE 17**

**DIPOLE MOMENTS OF FEW UNSYMMETRICAL COMPOUNDS (a)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dipole Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylphenylsilane</td>
<td>0.98</td>
</tr>
<tr>
<td>Triethylphenyltin</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethyltriphenyltin</td>
<td>0.73</td>
</tr>
<tr>
<td>Triethylphenyllead</td>
<td>0.86</td>
</tr>
<tr>
<td>Ethyltriphenyllead</td>
<td>0.81</td>
</tr>
</tbody>
</table>

(a) From L. Malatesta (146)

L. Malatesta and R. Pizzotti (148, 149)

**TABLE 18**

**THE EFFECTIVE METHYL MASS OF THE TETRAMETHYL DERIVATIVES OF THE ELEMENTS OF GROUP IV(a)**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Effective Methyl mass</th>
<th>Bond</th>
<th>$k_\text{st} \times 10^5$</th>
<th>$k_b \times 10^5$</th>
<th>$k_\text{st}/k_b$</th>
<th>$\chi_\text{M} - \chi_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(CH$_3$)$_4$</td>
<td>16.67</td>
<td>C-C</td>
<td>5.28</td>
<td>0.331</td>
<td>15.95</td>
<td>6.00</td>
</tr>
<tr>
<td>Si(CH$_3$)$_4$</td>
<td>16.04</td>
<td>Si-C</td>
<td>3.38</td>
<td>0.120</td>
<td>28.16</td>
<td>-0.75</td>
</tr>
<tr>
<td>Ge(CH$_3$)$_4$</td>
<td>15.83</td>
<td>Ge-C</td>
<td>2.72</td>
<td>0.0357</td>
<td>76.19</td>
<td>-0.85</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_4$</td>
<td>15.17</td>
<td>Sn-C</td>
<td>2.37</td>
<td>0.0313</td>
<td>75.72</td>
<td>-0.85</td>
</tr>
<tr>
<td>Pb(CH$_3$)$_4$</td>
<td>15.56</td>
<td>Pb-C</td>
<td>1.94</td>
<td>0.0307</td>
<td>63.19</td>
<td>-1.05</td>
</tr>
</tbody>
</table>

(a) From R.K.Sheline and K.S.Pitzer (210)

R.K.Sheline (211)
FIG. 2

- Stretching freq. ($\nu$)
- Deformation freq. ($\beta$)

FUNDAMENTAL FREQ. CM$^{-1}$

600
500
400
380

ATOMIC NO.

6 14 32 50 82
bending vibrations between 675 and 820 cm\(^{-1}\) decrease with reduced mass of the diatomic group \(H-C\), while the in-plane bending vibrations of the C-H bond is proportional with the square of the electronegativity of the atom \(N\).

The spectroscopic studies of the tetramethyl compounds have given rise to a number of interesting theoretical considerations. Sheline and Pitzer (210) have calculated what they termed "the effective methyl mass" which is of great use in the study of the spectra of polyatomic molecules whereby the methyl group is considered to have a point mass which "must give the correct force constant". By this procedure one reduces the tetramethyl compounds to pentatomic molecules, the spectroscopic analysis of which is considerably simplified. The "effective methyl mass" for the tetramethyl compounds of the elements of Group IV are given in Table 18. From this table it can be seen that the "effective methyl mass" approaches the sum of the atomic weights of the atoms of the methyl group, \(CH_3(15.0028)\), on descending the group. However, Rank, Saksena and Shull (181) have expressed serious doubts as to the value of these "effective methyl masses" on the ground that they invariably lead to highly inaccurate values for the force constants.

Sheline (211) made use of the ratio of the calculated stretching force constant \((k_{st})\) to the bending force constant \((k_b)\) for the particular bond to indicate the degree of covalent character of that bond. The values of \(k_{st}/k_b\) should only be considered as qualitative indication of the polarity of the bond, since the assumption that there is no interaction between non-bonded groups or atoms has been made in relating these values to the polarity of the bonds.
Sanderson (197, 198) using atomic charges, calculates for the methyl compounds the net charge on the methyl group which he considers a measure of the polarity of the bonds. However, he makes no effort to relate these values, either quantitatively or qualitatively, to the character of the bonds, although he does discuss such properties as the physical state, oxidation with carbon dioxide and hydrolysis.

The effect of the tin atom on an aromatic group attached to it is of great theoretical interest. It has been remarked earlier that the rather large size of the tin atom and also of silicon, germanium and lead makes the possibility of p-orbital overlapping to form \( \pi \)-bonds rather remote and therefore the formation of double bonds involving tin is considered unlikely. However tin, as well as silicon, germanium and lead has an empty d-orbital within its valency orbit (see Table 2), and it has been shown recently (40) that such d-orbitals can be utilised for bond formation. The resulting bond is a dative one and therefore, requires a donor atom or group; in the case of the phenyl group donating its \( \pi \)-electrons a \( d - \pi \) bond is formed (40).

Bowden and Braude (15) from a study of the phenyl derivatives \( \text{PhMR}_n \) (where \( M \) represents an elements of group IV and \( R \) an alkyl radical) have found that electronic interaction between \( M \), excepting carbon, and the \( \pi \)-electron centre in the phenyl group must be considered in order to account for the ultraviolet absorption spectra of these compounds. This interaction causes an auxochromic shift of the absorption band of the phenyl group.

Chatt and Williams (34) studied the dissociation constants of the
series of acids $\text{R}_2\text{MC}_6\text{H}_4\text{COOH}$ (where $M=$ C, Si, Ge and Sn and $R=$ Me or Et)
In this series the acid strength should be an indication of the strength of the $d\pi-p\pi$ bond, since the electrons forming this bond are supplied by the aromatic system as indicated in the diagram below (34):

This type of $\pi$-bond is similar to the $\pi$-bond formed between a transition metal and ligands containing bivalent carbon, where, in that case, the metal provides the $d$-electrons which are accommodated in the empty $p$-orbitals of the carbon atom e.g. the nickel-carbon bond in nickel carbonyl. Another suggestion (34) is that resonance occurs between the following forms:
The thermodynamic dissociation constants \( K_a \) of these acids in aqueous methanol solution are given in Table 19, where it can be clearly seen that the M-C\( _{\text{ar}} \) bond has some double bond character at least in the anion \( \text{p-R}_3\text{MC}_6\text{H}_4\text{COO}^- \), and therefore very probably in the acid (34).

From Table 19 it can be seen quite clearly that the replacement of one metal atom by another of the same group has little or no effect on the acid strength indicating that \( \pi^* - \pi \) bonding is apparently independent of the relative sizes of the bonded orbitals i.e. of the principal quantum number and the size of the atom M, as required by theory (34, 40).

Giacomello (68) has investigated the crystal structure of tetraphenyl compounds of silicon, tin and lead; and his values of the M-C\( _{\text{ar}} \) bond distances are compared in Table 20 with the theoretical values obtained from the sum of covalent radii of the atoms concerned.

One very interesting point that arises from Table 20 is the apparent anomaly of the Pb-C\( _{\text{ar}} \) bond. It should be worthwhile determining the dissociation constants of the acid \( \text{p-R}_3\text{PbC}_6\text{H}_4\text{COOH} \) for it seems very likely that different mechanism may be operating in the lead compound.

Referring to Table 19, it seems that the inductive effect which increases slightly in going from silicon to tin is balanced by the increase in the mesomeric effect. Supporting this argument is the work (52) on the ionization constants and absorption spectra of the trimethylsilylmethylbenzoic acids, \( \text{(CH}_3\text{)}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{COOH} \), where the presence of the methylene group \(-\text{CH}_2-\) eliminates the mesomeric effect \(-\text{M}\) of the silicon atom but only reduces the inductive effect \(+\text{I}\) with the result that these acids are weaker than the corresponding toluic acids.
TABLE 19
THERMODYNAMIC DISSOCIATION CONSTANTS ($K_a$) OF THE ACIDS

\[ P-\text{R}_2 \text{MO}_2 \text{H}_4 \text{COOH.}(a) \]

<table>
<thead>
<tr>
<th>M</th>
<th>$10^6 K_a$</th>
<th>R = Me</th>
<th>R = Et</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.70</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.11</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>1.07</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>1.05</td>
<td>(1.17)</td>
<td></td>
</tr>
</tbody>
</table>

(a) From J. Chatt and Williams (34)

TABLE 20
M-Car BOND DISTANCE IN Ph₄M MOLECULES

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å) from X-ray crystallographic measurements (a)</th>
<th>Theoretical single bond length (b)</th>
<th>Theoretical double bond length (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Car</td>
<td>1.88</td>
<td>1.94</td>
<td>1.73</td>
</tr>
<tr>
<td>Ge-Car</td>
<td>-</td>
<td>1.99</td>
<td>1.78</td>
</tr>
<tr>
<td>Sn-Car</td>
<td>2.07</td>
<td>2.17</td>
<td>1.96</td>
</tr>
<tr>
<td>Pb-Car</td>
<td>2.39</td>
<td>2.23</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) From G. Giacomello (68)
(b) From L. Pauling (174)
Further evidence for the interaction between the metal atom and the \( \pi \) electrons of the phenyl group is forthcoming from the studies (199a) of the scintillator counting behaviour of a number of substituted benzenes including tetraphenyltin. The scintillation efficiency of the compounds was correlated to the molecular structure and the mobility of the \( \pi \) electrons within the molecules.

The polarity of the Sn-C bond is emphasized when a functional group is attached to \( \alpha \)-carbon of the carbon chain as in trimethylcyanomethyltin \((\text{CH}_3)_3\text{SnCNCH}_2\text{CH} \), for instance (105). In such compound, and indeed in general, nucleophilic reagents are powerful tools for the fission of the Sn-C bond. The mechanism of the attack may be visualized:

\[
\begin{align*}
\text{Sn} & \quad \text{CN} \\
\uparrow & \\
\text{S}^+ & \quad \text{CN} \\
\end{align*}
\]

\text{nucleophilic reagent e.g. OH}^-

Thermodynamic investigations (100, 112, 140, 143, 224, 225, 226) have been carried out on a number of symmetrical organotin compounds with the object of determining their thermodynamic properties e.g. heats of combustion, transition and formation, heat capacities, entropies, vapour pressures, free energies etc.

Table 21 lists the values of some thermodynamic functions of symmetrical tetraalkyltin compounds. It will be noted that the heat of formation increases with increasing molecular weight, and there is a change from a negative heat of formation for the tetramethyltin to positive values for
### TABLE 21

SOME THERMODYNAMIC PROPERTIES OF ALKYL Tin COMPOUNDS (a)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of combustion Kcal/mole</th>
<th>Heat of formation Kcal/mole</th>
<th>Free energy of formation</th>
<th>Entropy of formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₄Sn</td>
<td>903 ± 10(b)</td>
<td>-13.6 ± 10(b)</td>
<td>19.0 ± 10 (b)</td>
<td>-109 (b)</td>
</tr>
<tr>
<td>(C₂H₅)₄Sn</td>
<td>1521</td>
<td>+ 59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n-O₂H₃)₄Sn</td>
<td>2163</td>
<td>+ 69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n-C₄H₉)₄Sn</td>
<td>2773</td>
<td>+ 111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n-C₅H₁₁)₄Sn</td>
<td>3384</td>
<td>+ 152</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) From W.J. Jones, D.P. Evans, T. Gulwell and D.G. Griffiths (100).

(b) From E.R. Lippincott and M. G. Tobin (140)

Lippincott and Tobin calculated the free energy and heat of formation and entropy of formation at three temperatures, the values listed in the table are those at 300 K.
Experiments on the determination of the melting point of tetramethyltin (224-6) showed that there were at least ten melting points for this compound. When the experiments were carried out on different samples in three types of apparatus, ten crystalline modifications were found, the melting points of which were found to lie between 138-148°C. Similar investigations on tetraethyllead revealed that there were seven melting points corresponding to at least seven crystalline modifications.

Experiments on the following compounds: Me₄Sn, Me₄Pb, Et₄Si, Et₄Ge and Et₄C, indicated, with the exception of tetraethyl germanium which has crystallized in two forms, only one melting point for each compound. Aston and Mosserly (5) and Aston Kennedy and Messerly (7) have investigated the thermodynamic properties of tetramethylmethane (neopentane) and tetramethylsilane respectively. For the former, one melting point was found, while for the latter two crystalline forms were found. Table 22 lists the known melting points of tetramethylsilane and the tetraethyls of germanium, tin and lead.

Table 23 gives the melting points and the entropies of fusion of the tetramethyls and tetraethyls of group IV together with the values of the tetrachlorides for comparison.

The main points only in the discussion of the above investigations will be outlined here, for further and fuller discussion reference should be made to the original papers (224-6).

French and Rasmussen (63) have shown that the potential barrier for free rotation of methyl groups about M-C bond decreases in going from carbon to lead as can be seen from Table 24. However, in the ethyl...
### TABLE 22
**MELTING POINTS OF SOME TETRAALKYL COMPOUNDS**

<table>
<thead>
<tr>
<th>compound</th>
<th>melting points °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₄Si</td>
<td>174.12 171.04</td>
</tr>
<tr>
<td>Et₄Ge</td>
<td>183.2 180.47</td>
</tr>
<tr>
<td>Et₄Sn</td>
<td>147.1 145.3 144.1 143.15 142.12 141.07 140.6 139.8 138.7 138.1</td>
</tr>
<tr>
<td>Et₄Pb</td>
<td>142.9 141.5 139.3 138.55 or 138.2 137.4 - 136.6 135.6 - -</td>
</tr>
</tbody>
</table>

### TABLE 23
**MELTING POINTS AND ENTROPIES OF FUSION FOR THE TETRACHLORIDES, TETRAMETHYLIS AND TETRAETHYLIS OF THE ELEMENTS OF GROUP IV. (a)**

<table>
<thead>
<tr>
<th>M</th>
<th>Cl</th>
<th>Me</th>
<th>Et</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M.pt °K</td>
<td>S_f</td>
<td>M.pt °K</td>
</tr>
<tr>
<td>C</td>
<td>250.23</td>
<td>7.10(b)</td>
<td>256.52</td>
</tr>
<tr>
<td>Si</td>
<td>205.5</td>
<td>9.06</td>
<td>174.12(o) 9.465</td>
</tr>
<tr>
<td>Ge</td>
<td>233.6</td>
<td>-</td>
<td>185</td>
</tr>
<tr>
<td>Sn</td>
<td>239.9</td>
<td>9.11</td>
<td>218.18</td>
</tr>
<tr>
<td>Pb</td>
<td>258</td>
<td>-</td>
<td>242.92</td>
</tr>
</tbody>
</table>


(b) Combined entropies of fusion and transition.

(c) Melting points of form for which thermodynamic data are available.
### TABLE 24

**POTENTIAL BARRIERS FOR FREE ROTATION ABOUT M-C BOND OF THE METHYL GROUPS IN (CH$_3$)$_n$M COMPOUNDS (a)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Potential barrier Cal.</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>4800</td>
<td>measured</td>
</tr>
<tr>
<td>Si-C</td>
<td>1100-1500 *</td>
<td>measured</td>
</tr>
<tr>
<td>Ge-C</td>
<td>1200</td>
<td>calculated</td>
</tr>
<tr>
<td>Sn-C</td>
<td>0</td>
<td>calculated</td>
</tr>
<tr>
<td>Pb-C</td>
<td>0</td>
<td>calculated</td>
</tr>
</tbody>
</table>

(a) From F.H. French and R.S. Rasmussen (63)

*Kilb & Pierce (106b) determined the energy barrier of internal rotation about the Si-C bond in methyl silane from microwave spectroscopic data to be 1700 ± 100 cal.*
compounds (CH₃CH₂)₄M, there is a marked overlapping of the van der Waals fields of force of the peripheral methyl groups and therefore the potential barrier for free rotation must be higher in the ethyl derivatives than in the methyl (225). The rather large central atom renders the molecules, other than those of carbon compounds, less spherical and looser and hence interlocking becomes possible. All the above factors acting together produces a resultant effect which is critical in the transition from germanium to tin, and thus polymorphism arises. It is, therefore, rotational isomerism (225, 226) i.e. isomerism produced by the different rotational positions of the molecules which are held in position by the intermolecular interlocking especially in the solid state and to a lesser extent in the liquid phase (80).

Ultraviolet absorption spectra of tetramethy (183, 236) tetraethyl- (183) and of tetrapheny tin (158) showed that they photo-decomposed in ultraviolet light. Similar effects have been found in the tetramethyls and tetraethyls of germanium and lead (51, 127, 183, 235, 236) and in tetraphenyllead (127). Table 25 lists the absorption limits for these compounds as determined by the various investigators.

Riccoboni's mechanism for the photolysis of tetraethyltin is similar to the mechanism of the thermal decomposition of the analogous mercury compound i.e. free radical chain reaction (183), the first stage in the reaction is probably:

$$\text{Sn(C}_2\text{H}_5)_4 + \text{hv} \rightarrow \text{C}_2\text{H}_5 + (\text{C}_2\text{H}_5)_3\text{Sn}$$

followed by:

$$2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$$
<table>
<thead>
<tr>
<th>Compound</th>
<th>Duncan &amp; Murray</th>
<th>Terenin &amp; Prilezhaeva</th>
<th>Leighton &amp; Mortensen</th>
<th>Thompson &amp; Idnnett</th>
<th>Riccoboni</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_4\text{C}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No absorption limit</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{Ge}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2330</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{Sn}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>ca 2330</td>
<td>-</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{Sn}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2420 in aceton</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2520 in methanol</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{Pb}$</td>
<td>ca 2330</td>
<td>-</td>
<td>2800 vap.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3100 soln.</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{Pb}$</td>
<td>-</td>
<td>2650</td>
<td>3500 vap.</td>
<td>2350</td>
<td>3470 in aceton</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3500 soln.</td>
<td></td>
<td>3490 in methanol</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_4\text{Pb}$</td>
<td>-</td>
<td>-</td>
<td>2800</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
From the limit of continuous absorption, Riccoboni (183) deduced that the overall activation energy was 117 Kcal. As the activation energy of the second stage is of the order of 8 Kcal this gives a value of 109 Kcal for the dissociation energy of Sn-C bond compared with the value of 81 Kcal given by Long and Norrish (143).

In the following paragraphs cleavage reactions will be discussed only very briefly; fuller surveys of this field may be found in the reviews of Luijten and van der Kerk (144, 145) and in Krause and von Grosse book (122).

Manulkin in a series of articles (1941-1950) (150-56) has reported his investigations on the cleavage of organotin compounds and similar compounds of lead and silicon. The first reaction studied was between iodine and symmetrical organotin compounds, where, an alkyl or aryl radical was eliminated according to the equation:

$$R_4M + I_2 \rightarrow R_2M + RI$$

Manulkin found that while the splitting off of the first two radicals was stepwise, the remaining two were split off simultaneously.

$R_4Sn$ and $R_2SnR$ type of compounds were next investigated where $R$ varied from $C_1$ to $C_6$ inclusive. Manulkin found that while in the lower members ($C_1$ to $C_6$) the ease of cleavage by iodination decreased with increasing number of carbon atoms in the radical for the two higher members of the series, in which $R$ contained 7 and 8 carbon atoms respectively, only slight differences were observed. With the compound tributyl-sec-butyltin the secondary alkyl radical was eliminated first, but with triethyl-iso-propyltin conflicting evidence as to the course of the elimination was obtained the products were triethyltin iodide as well as diethyl-iso-
propyltin iodide.

The heat of reaction of bromine vapour with tetramethyltin and the heat of reaction of bromine and iodine with hexamethyldistannane in cyclohexane solution have been investigated (176a). Values were derived for the heats of formation of trimethyltin bromide and iodide and of hexamethyldistannane assuming the value for the heat of formation of tetramethyltin (i.e. $-13.6 \pm 10$ kcal/mole at 300°K) reported by Lippincott and Tobin (140).

Manulkin also studied cleavage using other reagents, such as hydrogen chloride, mercuric chloride, aluminum chloride, ferric chloride and bismuth trichloride. He found that hydrogen chloride was as effective as iodine, but Kipping (106c) has found that while iodine cleaved one radical hydrochloric acid cleaved two radicals simultaneously. Manulkin has also found that mercuric chloride was more effective than either, and that bismuth trichloride dealkylated $R_4\text{Sn}$ less actively than aluminum chloride but it was just as active as mercuric chloride. In all the above reactions the temperature effect was quite pronounced.

Aluminum chloride and benzyl chloride were found (128) to be capable, under certain conditions, of totally cleaving tetraaryltin.

In the study of cleavage reactions using carboxylic acids a relationship has been found (129, 199b) between the ionization constant of the acid and the degree of cleaving. Further, a correlation has been noted (130) between the volume of alkane liberated by cleaving $R_4\text{Sn}$ (where $R$ is an alkyl radical) by a carboxylic acids and the basicity of the solvent. The more basic the solvent the more suppressed was the cleavage.

A quantitative study has been made (131) of the reaction between
Et_3PhSn, Et_2Ph_2Sn, EtPh_3Sn and the corresponding n-propylphenyl derivatives and silver nitrate in absolute alcohol at 25°C. The behaviour of the tri-alkyl and the diakyl compounds was found to be markedly different from that of the monoalkyl compounds. The inductive effect (+I) of the alkyl group may be held responsible for this phenomenon.

Kocheshkov (107,110) has studied the reaction between tetraalkyltin and stannic halides. The following equations represent the course of the reactions:

\[ 3R_4Sn + SnX_4 \rightarrow 4R_3SnX \]  \hspace{1cm} (I)
\[ R_4Sn + SnX_4 \rightarrow 2R_2SnX_2 \]  \hspace{1cm} (II)
\[ R_4Sn + R_2SnX_2 \rightarrow 2R_3SnX \]  \hspace{1cm} (III)

\( X \) being chlorine, bromine or iodine. Reactions I and II were found to be exothermic while reaction III endothermic. Reactions II and III may be intermediate reaction stages in I. However, when equimolecular proportions of \( R_4Sn \) and \( SnX_4 \) are allowed to react the main product is \( R_2SnX_2 \):

\[ R_4Sn + SnX_4 \rightarrow 2R_2SnX_2 \]  \hspace{1cm} (I)
\[ R_4Sn + SnX_4 \rightarrow R_3SnX + RSnX_3 \]  \hspace{1cm} (II)
\[ 2R_3SnX + SnX_4 \rightarrow 3R_2SnX_2 \]  \hspace{1cm} (III)
\[ R_4Sn + 2RSnX_3 \rightarrow 3R_2SnX_2 \]  \hspace{1cm} (IV)
\[ R_3SnX + RSnX_3 \rightarrow 2R_2SnX_2 \]  \hspace{1cm} (V)

The only exothermic reactions in this case are reactions I and II.
The heat of the gaseous redistributions reaction:

\[ \frac{3}{4}\text{Sn(CH}_3\text{)}_4 + \frac{1}{4}\text{SnBr}_4 \rightarrow (\text{CH}_3)_3\text{SnBr} \]

has been derived from the heats of formation of tetramethyltin and trimethyltin bromide and the value for \( \Delta H \), was found to be \(-10.8 \pm 3\) Kcal/mole which confirms Kocheshkov findings and requires the Sn-CH\(_3\) or the Sn-Br (or both) bond energy terms values to be enhanced in the trimethyltin bromide over those in tetramethyltin (176a).

In the case of tetraaryltin (108) the above reactions are less energetic than in the case of tetraalkyltin, thus tetraphenyltin does not react readily with stannic chloride at room temperature, but tetra-\( m \)-tolyltin reacts easily with evolution of heat giving mono- and di-\( m \)-tolyltin chlorides.

The action of carbon tetrachloride on tetraphenyltin has been studied (171) where on refluxing, in the presence of acetyl peroxide, \( \text{C}_2\text{Cl}_6 \) and 94% unreacted tetraphenyltin were obtained.

Investigations (182a) of the reactions between the tetraphenyl derivatives of tin and lead with a number of transitional metal chlorides indicated that in the case of the tin compounds total cleavage took place.

Although tetraethyltin does not react with phosphorus trichloride even under reflux phosphorus tribromide or a mixture of phosphorus and iodine attacks tetraethyltin giving triethyltin bromide and triethyltin iodide respectively (191).

Water and aqueous methanol were found (286) to be active cleaving reagents for the compounds \( \text{Ph}_2\text{SnR}, \text{Ph}_2\text{SnR}_2, \text{PhSnR}_3 \) and \( \text{R}_4\text{Sn} \) (where \( \text{R} \) = 9-fluorenyl or 1-indenyl group). Towards HgI, the compounds of both series
behaved differently; in the indene series the indenyl group was cleaved first, but in the fluorene series the phenyl group was cleaved first (266).

Photochemical reactions (182) between diethylidiphenyltin and carbon tetrachloride, chloroform or methanol proceeds through the cleavage of the phenyl radical which then reacts with solvent to give respectively chlorobenzene and benzene. The action of light on solutions of dibenzylidiphenyltin in various solvents has been studied (182) but in most cases no significant amount of bibenzyl could be isolated.

Aldridge and Cremer (1) have reported recently that tetraethyltin slowly liberates "triesthyltin upon storage under laboratory conditions either neat or in chloroform solution". Harada has reported similar results (81).

Calingaert and Beatty (23) have studied a new type of reaction "in which all the radicals or atoms of one kind, present in a mixture in which they are linked to one or more central groups or atoms of another kind, are interchanged between all the central groups present. This process, which is termed 'redistribution reaction' takes place smoothly at low temperature in the liquid phase and under the influence of a catalyst. The yield is quantitative, and the composition of the resulted mixture can be calculated from that of the reactents on the basis of random distribution of the interchanged radicals or atoms: this reaction product is therefore termed 'random equilibrium mixture'".

In general, the following reaction will take place between $R_nM$ and $R'_nM'$ in the presence of a catalyst under suitable conditions:

$$R_nM + R'_nM' \rightarrow R_nM + R_{n-1}R'M + R_{n-2}R'M' + \cdots + R'R_{n-1}M + R'nM + R_nM' + R'nM'$$

$$+ R'_{n-1}R'M' + R'_{n-2}R'M' + \cdots + R'R'n'_{n-1}M' + R'n'M'$$
Most of the systems that have been studied (23-8) were tetraalkylleads and alkyllead halides also. A few tetraalkyltin compounds (29) have been investigated. In particular, the systems Me₄Sn, Et₄Sn and Me₄Sn, Et₄Pb have been studied and for the latter, it has been found that the affinity of tin and lead for the methyl and ethyl groups was the same. However, it has been shown (30) that mercury has a greater affinity than lead for the methyl group with respect to the ethyl group. It is interesting to note that alkylsilicon compounds behave in a similar fashion to the lead and tin analogues. The redistribution reaction also takes place in aliphatic halides and esters (31).

The thermal decomposition of metal alkyls is considered in the majority of cases to proceed through the formation of free radicals (227). It has been shown earlier that the photolysis of organotin compounds, as well as those of germanium and lead, also proceeds via free radical chain reaction (51,183,236).

However, Waring and Horton (252) have decided upon a rearrangement mechanism for the thermal decomposition of tetramethyltin and for a number of organometallic compounds of silicon (251). Other workers have suggested similar mechanisms for tetraethylgermanium (66). Waring and Horton (252) discussed their results on the basis of the high activation energies which, in their opinion, favour this type of mechanism over a free radical chain mechanism which does not require high activation energy. However, their conclusion has been disputed (200) and their experimental results which they fitted to a first order rate constant at high initial pressures, approaching a second order rate at low initial pressures, have been better fitted to a three halves order rate constant. It has also been pointed out that a free
radical chain reaction may require high activation energy. Further, Waring and Horton (252) in their discussion of the activation energies of the thermal decomposition of the tetraalkyls of silicon, germanium, tin and lead could not explain the rather low activation energy for tetraethyllead. The activation energies of a number of tetraalkyls are given in Table 26. It is interesting to note the decrease in the activation energy for the silicon compounds as the number of carbon atoms in the allyl chain increases. This tendency may be caused by the negative effect of the methyl group (251, 252).

The rearrangement mechanism suggested by Waring and Horton (252) for the thermal decomposition of tetramethyltin is given by the following equations:

\[ \text{Sn} + 2\text{C}_2\text{H}_4 + 2\text{H} \quad \text{.........I} \]
\[ \text{Sn(\text{CH}_3)_4} \rightarrow \text{Sn} + \text{C}_2\text{H}_4 + 2\text{OH}_4 \quad \text{.........II} \]
\[ \text{Sn} + \text{C} + 3\text{CH}_4 \quad \text{.........III} \]

At high initial pressures, the ratio of final to initial pressures points to reaction III as the principal stoichiometric reaction with reaction I second in importance. However, at low initial pressures, the ratio increases and more complicated reactions may take place.

As Sathyamurti et al (200) points out a better explanation of Waring and Horton's experimental results would be obtained if a free radical mechanism operated.

Waring and Horton (252) themselves suggested its presence but concluded that it only takes place to a very limited extent. This mechanism is supported by the fact that the majority of organometallic
### Table 26

**Activation Energies for the Decomposition of Tetralkyl Compounds of Silicon, Germanium, Tin and Lead**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Activation energy $E_a$ cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_4\text{Si}$</td>
<td>79000 (a)</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{Sn}$</td>
<td>82000 (b)</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{Si}$</td>
<td>51000 (c)</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{Ge}$</td>
<td>51000 (d)</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{Pb}$</td>
<td>37000 (e)</td>
</tr>
<tr>
<td>$(\text{n-C}_3\text{H}_7)_4\text{Si}$</td>
<td>46000 (c)</td>
</tr>
</tbody>
</table>

(a) D. Helm and E. Mack (84).
(b) C.E. Waring and W.S. Horton (252).
(c) C.E. Waring (251).
(d) R.L. Geddes and E. Mack (66).
(e) J.A. Leermakers (126).
compounds are found to decompose through free radical chain reactions (227, 261). Also, mass spectra (49) of the tetramethyls of carbon, silicon, germanium, tin and lead have shown that the main product of the decomposition was \((\text{CH}_3)_2\text{M}\). Paneth and Leutsch (173) have been able to produce a relatively stable benzyl radical from the decomposition of tetrabenzyltin. However the work of Gordy and McCormick (79) on the paramagnetic resonance spectrum of X-irradiated frozen (at 77\(^\circ\)K) tetramethyltin has failed to identify the radicals formed but one type appears to be \((\text{C}_2\text{H}_4)^+\). This finding although is inconclusive might be an indication of the possible correctness of Waring and Horton rearrangement mechanism.

The following equations represent the postulated free radical chain mechanism for the thermal decomposition of tetramethyltin (200):

\[
\text{(CH}_3)_4\text{Sn} \rightarrow \text{Sn(CH}_3)_3 + \text{CH}_3 \quad \quad \quad \quad \quad I
\]

Sn(CH\(_3\)_3 may further break down and give more methyl radicals and finally metallic tin.

\[
\text{Sn(CH}_3)_4 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{Sn(CH}_3)_2\text{CH}_2 \quad \quad \quad \quad \quad \text{IIa}
\]

\[
\text{Sn(CH}_3)_2\text{CH}_2 \rightarrow \text{CH}_3 + \text{(CH}_3)_2\text{Sn=CH}_2 \quad \quad \quad \quad \quad \text{IIb}
\]

The unsaturated product may undergo further reaction or polymerization accounting for the solid product obtained in the reaction. Reactions IIa and IIb constitute the chain propagation stage. The chain breaking stage is the recombination of the methyl radicals:

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad \quad \quad \quad \quad \text{III}
\]

The presence of hydrogen and ethylene in the reaction product is accounted for by a rearrangement reaction as suggested by Waring and Horton (252) but it is not the prominent reaction.
One important objection, however, to the above mechanism is the postulated intermediate in reaction IIb which, according to the discussion presented in section ... seems to be highly improbable.

The heat of formation of some tin tetraalkyls have been calculated (49a) from the heat of combustion and the available data are given in Table 26a.

The catalytic decomposition of organometallic compounds of tin have been investigated (113a, 181a, 181b) and it have been found that the addition of metal powders lowers the decomposition temperature of tetraphenyltin to 175°C under hydrogen pressure.

B. COMPOUNDS CONTAINING Sn-Sn BOND.

A number of compounds with Sn-Sn bonds has been prepared including both alkyls, aryls and mixed alkyl-aryls. Also compounds with 3, 4 and 5 tin atoms in a chain have been prepared in the alkyl series (118,119, 212).

The ditin compounds are quite stable and distil unchanged, but the hexaalkyltin compounds are oxidized by air to form the oxide R₂Sn₂O₃. Other reagents attack the Sn-Sn bond e.g. mercuric chloride and bromide sodium in liquid ammonia, ethyl iodide and methyl iodide. It is interesting to note that ethyl iodide is converted into butane while methyl iodide adds to Et₂Sn₂SnEt₂ to form Et₂SnI and MeEt₂Sn. Hexaphenylditin, on the other hand, is more stable in air, but the Sn-Sn bond is cleaved by bromine solution in chloroform and by silver nitrate solution in alcohol (212).

Alkylpolystannanes i.e. with more than one Sn-Sn bond in a chain are known. They are, in general, colourless oily liquids, oxidizable by...
### TABLE 26a.

HEATS OF COMBUSTION AND HEATS OF FORMATION OF SEVERAL TIN TETRAALKYLIS AT 300°K AND 760 mm Hg.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta H$ Comb.</th>
<th>Calc'd $-\Delta H$ Comb(a)</th>
<th>Form. $-\Delta H$ Comb(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kcal/mole</td>
<td>Kcal/mole(a)</td>
<td>Kcal/mole(a)</td>
</tr>
<tr>
<td>$\text{Me}_4\text{Sn}$</td>
<td>$934 \pm 3^a$</td>
<td>920</td>
<td>$+9$</td>
</tr>
<tr>
<td></td>
<td>$904 \pm 10^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Me}_3\text{SnEt}$</td>
<td>$1034 \pm 5^a$</td>
<td>1077</td>
<td>$+53$</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SnEt}_2$</td>
<td>$1221 \pm 5^a$</td>
<td>1234</td>
<td>$+28$</td>
</tr>
<tr>
<td>$\text{Me}_3\text{SnEt}_3$</td>
<td>$1358 \pm 1^q$</td>
<td>1391</td>
<td>$+54$</td>
</tr>
<tr>
<td>$\text{Et}_4\text{Sn}$</td>
<td>$1547 \pm 2^a$</td>
<td>1598</td>
<td>$-27$</td>
</tr>
<tr>
<td></td>
<td>$1521^c$</td>
<td>$-39^c$</td>
<td></td>
</tr>
<tr>
<td>$\text{Et}_2\text{SnBu}_2$</td>
<td>$2170 \pm 2^a$</td>
<td>2176</td>
<td>$-54$</td>
</tr>
<tr>
<td>$\text{Bu}_4\text{Sn}$</td>
<td>$2816 \pm 4^a$</td>
<td>2804</td>
<td>$-57$</td>
</tr>
<tr>
<td></td>
<td>$2773^c$</td>
<td>$-111^c$</td>
<td></td>
</tr>
<tr>
<td>$(\text{C}<em>6\text{H}</em>{13})_4\text{Sn}$</td>
<td>$4060^a$</td>
<td>$4060$</td>
<td>$-119$</td>
</tr>
</tbody>
</table>


(b) E.R. Lippincott and M.C. Tobin (140)

(c) W.J. Jones, D.P. Evans, T. Gulwell and D.C. Griffith (100).
air to white solids. No arylpolystannane has been prepared (212).

Although the structure of the ditins has not been determined, it can be considered to be similar to that of the dilead compounds. Lead, in hexamethyldiyllead, has been found (214) by electron diffraction methods to have a tetrahedral configuration.

Some of the most interesting problems of organotin chemistry are the molecular weight determinations and magnetic measurements on the alkyl- and hexaaryl-ditins (212). The vapour density of Et₆Sn₂ at 225°C was found (212) to agree with the dimeric formula. However, the results obtained in solutions are conflicting. While it was found that Et₆Sn₂ is about 50% dissociated to the monomers (Et₃Sn) in 2% boiling ether solution, in 1.3% freezing benzene solution it was very little dissociated. Kraus (117) using the ebullioscopic method found that at the boiling point of benzene, hexamethylditin is almost completely dissociated to the monomer at low concentration and dimeric at high concentration. However, Morris, Byerly and Selwood (154) have carried out ebullioscopic measurements on hexamethyl-ditin in benzene solution and found that the elevation of the boiling point of benzene was always lower than that calculated for complete dissociation and failed rapidly with time indicating the unreliability of such methods in the study of these compounds. Other investigators (99) have found that the cryoscopic measurements on some dihalotetraalkylditins, such as 1,2-dichlorotetra-n-butyliditin, in benzene or dioxan solutions did not give the monomeric molecular weights but varied over a wide range indicating again that these methods should only be considered with reserve. Harada (81) has found similar trends in his values of
cryoscopically determined molecular weights.

Magnetic measurements (101, 163, 164) on the other hand, have shown the absence of any monomeric forms, not only in the case of hexamethylditin but also in hexa-o-tolyliditin which were found to be diamagnetic and any dissociation, even of a few percents, would have been detected.

Exactly similar situation exists in the analogous compounds of germanium and lead (62,95,163,164,179,207).

It has been found (69) that when hexaphenyldilead is allowed to react with maleic anhydride, compound I is obtained instead of the expected compound II, indicating that hexaphenyldilead is behaving like hexaphenylethane, although magnetic measurements (179) indicated no dissociation of the lead compounds. It would be interesting to see whether the analogous germanium and tin compounds behave similarly.

In an endeavour to explain the apparent controversy over the nature of the Sn-Sn bond, few suggestions have been put forward (163,164,167). One line of approach is to explain the apparent instability of organo-
metallic radicals of geranium, tin and lead by suggesting that the increase in the size of the central atom in descending the group increases the possibility of collision of these organometallic radicals, if they be formed, and this hastens their subsequent recombination. This is assisted by the fact that steric hinderance is substantially reduced and repulsion between the non bonded groups or atoms in the dimeric form, which operate in the hexa-substituted ethanes and tends to weaken the C-C bond, does not operate in the analogous germanium, tin and lead compounds. The second line of approach is to explain away the molecular weights of these compounds as determined by cryoscopic and ebullioscopic methods, by suggesting (163, 164) that these compounds decompose in solution but no experimental evidence is available to verify it.

The bond energies and bond lengths for the M-M bonds of group IV are given in Table 27 where the variation in bond energy with bond length can be noted.

C. COMPOUNDS CONTAINING Sn-H BONDS:

Alkyl and aryl tin hydrides can be considered as derivatives of stannane SnH₄. Although the monohydride SnH has been detected and studied spectroscopically (67, 88, 253-255) and the hydrides of silicon and germanium are well known (94, 228, 237), no spectral data are available for stannane.

Paneth obtained SnH₄ by electrolytic reduction, but the yield was very poor (212). Later, reduction of anhydrous stannic chloride with lithium aluminum hydride or lithium hydride was employed with some success (61). Recently (203) an acid solution of tin has been reduced by sodium
### Table 27

**Bond energy and bond length of M-M bonds of Group IV elements**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length Å</th>
<th>Bond energy Kcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>1.541 (a)</td>
<td>66.2 (c)</td>
</tr>
<tr>
<td>Si-Si</td>
<td>2.346 (a)</td>
<td>45 (d)</td>
</tr>
<tr>
<td>Ge-Ge</td>
<td>2.446 (a)</td>
<td>44.6 (d)</td>
</tr>
<tr>
<td>Sn-Sn</td>
<td>2.811 (a)</td>
<td>35.0 (d)</td>
</tr>
<tr>
<td>Pb-Pb</td>
<td>2.88 (b)</td>
<td></td>
</tr>
</tbody>
</table>

(a) From E.C. Baugham (11). These values were obtained from the pure elements in the solid state (the diamond form).

(b) From H.A. Skinner and L.E. Sutton (214). This value was obtained from electron diffraction experiments on gaseous hexamethyldiethane.

(c) From T. L. Cottrell (39).

(d) From H.O. Pritchard and H.A. Skinner (180).
borylhydride to $\text{SnH}_4$ in as high a yield as 84%.

The stability of the hydrides of group IV elements decreases on descending the group. There is a big jump in the strength of the $\text{M-H}$ bond between carbon and silicon (see Table 16). Taft and Sisler (231) have compared some of the physical properties of these hydrides. Table 28 gives the melting and boiling points of the hydrides and their decomposition temperatures.

The kinetics of the decomposition of tin hydride ($\text{SnH}_4$) has been studied by Tamaru (233) who found that it was a first order reaction with an activation energy of 9.1 Kcal/mole. It has also been found that the decomposition took place on the initially deposited tin film on the wall of the reaction vessel and thus there was an induction period. The introduction of oxygen stopped the reaction by forming an oxide film over the tin film. In the case of germane ($\text{GeH}_4$) it has been found (60,232) that it was a zero order reaction with respect to germane, and an activation energy of 41.2 Kcal/mole was obtained. The introduction of oxygen in this case accelerated the reaction and lowered the activation energy to 38.2 Kcal/mole, indicating a totally different mechanism for the decomposition of the two hydrides.

The alkyl and aryl tin hydrides are more stable than stannane and the stability increases as a number of substituents increases (49a, 61).

The addition of organotin hydrides of the general formula $\text{R}_2\text{SnH}$ to olefinic double bond is of great interest (106). While the addition of polyhalomethane, trichlorosilane and trichlorogermane to an olefin with a terminal double bond proceeds via free radical type mechanism, the addition of the organotin hydrides seems to occur by an ionic
TABLE 28

FEW PHYSICAL CONSTANTS OF THE HYDRIDES MH₄. (a)

<table>
<thead>
<tr>
<th>MH₄</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>-161.3</td>
<td>-111.9</td>
<td>-90</td>
<td>-52</td>
<td>ca  -13</td>
</tr>
<tr>
<td>Melting point</td>
<td>-182.7</td>
<td>-185</td>
<td>-165</td>
<td>-150</td>
<td>-</td>
</tr>
<tr>
<td>Decomposition temperature</td>
<td>800</td>
<td>450</td>
<td>285</td>
<td>150</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) From N.V. Sidgwick (212)
type mechanism. Both alkyl and aryl derivatives can undergo the reaction which can be presented as:

\[ \text{R}_3\text{SnH} + \text{CH}_2=\text{CHX} \rightarrow \text{R}_3\text{SnC}_2I_2-\text{CH}_2X \]

where \( X \) is a functional group.

Gilman and Rosenberg (74) have studied the reaction of triphenyl tin hydride with methylithium and found that it reacts in a similar way to the reaction of analogous compounds of group IV elements i.e.:

\[ \text{Ph}_3\text{SnH} + \text{MeLi} \rightarrow \text{Ph}_3\text{SnMe} + \text{Ph}_4\text{Sn} + \text{LiH} \]

contrary to previously reported reaction (74):

\[ \text{Ph}_3\text{SnH} + \text{MeLi} \rightarrow \text{Ph}_3\text{SnLi} + \text{CH}_4 \]

Lide (137) has measured the microwave spectrum of methylstannane (\( \text{CH}_3\text{SnH}_3 \)) and found that it has a dipole moment of \( 0.68 \pm 0.03 \) Debye unit.

Some of the physical properties of alkyl and aryl tin hydrides are listed in Table 29.

D. COMPOUNDS CONTAINING Sn-Hal BONDS.

Electron diffraction measurements have shown that organotin halides (20,141,215) like the tetrahalides (17,18,19) have tetrahedral configuration.

Dipole moment measurements on the tetrahalides and organotin halides have supported the tetrahedral configuration. However, the slight moment (0.8 Debye unit) of stannic chloride was thought, at first (13,14), to be caused by a pyramidal structure of the stannic chloride molecule rather than a tetrahedral structure as in CCl\(_4\) and SiCl\(_4\), which have zero dipole moment (123, 223,241-2). Later, the rather small moment of SnCl\(_4\) was explained as being caused by molecular compound formation with the solvent molecules e.g. benzene, dioxane etc. The formation of these
### Table 29

**Physical Constants of Some Alkyltin Hydrides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling point°C</th>
<th>Heat of vaporization cal/mole</th>
<th>Traunton constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃SnH₃ (a)</td>
<td>0</td>
<td>5750</td>
<td>21.0</td>
</tr>
<tr>
<td>(CH₃)₂SnH₂ (a)</td>
<td>35</td>
<td>6790</td>
<td>22.1</td>
</tr>
<tr>
<td>(CH₃)₃SnH (a)</td>
<td>59</td>
<td>7240</td>
<td>21.8</td>
</tr>
<tr>
<td>C₂H₅SnH₃ (b)</td>
<td>35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C₂H₅)₂SnH₂ (b)</td>
<td>99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C₅H₅)₃SnH (b)</td>
<td>142</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C₆H₅)₂SnH₂ (c)</td>
<td>Unstable</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C₆H₅)₃SnH (c)</td>
<td>173/6 mm</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) From A.E. Finholt, A.C. Bond, K.E. Wilzbach and H.I. Schlesinger (61)

(b) C.R. Dillard, E.H. McNeill, D.E. Simmons and J.B. Yeldell (49a)

(c) From N.V. Sidgwick (212).
molecular compounds has been found (124, 190, 240) in a number of cases and electronic absorption spectra have supported their presence.

In the tin compounds (136, 220, 223) there is no marked deformation of the tetrahedral angles unlike the analogous compounds of carbon, silicon and germanium. This is, undoubtedly, due to the larger size of the tin atom which increases the distance between the attached dipoles and evidently decreases the mutual inductive effect of these dipoles.

Electron diffraction data have shown that the Sn-Hal bond distance is less than the sum of the covalent radii, this has, also, been found in the case of other halides of group IVB elements. Table 30 compares the measured bond lengths with the values calculated from Pauling's covalent radii.

Electric dipole moment measurements have indicated that the M-Hal bond (where M = Ge, Sn or Pb) possesses a rather high percentage of ionic character which is contributed by the electronegativity differences of the bonded atoms. Table 31 gives the electric dipole moments for a number of organotin halides and their silicon, germanium and lead analogues. The bond moments and percentage ionic character of the bonds calculated from the former and from electronegativities are given in Table 32 (104, 135, 136, 146-9, 170, 218-22).

Two approaches were made to explain the bond shortening in the organometallic halides. Figure 3 in which percentage contraction is plotted against number of halogen atoms in the molecule indicates the general trend.

Brockway (17, 18, 20, 21) suggested, on the basis of the rather low value for the dipole moment of chlorosilane compared with the chloromethanes,
TABLE 30
THE M-Hal bond lengths for the elements of group IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>Obs. l(_{\text{M-Hal}})</th>
<th>Calcd l(_{\text{M-Hal}})</th>
<th>(\frac{\text{Obs.}}{\text{Calcd}})</th>
<th>% contraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)F</td>
<td>1.42 (a)</td>
<td>1.41</td>
<td>0.01</td>
<td>0.71</td>
</tr>
<tr>
<td>CF(_4)</td>
<td>1.36 (a)</td>
<td></td>
<td>-0.05</td>
<td>-3.5</td>
</tr>
<tr>
<td>CH(_2)Cl</td>
<td>1.77 (a)</td>
<td>1.76</td>
<td>0.01</td>
<td>0.56</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>1.77 (a)</td>
<td></td>
<td>0.01</td>
<td>0.56</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>1.77 (a)</td>
<td></td>
<td>0.01</td>
<td>0.56</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>1.76 (a)</td>
<td></td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>CH(_2)Br</td>
<td>(2.06) (a)</td>
<td>1.91</td>
<td>(0.15)</td>
<td>(7.9)</td>
</tr>
<tr>
<td>CH(_2)Br(_2)</td>
<td>1.91 (a)</td>
<td></td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>CHBr(_3)</td>
<td>(2.03) (a)</td>
<td></td>
<td>(0.12)</td>
<td>(6.2)</td>
</tr>
<tr>
<td>CBr(_4)</td>
<td>1.94 (a)</td>
<td></td>
<td>0.03</td>
<td>1.6</td>
</tr>
<tr>
<td>CH(_3)I</td>
<td>(2.28) (a)</td>
<td>2.10</td>
<td>(0.18)</td>
<td>(8.5)</td>
</tr>
<tr>
<td>CH(_2)I(_2)</td>
<td>(2.28) (a)</td>
<td></td>
<td>(0.18)</td>
<td>(8.5)</td>
</tr>
<tr>
<td>CHI(_3)</td>
<td>2.12 (a)</td>
<td></td>
<td>0.02</td>
<td>0.95</td>
</tr>
<tr>
<td>CI(_4)</td>
<td>2.15 (b)</td>
<td></td>
<td>0.05</td>
<td>2.4</td>
</tr>
<tr>
<td>SiH(_3)Cl</td>
<td>2.06 (c)</td>
<td>2.16</td>
<td>-0.10</td>
<td>-4.6</td>
</tr>
<tr>
<td>SiH(_2)Cl</td>
<td>2.02 (c)</td>
<td></td>
<td>-0.14</td>
<td>-6.5</td>
</tr>
<tr>
<td>SiHCl(_3)</td>
<td>2.01 (c)</td>
<td></td>
<td>-0.15</td>
<td>-6.9</td>
</tr>
<tr>
<td>SiCl(_4)</td>
<td>2.00 (c)</td>
<td></td>
<td>-0.16</td>
<td>-7.4</td>
</tr>
<tr>
<td>SiBr(_4)</td>
<td>2.152 (b)</td>
<td>2.31</td>
<td>-0.16</td>
<td>-6.9</td>
</tr>
<tr>
<td>SiI(_4)</td>
<td>2.43 (b)</td>
<td>2.50</td>
<td>-0.07</td>
<td>-2.8</td>
</tr>
<tr>
<td>GeHCl(_3)</td>
<td>2.1139 (d)</td>
<td>2.21</td>
<td>-0.10</td>
<td>-4.5</td>
</tr>
</tbody>
</table>
### TABLE 30 (Concluded)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Obsd. $M_{\text{Hal}}$</th>
<th>Calcd. $M_{\text{Hal}}$</th>
<th>$\frac{\text{Obsd.} - \text{Calcd.}}{\text{Calcd.}}$</th>
<th>% concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeCl$_4$</td>
<td>2.08 (a)</td>
<td></td>
<td>-0.13</td>
<td>-5.9</td>
</tr>
<tr>
<td>GeBr$_4$</td>
<td>2.29 (b)</td>
<td>2.36</td>
<td>-0.07</td>
<td>-3.0</td>
</tr>
<tr>
<td>GeI$_4$</td>
<td>2.50 (b)</td>
<td>2.55</td>
<td>-0.05</td>
<td>-2.0</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_2$Cl</td>
<td>2.37 (e)</td>
<td>2.39</td>
<td>-0.02</td>
<td>-0.8</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_2$Cl$_2$</td>
<td>2.34 (e)</td>
<td></td>
<td>-0.05</td>
<td>-2.1</td>
</tr>
<tr>
<td>Sn(CH$_3$)Cl$_3$</td>
<td>2.32 (e)</td>
<td></td>
<td>-0.07</td>
<td>-2.9</td>
</tr>
<tr>
<td>SnCl$_4$</td>
<td>2.30 (a)</td>
<td></td>
<td>-0.09</td>
<td>-3.8</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_3$Br</td>
<td>2.49 (e)</td>
<td>2.54</td>
<td>-0.05</td>
<td>-2.0</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_2$Br$_2$</td>
<td>2.48 (e)</td>
<td></td>
<td>-0.06</td>
<td>-2.4</td>
</tr>
<tr>
<td>Sn(CH$_3$)Br$_3$</td>
<td>2.45 (e)</td>
<td></td>
<td>-0.09</td>
<td>-3.5</td>
</tr>
<tr>
<td>SnBr$_4$</td>
<td>2.44 (b)</td>
<td></td>
<td>-0.10</td>
<td>-5.9</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_3$I</td>
<td>2.72 (e)</td>
<td>2.73</td>
<td>-0.01</td>
<td>-0.4</td>
</tr>
<tr>
<td>Sn(CH$_3$)$_2$I$_2$</td>
<td>2.69 (e)</td>
<td></td>
<td>-0.04</td>
<td>-1.5</td>
</tr>
<tr>
<td>Sn(CH$_3$)I$_3$</td>
<td>2.68 (e)</td>
<td></td>
<td>-0.05</td>
<td>-1.8</td>
</tr>
<tr>
<td>SnI$_4$</td>
<td>2.64 (b)</td>
<td></td>
<td>-0.09</td>
<td>-3.3</td>
</tr>
<tr>
<td>PbCl$_4$</td>
<td>2.43 (b)</td>
<td>2.45</td>
<td>-0.02</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

(a) From L.O. Brockway, (19).
(b) From M.W. Lister and L.E. Sutton, (141).
(c) From L.O. Brockway and I.E. Coop, (21).
(d) From P. Venkatesworlu, R.C. Mockler and W. Gordy (245).
(e) From H.A. Skinner and L.E. Sutton (215).
### TABLE 31
ELECTRIC DIPOLE MOMENTS OF $R_nMHal_{4-n}$ COMPOUNDS OF GROUP IV

<table>
<thead>
<tr>
<th>Alk$_3$MHal</th>
<th>Me$_2$CCl</th>
<th>Me$_2$CBr</th>
<th>Me$_2$Cl</th>
<th>H$_2$SiCl</th>
<th>Et$_3$SiCl</th>
<th>H$_2$GeCl</th>
<th>Me$_2$SnBr</th>
<th>Et$_3$SnCl</th>
<th>Me$_2$PbCl</th>
<th>Et$_3$PbCl</th>
<th>Et$_3$PbBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound</td>
<td>2.15 (a)</td>
<td>2.21 (a)</td>
<td>2.13 (a)</td>
<td>1.28 (a)</td>
<td>2.07 (b)</td>
<td>2.03 (a)</td>
<td>3.32 (c)</td>
<td>3.44 (a)</td>
<td>4.47 (b)</td>
<td>4.39 (a)</td>
<td>4.46 (a)</td>
</tr>
<tr>
<td>max $\times 10^{18}$</td>
<td>1.95 (a)</td>
<td>1.99 (a)</td>
<td>1.99 (a)</td>
<td>1.17 (a)</td>
<td>2.35 (a)</td>
<td>2.21 (a)</td>
<td>3.28 (a)</td>
<td>3.44 (a)</td>
<td>4.21 (a)</td>
<td>4.32 (b)</td>
<td>4.39 (a)</td>
</tr>
</tbody>
</table>

- (a) From G.L. Lewis and C.P. Smyth, (135).

- (b) From L. Malatesta and R. Pizzotti, (147 - 9).
- (c) From M.E. Spaght, F. Hein and H. Pauling, (223).
### Table 32

**Bond Moments and Ionic Character of the M-Hal, Bonds.**

<table>
<thead>
<tr>
<th>Bond</th>
<th>min. bond moment (a)</th>
<th>min. % ionic character (a) from bond moments</th>
<th>electro-negativity difference (b)</th>
<th>% ionic character from electronegativity (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-Cl</td>
<td>2.0</td>
<td>19</td>
<td>1.3</td>
<td>35</td>
</tr>
<tr>
<td>Ge-Br</td>
<td>2.0</td>
<td>17</td>
<td>1.1</td>
<td>35</td>
</tr>
<tr>
<td>Sn-Cl</td>
<td>3.1</td>
<td>27</td>
<td>1.3</td>
<td>35</td>
</tr>
<tr>
<td>Pb-Cl</td>
<td>4.1</td>
<td>34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-Br</td>
<td>4.0</td>
<td>31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-I</td>
<td>3.4</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na-I</td>
<td>4.9</td>
<td>35</td>
<td>1.5</td>
<td>43</td>
</tr>
<tr>
<td>K-I</td>
<td>6.8</td>
<td>44</td>
<td>1.6</td>
<td>47</td>
</tr>
<tr>
<td>K-Cl</td>
<td>6.3</td>
<td>47</td>
<td>2.2</td>
<td>70</td>
</tr>
</tbody>
</table>

(a) From G.P. Smyth, (221)

P.F. Oesper and G.P. Smyth, (170)

(b) From L. Pauling, (174)
Fig. 3

- $\text{H}_n\text{SiCl}_{4-n}$
- $\Delta \text{H}_n\text{GeCl}_{4-n}$
- $\Box \text{Me}_n\text{SnCl}_{4-n}$
- $\times \text{Me}_n\text{SnBr}_{4-n}$
- $\triangledown \text{Me}_n\text{SnI}_{4-n}$
and the fact that in the tetramethyl derivatives of silicon, germanium, tin and lead no bond contraction has been observed, that the polarity of the bonds does not affect their length to any considerable extent. Both, the bond moments and bond lengths appear to be affected by a partial back coordination producing a double bond character in the bond, which is at its maximum in silicon (c.f. $M-C_{ar}$ bond discussed in section A).

Skinner and Sutton (215), on the other hand, supported, with some reservations, the opinion that bond shortening is due to the ionic character of the bond. They base their objection to the double bond character theory on the ground, that as the number of halogens in the molecule increases, the percentage contraction increases and since the double bond character theory requires a negative charge on the central metal atom for every double bond formed, it seems that the more negative the central atom gets the more it attracts negative charges this is contrary to experience. However, Skinner and Sutton have qualified the theory based on the electronegativity difference of the bonded atoms in such a way as to come to the conclusion that there are in fact two processes going on consecutively, the primary one is an ionization process which permits as a secondary one the formation of double bond from the halogen to the central atom, and it is to the last process the contraction of the bond length is due. The ionization process is important in order to offset the accumulation of negative charge on the central metal atom. However, the second process of rather less importance in the monohalides. In the dihalides, forms as $R-Sn-X^+$ contribute substantially to the structure of the molecule (215).
It is important to notice that in all the above discussions on bond contraction the fact remains that the value of the contraction is based on Pauling's covalent radii (174) which were determined from homopolar covalent bonds and therefore must be considered with some caution. The change in atomic radius with changes in bond number, coordination number and valency has been pointed out by Pauling (175). Work on the magnetic susceptibility (103,104) and molar refraction (49a) of organotin halides suggests that a compression of the central atom takes place as a halogen atom replaces an alkyl group and further compression takes place upon the replacement of a second alkyl group by another halogen atom.

Bayliss (12) from a consideration of atomic parachors as a measure of atomic volume calculated covalent radii for Si, Ge, Sn and Pb from their tetrachlorides and tetraethyls and showed that they are in good agreement with values obtained from electron diffraction experiments provided that the halogen or the carbon covalent radii were considered to remain constant.

Sanderson (193,195) used his concept of electronegativity to calculate the variation in the radius of an atom in a molecule with respect to its electronic environment and applied it to the case of bond shortening in the gaseous alkali halides. It would be interesting however to see if his argument will apply to the case of bond contraction in the organometallic halides of group IVB elements. The real problem is, in fact, the inadequacy of present day chemical theory rather than any misinterpretation of it. For even the theory of Skinner and Sutton fails to explain the change in the slope of the curves in figure 3 (showing % contraction against number of halogen atom) in going from dihalides to
trihalides. In fact their theory suggests that the monohalides should lie below a smooth curve connecting the di-, tri- and tetra- halides.

The infrared and Raman spectra for a group of organotin halides have been investigated (139, 250). A comparison of some of the fundamental frequencies of the series \((\text{CH}_3)_x\text{SnCl}_{4-x}\) \((x=4, 3, 2, 1\text{ or } 0)\) is shown in figure 4.

The Raman spectra of methylchlooroform of germanium and tin have been investigated by Volkriver, Tchakirian and Freymann (248) who suggested the ionic formula \(\text{H}^+(\text{MCl}_3^-)\) (where \(\text{M} = \text{Group IV element}\)). However, the covalent character of chloroform and the analogous compounds of silicon and germanium has been well established (44, 48, 58, 160, 245), but there is chemical evidence that in the case of germanochloroform in aqueous or alcoholic media ionization sets (59) giving rise to the equilibrium:

\[
\text{GeCl}_3 \rightleftharpoons \text{H}^+ + \text{GeCl}_3^-
\]

In the case of tin the tendency for ionization into \(\text{H}^+\) and \(\text{SnCl}_3^-\) is so great that covalent trichlorostannane is unknown. However, the chlorostannite ion \((\text{SnCl}_3^-)\) is readily hydrolysed to stannous oxide (58).

Exchange reaction between the halides of group IV elements have been studied (42-9, 203) and also among the halohydrides of the general formula \(\text{MHX}_3\). Halogens were found to be more mobile in \(\text{MHX}_3\) molecules than in \(\text{MX}_4\) and the mobility of the halogens increases in the halides in the following order \(\text{C} < \text{Si} < \text{Ge} < \text{Sn}\). The stability of the mixed halides, on the other hand, decreases in the order \(\text{Sn} < \text{Ge} < \text{Si} < \text{C}\).

Exchange reaction between anhydrous stannic chloride and organic chlorides have been investigated (82, 83, 87) and indeed many organic
reactions in which SnCl₄ takes part as a catalyst involves such exchange.

Kraus and Callis (114) and Kraus and Greer (115, 116) have investigated the electrochemical behavior of organotin halides of the type R₃SnHal, and considered them as "pseudo-electrolytes" since they have very low specific conductance in the pure state and in non-basic solvents such as nitrobenzene even though the dielectric constant of the solvent may be high. On the other hand, solution in basic solvents such as alcohols and amines are relatively good conductors. This behavior was attributed to the formation in the basic solvent of more electronegative groups by combination of the trialkyltin group with solvent molecule giving rise to ammonium or oxonium type salts. Compounds of these types formed between Me₃SnCl and Me₃SnI and amonia, aniline and pyridine have been separated. Study of the conductance of trimethyltin chloride in mixed solvents also supports the contention that the electrolytic behavior of these compounds in solutions is due to the formation of compounds of the oxonium and ammonium type.

However, recent work on the conductance of stannic chloride in thionyl chloride indicates the formation of Werner type complex (176) between SnCl₄ and pyridine, thus:

$$\text{C}_5\text{H}_5\text{N} + \text{SnCl}_4 \rightleftharpoons \text{C}_5\text{H}_5\text{N}:\text{SnCl}_3^{\text{+}} + \text{Cl}^-$$

$$\text{C}_5\text{H}_5\text{N}:\text{SnCl}_3^{\text{+}} + \text{C}_5\text{H}_5\text{N} \rightleftharpoons (\text{C}_5\text{H}_5\text{N}:)_2\text{SnCl}_4$$

Spectrophotometric studies of the ionization of triphenyl ethyl bromide (Ph₃CBr)(59) by stannic bromide in various solvents such as benzene and ethyl bromide indicate that the following reaction may take place:

$$\text{(C}_6\text{H}_5)_3\text{CBr} + \text{SnBr}_4 \rightleftharpoons \left[(\text{C}_6\text{H}_5)_3\text{C}^{\text{+}} \text{SnBr}_5^{-}\right]$$

$$\left[(\text{C}_6\text{H}_5)_3\text{C}^{\text{+}} \text{SnBr}_5^{-}\right] \rightleftharpoons \left[(\text{C}_6\text{H}_5)_3\text{CBr} \cdot \text{SnBr}_4^{-}\right]$$
If the tetrabromide is replaced by $\text{MeSnBr}_3$, the ionization of $\text{Ph}_3\text{CBR}$ in benzene solution is destroyed.

Compounds of the type $\text{R}_2\text{SnCl}_2$ have been studied (76,186) electrochemically and a number of theoretically important results were obtained. While organosilicon compounds hydrolyse readily and completely, the tin analogues can be handled quite easily in acid solutions and a number of salts of the type $\text{R}_2\text{SnX}_2$ and $\text{R}_2\text{SnX}_2$ have been prepared. Similarly, the tetrahalides of silicon hydrolyse much more rapidly than the stannic halides, also the mechanisms of the hydrolysies are markedly different (89).

It has been shown (76,186) that dimethyltin dichloride in water produces chloride ions and doubly charged dimethyltin ions ($\text{Me}_2\text{Sn}^{++}$) together with some hydrolysis products according to the equations:

$$(\text{CH}_3)_2\text{SnCl}_2 + n\text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{Sn(H}_2\text{O})_{n}^{++} + 2\text{Cl}^-$$

$$(\text{CH}_3)_2\text{Sn(H}_2\text{O})_{n}^{++} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{Sn(H}_2\text{O})_{n-1}\text{(OH)}^+ + \text{H}_3\text{O}^+$$

Cryoscopic measurements and hydrolysis constant determinations (186) indicate that in a 0.063 M solution at 25°C as little as 10.5% is hydrolysed. Further, hydrolysis of $\text{Me}_2\text{SnCl}_2$ with a base has been studied and it has been found that a precipitate was formed after the addition of one equivalent of the base, but it dissolved in two equivalents, indicating a reaction of the following type:

$$(\text{CH}_3)_2\text{Sn(H}_2\text{O})_{n}^{++} + 4\text{OH}^- \rightarrow (\text{CH}_3)_2\text{Sn(OH)}_{4}^{--} + n\text{H}_2\text{O}.$$ (n may be 4 or 6)

The ion ($\text{Me}_2\text{Sn}^{++}$) has been isolated (186) on a cation exchange column by running through an aqueous solution of $(\text{CH}_3)_2\text{SnCl}_2$.

Nevertheless, Thomas and Rochow (235a) have found that in N,N-dimethylformamide solutions the triphenyl chlorides of carbon, silicon, germanium and lead did not dissociate into organometallic cations and
chloride anions. Water may be responsible for the hydrolysis which causes the finite conductivity observed. However, some evidence was found for the ionization of organotin compounds in acetonitrile and in pyridene-nitrobenzene mixture. There is no doubt that under suitable conditions of solvation, organotin halides may be capable of ionization. Studies on the analogous silicon compounds showed that they do not produce organosilicon cation in pyridene, nitrobenzene, pyridene-nitrobenzene mixtures, nitrobenzene-aluminium trichloride mixtures and in liquid sulphur dioxide solutions. Thomas and Rochow (235b) have concluded from their conductimetric work that "the nonexistence of resonance-stabilized triphenylsiliconium ion and the lack of evidence for a similar ion from tris-$p$-dimethylaminophenylchlorosilane in systems which produce large amounts of analogous carbonium ions (support) the contention that silicon does not form double bonds with carbon of the $\pi$-type". The findings have strong bearing on the discussion presented earlier on the dissociation constants of the acids $p$-$R_3MO_2H_4COOH$ and the possibility of a $\pi$-$\pi$-bonding between atoms of Group IV and carbon.

Further studies of the dimethyltin cation led Rochow, Seyferth and Smith (187) to conclude that "in water and amines or amides the solvated cation probably remains tetrahedral, but we think that in anhydrous salts the $(CH_3)_2Sn^{++}$ ion resembles $:Sn^{++}$ (where the pair dots indicate the unused $5s^2$ electrons in the latter), and should also resemble $:Pb^{++}$ and $:Tl^{+}$ in structure.

Polarographic behaviours of trimethyltin, tri-$n$-propyltin and tri-$n$-butyltin halides have been studied in aqueous alcoholic solutions (37,38). They were found to be electroreducible and give well defined
polarographic waves which were similar for all these compounds. However, the reducing potential becomes more negative with rise in the electronegativity of the alkyl radical, for the same halide, in the following order:

\[(n-C_4H_9)_3Sn < (n-C_3H_7)_3Sn < (C_2H_5)_3Sn\]

Under suitable experimental conditions, three polarographic waves were obtained. The first two waves corresponded to the acquiring of one, two electrons per molecule respectively. The following electro-reduction mechanism was suggested (37):

\[
\begin{align*}
(1) & \quad 2(C_2H_5)_3Sn^+ + 2e^- \rightarrow \text{-1.1 volt} \rightarrow (C_2H_5)_6Sn_2 \\
(2) & \quad (C_2H_5)_3Sn^+ + 2e^- \rightarrow \text{-1.5 volt} \rightarrow (C_2H_5)_2Sn + C_2H_5^- \\
& \quad \quad \quad \quad \quad \rightarrow (C_2H_5)_4Sn + Sn
\end{align*}
\]

Processes (1) and (2) were found to be independent of one another but dependent on the cathode potential.

Polarographic investigations (238) on the dialkytin dihalides and on alkytin triiodides gave similar results to those obtained for the trialkylhalides. As in the work mentioned above, it has been found that the reduction potential of the metal in the organic compounds is different from that of the metal in an inorganic simple ion; and that it is a function of pH; and that the diffusion current limit is proportional, in many cases, to the concentration (238).

Aldridge and Cremer (1) have examined the action of sun light on triethylin tin dithizone complex in buffered solution in chloroform. They found that an exposure to sunlight triethyltin dithizone was converted into diethyltin dithizone.

Organotin compounds with ethylenic double bonds in the carbon chains have been prepared (168-9) and they were found to show cis-trans isomerism
e.g. \((\mathrm{ClCH=CH})_2\mathrm{SnCl}\) have been prepared in the \textit{cis}- and \textit{trans}- forms from the corresponding \(\mathrm{ClCH=CHHgCl}\). Irradiation of the molten \textit{trans}-isomer with ultraviolet light for 25 hours gave 40\% \textit{cis}-isomer. Compound with two or three chlorine atoms have been prepared in both \textit{cis}- and \textit{trans}- forms.

Although organotin trihalides are well known, their physical properties have not been studied to any great extent. The ultraviolet spectrum of methyltin triiodide has been measured by Allsop (2) who found that it resembles the ultraviolet spectra of other triiodides e.g. AsI\(_3\), BiI\(_3\), CHI\(_3\), etc. Thus indicating that the absorption bands can have the same origin, namely in the simultaneous production during irradiation of iodine atoms in the normal and the excited metastable state.

The thermal decomposition of dimethyltin dichloride have been studied (179a) by the toluene carrier technique between 554 and 688\(^\circ\)C. The results can be satisfactorily interpreted in terms of the following simple equations:

\[
\begin{align*}
(\text{CH}_3)_2\text{SnCl}_2 & \rightarrow \text{CH}_3\text{SnCl}_2 + \text{CH}_3 \\
\text{CH}_3\text{SnCl}_2 & \rightarrow \text{SnCl}_2 + \text{CH}_3 \\
\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{CH}_4 + \text{C}_6\text{H}_5\text{CH}_2 \\
2\text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \\
2\text{C}_6\text{H}_5\text{CH}_2 & \rightarrow (\text{C}_6\text{H}_5\text{CH}_2)_2
\end{align*}
\]

and they can be fitted to a first order rate equation. The rate constant of the overall reaction contained at pressure of 16.1 mm of Hg is given by:

\[
\log_{10} k = (13.52 \pm 0.1) - (56100 \pm 40/2.303RT)
\]
The activation energy (56.1 Kcal/mole) can be assumed equal to the dissociation energy $D(H_2C-Sn(CH_3)Cl_2)$. This dissociation energy is higher than the mean energy from Sn-O bonds in tetramethyltin which has been reported (176a) to be 53.5 3 Kcal/mole. This finding is in keeping with the observation that the redistribution reaction of tin tetrahalides with tin alkyls is exothermic (107, 110, 176a).

E. COMPOUNDS CONTAINING Sn-O BONDS:

Organotin compounds with hydroxyl groups attached to tin have been known for some time as the product of hydrolysis of the corresponding halides; and compounds of the type $R_3SnOH$ are also known in the alkyl series (212). They resemble the hydroxides (and in actual fact behave as such) rather than the alcohols. All three classes i.e. $R_3SnOH$, $R_2Sn(OH)_2$ and $RSn(OH)_3$ are known, but the monohydroxides are the most stable in the series, their stability decreasing in the order in which they are given. They all lose water on heating forming oxides in the case of the mono- and di-hydroxides or stannonic acids in the case of the trihydroxides. The oxides of the type $Ph_3Sn.O.SnPh_3$ behave as oxides rather than ethers, e.g. they hydrolyse. The monohydroxides dissolve in water, and the dissociation constants of the trimethyltin hydroxide and triethyltin hydroxide are $1.7 \times 10^{-5}$ and $\sim 10^{-5}$ respectively (212).

The monohydroxides disproportionate (202) on heating to high temperatures (for $Me_3SnOH$ 100°C and for $Ph_3SnOH$ 130-140°C.) giving tetramethyl and tetraphenyl tin respectively, together with the oxide $R_2SnO$:

$$2R_3SnOH \rightarrow R_4Sn + R_2SnO + H_2O.$$ 

The dipole moments of trimethyltin hydroxide and triphenyltin...
### Table 33

**Dipole Moments of Few Hydroxy Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu \times 10^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_3\text{COH}$</td>
<td>1.66 (a)</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_3\text{SiOH}$</td>
<td>1.50 (b)</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_3\text{SiOH}$</td>
<td>1.45 (b)</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_2\text{SnOH}$</td>
<td>1.91 (c)</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_2\text{SnOH}$</td>
<td>1.98 (c)</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_3\text{PbOH}$</td>
<td>2.4 (d)</td>
</tr>
</tbody>
</table>

(a) From J.W. Smith (217).
(b) From L. Malatesta and R. Pizzotti (147).
(c) From L. Malatesta and R. Pizzotti (148).
(d) From L. Malatesta and R. Pizzotti (149).
hydroxide have been measured (147-9) and found to approximate to the values for the alcohols rather than to the silanols, as can be seen from Table 33.

A number of salts have been prepared both from $\text{R}_3\text{Sn}^+$ and $\text{R}_2\text{Sn}^{++}$. Salts of $\text{R}_2\text{Sn}^{++}$ behave in general like the corresponding salts of $\text{Pb}^{++}$ and $\text{Tl}^+$ (187).

Stannonic acids are powders and generally insoluble and infusible materials. Phenyl stannonic acid reacts with mercuric oxide to give diphenylmercury. Similar reaction occurs with tolzystannonic acid (109,212).

The compound $(\text{CH}_3)_2\text{Sn}[,(\text{CH}_3)_3\text{Si}^2]_2$ has been prepared and its properties and infrared absorption spectrum have been studied (234).

Compounds of the general formula $\text{Sn}(\text{OR})_4$, where $\text{R}$ is an alkyl group, have been prepared (15a,15b) and some of their physical properties (densities and parachors) have been investigated.

F. COMPOUNDS CONTAINING Sn-M BONDS: (M=alkali metal)

A number of compounds containing Sn-Na and Sn-Li bonds are known (70,73,117). Generally the Sn-M bond is so unstable that if the compound is crystallized it will decompose rapidly giving hydrocarbon and an alloy of tin and the alkali metal. These compounds are highly coloured both in solutions and in the crystalline state.

Conductivity measurements (120,121) in liquid ammonia show that these compounds are good conductors especially triphenyltin sodium with dissociation constant 14.0 (c.f. trimethyltin sodium 0.36).

It has been found (72) that triphenyl tin lithium does not possess sufficient activity to add to the carbon-carbon double bond of trans-stilbene.
or to the carbon-oxygen double bond of carbon dioxide, benzophenone or benzalacetophenone, but it attacks the oxirane ring successfully.

G. COMPOUNDS CONTAINING BONDS BETWEEN TIN AND VARIOUS OTHER ELEMENTS:

Although there are a few organotin compounds containing bonds between tin and other elements such as Si, P and S other than those discussed in the previous sections, their physical properties have not been satisfactorily studied.

A number of compounds containing Sn-S bonds are known which are analogous to the oxides, but in general they have lower melting points than the oxides and therefore the Sn-S bond may be highly covalent (212).

Organophosphorus tin compounds of the general formula $R_2Sn(PO_2R')_2$ and $R_2Sn(PO_2R_2)_{2+}$ have been prepared (3,4) by applying the Arbuzov reaction to organotin halides e.g. $R_2SnX$ with $P(OR')_3$. These compounds decompose on heating and hydrolyse rapidly with dilute hydrochloric acid, HBr and dilute caustic soda. The former give the halides and the latter give the oxide $R_2SnO$. It is interesting to note that no compound was obtained by applying Arbuzov reaction to triphenyltin halides or to organolead compounds.
The configuration of bivalent tin has been discussed earlier. Bivalent tin is rather unstable in the covalent compounds and tends to oxidise itself to the quadivalent state (212).

\[ 2R_2Sn \rightarrow R_4Sn + Sn \]

The alkyl derivatives have never been isolated in the pure state but dimethyl and diethyl tin appear to be highly coloured compounds (212).

Dicyclohexyltin and diaryltin have been isolated as yellow crystals. They give bright yellow solutions in benzene. Their actual structure is not yet settled but it is very likely that they are polymeric in nature. Diphenyltin has been found (95) to be diamagnetic both in benzene solution and in the solid state. Cryoscopic measurements in benzene solution show that the compound is monomeric in fresh solution and polymerizes on standing, similar behaviour was exhibited by diethyltin in naphthalene (81). Diphenyltin has a dipole moment of 1 'Debye unit independent of the degree of polymerization. Jensen and Clausen-Kaas (95) explained the above properties on the basis of a biradical structure with formal bonds:

```
R R
R:Sn:Sn:R
```

or

```
R
R:Sn
```

III

or

```
R
R:Sn:Sn:R
```

or

```
R
R:Sn
```

IV

The alternative arrangement suggested by Leeper, Summers and Gilman (125) is:

```
C_6H_5-Sn: + Sn-C_6H_5 \rightarrow C_6H_5-Sn-Sn-C_6H_5 \rightarrow \text{higher polymer}
```

```
C_6H_5
```

V
in which complete disappearance of the formal charge separation, because of resonance, is prevented for steric reasons, since the valence state of the first tin atom in the dimer or polymer is different from that of the second tin atom; the former is in the sp$^2$, planar, state while the latter has the p$^3$, pyramidal, configuration (35, 125).

The decomposition of diphenyltin has been found (181b) to proceed via the formation of free radical, while the decomposition of dibenzyltin is a pure pyrolytic reaction.
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PART TWO

II.1. PREPARATION OF ORGANOTIN COMPOUNDS.

II.2. ABSORPTION SPECTROSCOPIC MEASUREMENTS.
THE most widely used method for the preparation of organotin compounds is the exchange reaction of tin tetrachloride and organomagnesium halide (9a). Other organometallic compounds have also been used such as dialkylzinc and organolithium compounds (9a). The latter has been used (1, 2) largely for the preparation of organotin compounds containing a functional group in the organic moiety such as -COOH, -N(CH₃)₂, -CH₂OH.

For the reaction:

$$\text{SnCl}_4 + 4\text{RMgX} \rightarrow \text{R}_4\text{Sn} + 4\text{MgXCl} \quad \ldots \ldots (1)$$

to proceed to completion and a good yield of the symmetrical organotin compounds $\text{R}_4\text{Sn}$ to be obtained, an excess of Grignard reagent has to be used, and the reaction has to be carried out in some cases at high reflux temperature e.g. at the reflux temperature of dibutyl ether or xylene. In the case of aryltin compounds, however, diethyl ether has been found to give an adequate reflux temperature. The yield in general of the aryl derivatives of tin is much higher than the yield of alkyltin compounds.

The above reaction is considered to proceed stepwise involving the formation of organotin halides (such as $\text{R}_2\text{SnX}_2$, $\text{R}_3\text{SnX}$) as intermediates. Hence excess Grignard reagent is required. In the case of aryltin compounds the reaction has been found to proceed to completion much easier than for alkyltin compounds.

For the preparation of aryltin halides, the Kocheshkov reaction
was used (See Part One p 55):

\[
\begin{align*}
3R_4Sn + SnCl_4 & \rightarrow 4R_3SnCl \\
R_4Sn + SnCl_4 & \rightarrow 2R_2SnCl_2 \\
R_4Sn + 3SnCl_4 & \rightarrow 4RSnCl_3
\end{align*}
\]

with good yield of the required product.

Difficulties, however, have been encountered in the preparations of dibenzyltin dichloride and benzyltin trichloride from the appropriate mixtures of tetrabenzyltin and tin tetrachloride. All attempts at separating a single product were unsuccessful. But, tribenzyltin chloride was obtained in good yield either from tetrabenzyltin and tin tetrachloride by utilizing reaction (2), or directly from an excess of tin tetrachloride and benzylmagnesium chloride in ether.

Both tetra-\(p\)-tolyltin and tetrakis-\(p\)-chlorophenyltin were prepared with reasonable yield from tin tetrachloride and Grignard reagents.

The preparation of triethyltin phenoxyde and of \(N\)-triethyltin phthalamido are straightforward and involve the condensation reactions of triethyltin hydroxide with phenol to obtain the phenoxyde and with phthalamido to obtain the \(N\)-substituted phthalamido.

**PHENYL Tin COMPOUNDS.**

Tetraphenyltin was prepared according to the method of Pfeiffer and Schurmann (12) as outlined by Luijten and van der Kerk (10) with some minor modifications, from phonylmagnesium bromide and tin tetrachloride.

The Grignard reagent was prepared in 2 litre three-necked flask from Mg turnings (47 gm, 2 gm atoms) and bromobenzene (200 ml, 292 gm,
2 mole) in 850 ml of anhydrous diethyl ether. The bromobenzene used has been especially dried and distilled prior to usage in the preparation. The bromobenzene was added dropwise after the reaction has been induced to start by adding few drops of bromine. The addition of bromobenzene was continued for 3½ hours while the reaction was proceeding at the reflux temperature of ether. The contents of the reaction vessel was then further refluxed for ½ hour and afterwards allowed to cool.

In the course of ½ hour tin tetrachloride (40 ml, 0.034 mole) was added dropwise, the flask being cooled with ice during the addition. The mixture was then refluxed for 6 hours and then allowed to cool. The excess Grignard reagent was decomposed using ice-cold water (100 ml) and 10% hydrochloric acid (500 ml) added dropwise while the flask was cooled in ice.

The etheral and the aqueous layers were then sucked away and the residue was digested four times with benzene (1200 ml) and filtered. The solution was then dried over anhydrous calcium chloride. Some of the benzene (1000 ml) was removed by distillation and the remainder (200 ml) was allowed to cool when tetraphenylditin was crystallized out (63.43 gm) m.p. 233°C. The ether was distilled from the etheral layer which has been dried over calcium chloride and the residue was recrystallized from benzene m.p. 231°C. The aqueous layer was treated with hot benzene to extract any product which was kept in suspension. The benzene extract was then dried over calcium chloride. Some of the benzene was distilled off and the product was deposited, m.p. 230°C.
The combined tetraphonyltin extracted from the etheronal and aqueous layers weighed 38.0 gm. The total yield of pure tetraphonyltin was 100.4 gm (74% of the theoretical amount) m.p. 235°C.

Triphonyltin chloride and phonyltin trichloride were prepared from mixtures of tetraphonyltin and tin tetrachloride by the method described by Idjton and van der Kork (10).

Diphonyltin dichloride was prepared according to Kochoshkov (4) from a mixture of tetraphonyltin and tin tetrachloride.

The yield and some physical constants of the phonyltin compounds are given below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p.</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraphonyltin</td>
<td>235°C</td>
<td>74%</td>
</tr>
<tr>
<td>Triphonyltin chloride</td>
<td>103</td>
<td>49</td>
</tr>
<tr>
<td>Diphonyltin dichloride</td>
<td>42</td>
<td>61</td>
</tr>
<tr>
<td>Phonyltin trichloride</td>
<td>136</td>
<td>57</td>
</tr>
</tbody>
</table>

**BENZYLITIN COMPOUNDS**

Tetrabenzyltin was prepared from tin tetrachloride and benzylmagnesium chloride following two different techniques. It was first decided to use the method of Smith and Kipping (13) who gradually added benzyl chloride (4 mole) to an etheronal 'solution' of tin tetrachloride (1 mole) in the presence of powdered magnesium (4 gm atom), they reported m.p. 42-43°C but did not report the yield of their preparations. However, several attempts were made to prepare tetrabenzyltin by the above method but the product always contained an appreciable amount of tribenzyltin chloride. Even when an excess of the benzyltin chloride and magnesium was used. The product of the reaction contained tribenzyltin chloride.
(29.6% yield based on the amount of tin tetrachloride used) m.p. 142°C; and tetrabenzyltin (34% yield) m.p. 44°C.

The second technique used is very similar to that outlined above for the preparation of tetraphenyltin. The product in this case contained very little tribenzyltin chloride and the yield of tetrabenzyltin was 43% of the theoretical amount.

Attempts at preparing dibenzyltin dichloride and benzyltin trichloride by following the method used for the analogous phonyltin compounds were unsuccessful. However, this was not unexpected for it is well known that the Kocheshkov reaction only proceeds to completion for aryltin compounds (3 - 7) and that for the alkyltin compounds the reaction seems to get complicated after the second stage.

**TETRAKIS-p-CHLOROPHENYL Tin:**

The preparation of this compound was carried out according to the method of Krauso and Weinberg (8) as outlined by Luijten and van der Kork (10). The product gave 30.5 g of pure tetrakis-p-chlorophenyltin (45.4% of the theoretical amount) m.p. 197-80°C.

**TETRA-p-TOLYTIN**

This compound has been prepared by Talalceva and Kocheshkov (15) from the reaction of Sn/Hg in ether with Li and p-bromotoluene giving a yield of 39% of the theoretical amount and m.p. 238°C. It has also been prepared (11) from the reaction of Sn/Na alloy with p-tolylmercury chloride.

In the present work, tetra-p-tolylltin was prepared from p-tolylmagnesium bromide and tin tetrachloride in dry ether.
The Grignard reagent was prepared from magnesium (13.6 gm 0.56 mole) and p-bromotoluene (95.8 gm 0.56 mole) in 225 ml of dry ether in 1 litre three-necked flask. Few drops of bromine were added to start the reaction which proceeded thereafter for 1 hour while p-bromotoluene is being added dropwise. The contents were then heated to the reflux temperature of ether for 1½ hour.

Tin tetrachloride (182 gm, 8.2 ml, 0.07 mole) solution in 50 ml dry benzene was added to the reaction mixture with cooling in the course of 10 min. The reaction mixture was then refluxed for 3 hours after which it was allowed to cool and the excess Grignard reagent was decomposed with ice-cold water (100 ml) and ice-cold 5% hydrochloric acid (200 ml). The product was then separated and purified as outlined above for the preparation of tetraphenyltin. 18 gm of pure tetra-p-tolyltin was obtained 53.2% of the theoretical amount, m.p. 235°C.

TRIETHYL Tin DERIVATIVES

Triethyltin hydroxide has been kindly offered by Dr. Joan A Reid to whom grateful thanks are due.

Triethyltin phenoxyde and N: triethyltin phthalimide were prepared by the methods given by Hijten and van dor Kerk (10) from triethyltin hydroxide (triethyltin phenoxyde b.p. 0.88 mm 103°C; N:triethyltin phthalimide m.p. 71°C)
11.2. **ABSORPTION SPECTROSCOPIC MEASUREMENTS**

(1) **THE ULTRAVIOLET ABSORPTION MEASUREMENTS**

The UNICAM SP500 photoelectric spectrophotometer was used throughout in the measurement of the ultraviolet absorption spectra. The instrument consists of hydrogen discharge lamp for use in the range 320 m\(\mu\) to 200 m\(\mu\), and a tungsten lamp for the 1000-320 m\(\mu\) region; a monochromator with 30° quartz prism and interchangeable blue- and red-photocells. The photocells output current is measured by balancing the drop across a load resistance of 2000 megohm with a slide wire potentiometer calibrated in both percentage transmission and optical density.

The wave length scale of the instrument was calibrated initially and checked frequently using the hydrogen lines at 6563 Å (red photocell) and 4861 Å (blue-photocell).

The density/percentage transmission scale was calibrated using an aqueous solution of potassium chromate in 0.05 M potassium hydroxide which has been found (16) to be suitable standard to obey Beer's law.

Cells with fused silica windows were used with path length of 2, 10, and 40 mm. All cells were used in pairs and they were calibrated against each other. When special accuracy was needed as for example at bands maxima, the solution and the solvent were exchanged without altering the position of the cells and the average of the two results obtained was taken.

The instrument was kept in a thermostated room at a temperature of 23 ± 2°C. All spectral measurements were carried out at the above
Solutions were made with especially purified solvents (see later) by weighing not less than 0.025 gm of the compound. Graduated flasks of 10, 20, 50 and 100 ml capacities were used. They were all thoroughly cleaned, dried and flushed with dry nitrogen before use. Volumetric errors were avoided by measuring all dilutions by weight. The concentration of solution and the path length were chosen so that all measurements fall between the optical density range 0.1 to 1.4. At the position of maxima, the concentration and the path length were chosen such as to give density in the range 0.2–0.9, and so ensure maximum reproducibility.

The spectra of the compounds were measured in the range 200–400 μm using cyclohexane and chloroform as solvents. The former covers the whole range while chloroform only transmits down to 232 μm. The lower limit of the transmission of chloroform was reached by using 2mm cells (14).

(2) THE INFRARED ABSORPTION MEASUREMENTS:

The HILGER HBO0 double beam recording infrared spectrophotometer was used. It consists of Nernst heater as a source of infrared radiation, photoelectric unit based on the "Double Beam in Time" principle, a monochromator with rock-salt optics, the detection (thermopilo) and pre-amplification system, and a high speed recorder.

The spectrometer is of the Littrow type using 60° rock-salt prism and an off-axis paraboloid as collimator mirror. The scanning arrangement ensures a scale linear in wave number. The detector
used is a Schwarz thermopile which is connected to the pre-amplifier of the electric circuit via a step up transformer.

Scanning of the spectra is affected by the rotation of the Littrow mirror which is connected to the wave number cam. The wave number cam is driven by a synchronous motor via a gearbox and the rate of scanning can be selected; there are 8 such speeds ranging from 15 min. to 300 min. per full revolution of the cam.

The photoelectric part of the instrument is based on the "Double Beam in Time" principle. Two beams, the 'test' beam and the 'reference' beam are obtained from the Nernst lamp and are alternatively passed on to the entrance slit of the spectrometer by a vibrating mirror. Any difference of energy between the two beams produces an A.C. signal at the detector which is amplified and applied to a phase-sensitive servo motor which in turn drives a rectangular aperturc in the reference beam in such a direction as to reduce the energy difference. Thus the energies of the two beams are maintained at balance. The area of the aperturc is therefore a measure of the energy in the 'test' beam relative to that in the 'reference' beam at the same place in the spectrum i.e. it measures the percentage transmission of the sample placed in the 'test' beam. The size of the aperturc is continuously recorded on the recorder chart by means of a D.C. signal voltage derived from a potentiometer coupled to the drive of the aperturc. Even at 5% transmission the height of the aperturc is still 0.1" with the full width of nearly 2" so that dust and diffraction troubles are negligible in the measuring system.
In order to maintain an approximately constant reference energy level throughout each range of the optics used, a slit opening device is provided. The slit widths mostly used in the present work are the following:

- Range 4000 - 2500 cm$^{-1}$, slit width of 0.10 - 0.15 mm
- " 2000 - 1500 cm$^{-1}$, " " 0.15 - 0.25 mm
- " 1500 - 900 cm$^{-1}$, " " 0.25 - 0.40 mm
- " 900 - 650 cm$^{-1}$, " " 0.40 - 0.55 mm

The wave number scale of the instrument in the range 4000 - 650 cm$^{-1}$ was calibrated using the absorption of atmospheric carbon dioxide and water vapour by adjusting the instrument for single beam work. The spectra of CO$_2$ and H$_2$O in air cover most of this range, they give rise to the following bands at 3882, 3741 and 3617 cm$^{-1}$ and at 2367 and 2336 cm$^{-1}$.

Water vapour in air gives rise to an extensive spectrum in the range 1993 - 1396 cm$^{-1}$ of well defined bands. Atmospheric CO$_2$ absorbs at 720 and 668 cm$^{-1}$ (14).

The spectrum of polystyrene recorded on the double beam set up of the instrument is used as a confirmation and a supplement for the above calibration. Before and after the recording of a spectrum the wave number scale was checked by scanning a polystyrene spectrum. The following strong and medium absorption bands of polystyrene were used (9):

- 3029 cm$^{-1}$ s
- 2923 s
- 2851 m, s
- 1602 m, s
- 1493 m, s
- 1450 s
- 1376 m
- 1180 m, w
- 1154 m, w
The instrument was kept in a thermostated room at temperature 23 ± 2°C and all spectral measurements were carried out at that temperature care being taken to avoid serious rise in the temperature of the optics during a run.

A pair of variable space cells were used mostly in the present work. They were constructed from stainless steel body and rock-salt windows. To calibrate the cells, the optical density of cyclohexane lines at 905 cm⁻¹ and 1241 cm⁻¹ were measured at various thicknesses of the cell. The graph obtained by plotting optical density against the cell readings is then extrapolated to zero thickness. A pair of demountable fixed space (0.01 mm) cells were also used, as well as a pair of rock-salt plates which were used in the study of capillary liquid films and thin solid films of compounds of low melting point. All cells were thoroughly cleaned and kept in very dry atmosphere by storing them in a desiccator over calcium chloride. Complete dryness was ensured by baking the cells under an infrared lamp and allowing them to cool in a desiccator prior to use.

(3) **SOLVENTS:**

**Cyclohexane (B.D.H. Special for Spectroscopy)** was used for the ultraviolet absorption measurements as supplied by the manufacturers. It was found to be dry enough for most of the compounds studied.

However for the work with tin tetrachloride, the solvent was dried
ovor calcinated calcium oxide docanted and further dried over sodium and then distilled immediately before use.

CHLOROFORM B.P. was used after drying by refluxing over phosphorous pentoxide and distilled before use.

CARBON TETRACHLORIDE (Spectrosol) quality was used as supplied by the manufacturers.

CARBON DISULPHIDE (Analar) quality was used. However in some cases it was dried over anhydrous calcium chlorido to ensure the absence of any traces of water and then distilled before use.

The purity of all the above solvents was checked by measuring their infrared absorption spectra in the range 4000-650 cm⁻¹.

(4) INFRARED SPECTRA OF SOLID COMPOUNDS:

For the solid compounds with melting points below 100°C such as diphonyltin dichloride, tetrabenzyltin, N:triethyltin phthalimido, a thin solid film was prepared by melting few crystals of the solid on a rock-salt plate under the infrared lamp and rubbing the molten solid between the two plates until a nearly uniform film was obtained. It was then allowed to cool down slowly in the desiccator till the liquid solidified and the spectrum of the solid was then taken.

For the solid compounds in general the mill technique was used. To a finally divided powder few drops of Nujol were added and a smooth paste was made in an agate mortar. The paste was then made to spread on a rock-salt plate by pressing a pair of plates together and rubbing them until a nearly uniform film was obtained.
CLEANING OF FUSED SILICA CELLS:

All fused silica cells were cleaned before and after use by boiling nitric acid to remove all traces of grease and dirt. They were then rinsed several times with water, alcohol, acetone and dry ether and then flushed with dry nitrogen and kept in the oven at 110°C till they were required. Immediately before use they were kept in a desiccator to cool down. The cells were usually checked before use by comparing their percentage transmission against each other.

PRESENTATION OF THE SPECTRA:

The infrared absorption spectra are presented in tables of frequencies in cm$^{-1}$, relative intensity for the spectra of solids and Nujol mulls, and percentage absorption for liquids and solutions. Graphs of the spectra are also given for all the compounds, those graphs contain information as to the state of the compound, solvent used, concentrations of solutions and optical path length.

The ultraviolet absorption spectra are presented graphically as plots of log$\varepsilon$ (\(\varepsilon\) absorptivity i.e. extinction coefficient) against wave length in \(\text{m}\mu\). In most cases the vibrational fine structures are given in tables together with the values of the absorptivities.
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PART THREE

THE INFRARED ABSORPTION SPECTRA OF ORGANOTIN COMPOUNDS
III. INFRARED ABSORPTION SPECTRA OF ORGANOTIN COMPOUNDS

III.1. THEORETICAL INTRODUCTION:

The normal coordinates for the fundamental vibrations of monosubstituted benzenes have been determined by Liang and Krimm (36). Randle and Whiffen (46) have presented very approximate normal coordinates diagram for some of the vibrations, while Bailey, Gordon, halo, Harzfeld, Ingold and Poole (11) have discussed the case of monodeuterobenzene. An attempt will be made to determine approximately the normal coordinates for the fundamental vibrations of monosubstituted benzenes which will help later in the assignment of the fundamental frequencies of aryltin compounds investigated in this work.

The method employed here for the determination of the normal coordinates of molecular vibrations is that of Placzek which is based on the Theory of Groups (8). The method has been employed by Wilson (27), by Ingold and his coworkers (3-11, 30-1) by Pitzer and Scott (44) and by others (38-9, 54) to determine the normal coordinates for the vibrations of the benzene molecule. Several standard works (17, 29, 32, 52, 59) on the Theory of Groups and on molecular vibrations have been consulted. The nomenclature used here is that of Horzborg (29), slightly modified to allow for more recent terminology. The numbering of Horzborg for the normal coordinates of the vibration of the benzene molecule will be used.

The two normal coordinates diagrams viz: $\mathbf{a}_{12}^2$ and $\mathbf{a}_{14}^2$ given by Horzborg (29) and their correspondence to the frequencies assigned
to then by him are found to be unsatisfactory. It is true that both of those vibrations are doubly degenerate and they both belong to the same symmetry class namely $E$, and therefore in the case of benzene, at least, there exists some uncertainty as to the best normal coordinates for the particular vibration. Horzberg assigns to $\pi_{12}$ the frequency 3099 cm$^{-1}$ and to $\pi_{14}$ the frequency 1037 cm$^{-1}$ indicating that the former is mainly a C-H stretch ($\sigma$ C-H) and the latter a C-H in-plane deformation ($\beta$ C-H). A comparison of Horzberg’s normal coordinates diagrams $\pi_{12}$ and $\pi_{14}$ and of the corresponding diagram of Bailey, Ingold, Pook, and Wilson (8), with the original diagrams of Wilson (viz. $\pi_{18a}$ and $\pi_{20a}$) (57), and their development by Dopaign-Delay and Lacoste (viz. $\pi_{18a}$, $\pi_{18b}$, $\pi_{20a}$, and $\pi_{20b}$) (26) shows quite clearly that they are very similar indeed. However, it is well known in the case of degenerate vibrations that any linear orthogonal combinations of the normal coordinates of two modes is another mode with normal coordinates belonging to the same class of symmetry; and hence following the original suggestion of Wilson and the practice of Angus, Bailey, Halo, Ingold, Lockie, and Raisin (6) by taking the linear orthogonal sum and difference: $\pi_{12} + \pi_{14}$ and $\pi_{12} - \pi_{14}$ a better approximation is arrived at for the normal coordinates of the vibrations corresponding to frequencies 3099 and 1037 cm$^{-1}$. The former can now be assigned to $\sigma$ C-H and the latter to $\beta$ C-H. The normal coordinates diagrams of the vibrations of the benzene molecule are illustrated in Figure 1 which contain all the pairs of
FIG. 1

\[ \text{A}_{1g} \]
\[ \text{A}_{1g} \]
\[ \text{A}_{2g} \]
\[ \text{A}_{2u} \]
\[ \text{B}_{1u} \]
\[ \text{B}_{2g} \]
\[ \text{B}_{2u} \]
\[ \text{B}_{2u} \]
fig. 1 contd.
the degenerate vibrations indicated as subscript $a$ and $b$ to the number of the vibration. Those diagrams will facilitate the determination of the normal coordinates for the vibration of monosubstituted benzenes.

The loss of the $D_{6h}$ symmetry of benzene by substitution on the nucleus results in the molecule possessing fewer elements of symmetry than the parent molecule. In the case of monosubstituted benzenes the group symmetry is reduced to that of $C_{2v}$ which is a sub-group of $D_{6h}$. Even in the case where the substituent $X$ is not a single atom the local symmetry of the molecule can be regarded as approximating to group $C_{2v}$. In the monosubstituted benzene shown in Figure 2 the coordinates axes are arranged such that the plane of the molecule lies in the $xy$-plane with the $z$-axis perpendicular to the plane of the molecule and the $y$-axis passing through the $1:4$ positions. It can be seen clearly that such a molecule will have the following elements of symmetry:

(1) the identity element, $E$;
(2) a two-fold axis of symmetry along the $y$-axis, $C_2^y$;
(3) a plane of symmetry which is the plane of the molecule, $\sigma_{(xy)}$;
(4) a plane of symmetry at right angle to the plane of the molecule containing the two-fold axis of symmetry, $\sigma_{(yz)}$.

The above elements possess the fundamental group property that each is the product of two other elements. Those symmetry elements correspond to the following symmetry operations:

(1) the identity operation, $E$;
(2) $C_2^y$, a rotation about the two-fold axis by angle equal to $\pi$;
fig. 2

- Hydrogen
- Carbon
- Substituent
(3) $\sigma_{(xy)}$, a reflexion through the plane of the molecule $\sigma_{(xy)}$; 
(4) $\sigma_{(yz)}$, a reflexion through the plane $\sigma_{(yz)}$.

The following operational equations will be valid:

\[ C_2^y \cdot \sigma_{(xy)} = \sigma_{(yz)} \quad , \quad C_2^y \cdot C_2^y = E, \]

and therefore the two symmetry elements $C_2^y$ and $\sigma_{(xy)}$ can be considered as specifying set for the group.

The above elements of symmetry constitute a sub-group of group $D_{6h}$ which is the symmetry group of benzene. The symmetry properties of the benzene molecule are given in Table 1 for comparison purpose. The order of a group is equal to the number of symmetry operations and for the $C_{2v}$ group it is four, and is obviously a factor of the order of the $D_{6h}$ group which is 24 as shown in Table 1.

To investigate the results of applying the symmetry operations on the model group, the molecule is placed in "a potential hollow of its own" so that there will be $3N$ degrees of freedom corresponding to $3N$ normal vibrations of the molecule ($N=$number of atoms in the molecule). This procedure will effectively make the translational and rotational motions of the molecule a part of the normal vibrations.

The results of applying the above symmetry operations on the molecule is to alter its wave function $\Psi$ in one of the following ways:

(a) converting $\Psi$ into itself, (b) converting it into $-\Psi$, or (c) converting $\Psi$ into a different wave function, $\Psi'$, or into a linear combination of $\Psi$'s. According to what happens to the resulting wave function the vibration is said to be either (a) symmetrical (b) antisymmetrical or (c) degenerate with respect to the operation
<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>C2</th>
<th>2C3</th>
<th>2C6</th>
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<th>2S3</th>
<th>3Sv</th>
<th>3S''</th>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2u</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>T_z</td>
<td></td>
<td>I.R.</td>
</tr>
<tr>
<td>B1u</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>2</td>
<td>2</td>
<td></td>
<td>Inact.</td>
</tr>
<tr>
<td>B2u</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>2</td>
<td>2</td>
<td></td>
<td>Inact.</td>
</tr>
<tr>
<td>E1u</td>
<td>2</td>
<td>-2</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>4(2)</td>
<td>T_x,T_y</td>
<td>3(2)</td>
<td>I.R.</td>
</tr>
<tr>
<td>E2u</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2(2)</td>
<td></td>
<td></td>
<td>Inact.</td>
</tr>
</tbody>
</table>

\( \chi_r \) \text{, }36 0 0 0 0 -4 0 0 12 0 0 0 0 4

Non-degenerate vibrations 10, degenerate vibrations 10, vibrational degrees of freedom 30.

Total possible vibrational frequencies 20, active frequencies 11, inactive frequencies 9.


For details of the symmetry properties of benzene see reference 52.
However for degenerate vibrations to exist the model must have an axis of symmetry of higher order than two. Therefore in the case of the model considered all the vibrations can be either symmetrical or antisymmetrical and no degeneracy is possible. The behaviour of the model with respect to each of the symmetry operations makes it possible to divide the vibrations into different classes. Thus towards the elements of the Specifying Set for the symmetry group $C_{2v}$ the following symmetry classes are possible:

- $A_1 = \text{symmetrical to } C_2^y \text{ and symmetrical to } \sigma(\text{xy}),$
- $A_2 = \text{symmetrical to } C_2^y \text{ but antisymmetrical to } \sigma(\text{xy}),$
- $B_1 = \text{antisymmetrical to } C_2^y \text{ but symmetrical to } \sigma(\text{xy}),$
- $B_2 = \text{antisymmetrical to both } C_2^y \text{ and } \sigma(\text{xy}).$

The behaviour of the model with regard to the other two symmetry operations viz. $E$ and $\sigma(yz)$, can be determined either by inspection or by using the operational equations given above.

Now, to every group of symmetry elements there corresponds a set of representations $\Gamma_n$ which conforms to the operational rules of the group. These representations can be obtained by attaching vectors to each point in the model and writing out the matrices which correspond to the transformations of the vectors by the symmetry operations. These representations can be reduced by linear orthogonal transformations to irreducible representations which are unique for the group. It is most convenient to use the character $\chi$ of the matrix representation which is the sum of the diagonal elements of the matrix. Each irreducible representation will have a different set of characters,
and to those characters the rules of the original group apply. It is customary to label the normal vibrations of the molecule with the same symbols as the representations to which the vibrational wave functions belong. Thus in the case of $C_{2v}$, the characters of the irreducible representations will be either $+1$ or $-1$ depending on whether the wave function is symmetrical or antisymmetrical with respect to the operation.

In order to enumerate the number of normal vibrations which belong to a given representation use is made of the following formula (52):

$$a_i = \frac{1}{h} \sum_{R} \chi_i^{(R)} \chi_r^{(R)} \quad \ldots \ldots (1)$$

where $h$ is the order of the group, $\chi_i$ is the character of the irreducible representation $\Gamma_i$, and $\chi_r$ is the character of the reducible representation $\Gamma_r$, and the summation is carried out for the same representation over all the operations $R$. The number of the normal vibrations per representation $\Gamma_i$ will then be given by $a_i$.

The values of $\chi_i$ discussed above are given in Table 2 which also outlines the symmetry properties of Group $C_{2v}$ for a twelve-atoms molecule. In order to use equation (1) the values for $\chi_r$ have to be calculated; here use is made of the fact that terms will appear on the diagonals of the transformation matrices for the coordinates only for those atoms which are not shifted or permuted in the operation $R$ (52). For the case of the model in question, for the
identity operation E the transformation matrix for each atom taken separately is:

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

and the character is therefore 3, and since there are twelve atoms

\[\chi_r(E) = 36.\]

For the rotation of the molecule about the y-axis by 180°, the $C_2^y$ operation, only the 1-4 carbon atoms and the atoms X and H attached to them are not shifted. For each of those atoms the transformation matrix is:

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}
\]

the character is therefore equal to -1, and for the four atoms the value for $\chi_r(C_2^y) = -4$.

For the $\sigma(x,y)$ operation, i.e. reflexion in the plane of the molecule, the transformation matrix is

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}
\]

which gives +1 for the character of each unpermuted atom; and since there are twelve such atoms in this instance the total character

\[\chi_r(\sigma(x,y)) = 12.\]

For the operations $\sigma(yz)$, i.e. reflexion in the yz-plane, the transformation matrix for each unpermuted atom is given by:

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]
and since there are only four atoms which are not shifted after the operation the total character is therefore $\chi_r(\sigma - (yz))=4$. Those four atoms are the same as in the case of operation $C_2^y$.

Now, it is possible to calculate $a_1$ for each of the symmetry classes by using equation (1). The results are:

\[
\begin{align*}
a_1(A_1) &= \frac{1}{4} \cdot (36-4+12+4) = 12 \\
a_1(A_2) &= \frac{1}{4} \cdot (36-4-12-4) = 4 \\
a_1(B_1) &= \frac{1}{4} \cdot (36+4+12-4) = 12 \\
a_1(B_2) &= \frac{1}{4} \cdot (36+4-12+4) = 8
\end{align*}
\]

The $a_1$'s as calculated above include besides the number of the fundamental vibrations belonging to each of the representations, the number of translational ($T_x, T_y, T_z$) and rotational ($R_x, R_y, R_z$) motions. The symmetry class to which each of the above motions belong can be found by the following method (3, 52, 59).

For the translational motions of the molecule, it can be shown that the components of translational motions of the molecule in the $x, y, z$ directions will transform in a similar way to the transformations of the axes $x, y, z$ by the symmetry operations. The transformations characters for the coordinate axes are indicated in Table 2 wherefrom it can be seen that $T_x$ belongs to $B_1$, $T_y$ belongs to $A_1$ and $T_z$ belongs to $B_2$.

The characters for the rotational motions $R_x, R_y, R_z$ of the molecule as a whole about the axes $x, y, z$ are found in the following manner. Considering the components of the angular momentum $M$ of the
rotating molecule in planes perpendicular to the axes and taking $P_x, P_y, P_z$ as the components of the corresponding linear momentum in the $x, y, z$ directions, then the components $M_x, M_y, M_z$ of the angular momentum are given by the equations:

\[
\begin{align*}
M_x &= y P_z - z P_y \\
M_y &= z P_x - x P_z \\
M_z &= x P_y - y P_x
\end{align*}
\]

and that $R_x, R_y, R_z$ will transform like $M_x, M_y, M_z$ respectively. But since $P_x, P_y, P_z$ transform like the axes $x, y, z$, respectively, the transformation of each of the components of the angular momentum can be obtained from the product of the characters of the corresponding axes. Thus, $M_x$ will transform as $1, -1, -1, 1$ and $R_x$ will therefore belong to $B_2^*$. $M_y$ will transform as $1, 1, -1, -1$ and $R_y$ will belong to $A_2^*$; finally $M_z$ will transform as $1, -1, 1, -1$ and therefore $R_z$ belongs to $B_1^*$.

The intensities of transition between two energy levels of a molecule ($i$ and $j$) are determined (8, 29, 52, 59) by an integral of the form:

\[
p_{ij} = \int \psi_i^* P \psi_j \, dq
\]

where $\psi_i$ and $\psi_j$ are time-independent (amplitude) wave functions (wholly real) of the spatial coordinates $q$. $P$ can either be the dipole moment $M$ of the molecule in the case of infrared absorption spectra, or the polarizibility $\alpha_{pq}$ of the molecule in the case of Raman transition. For an infrared absorption band corresponding to a
particular vibration to appear on one component at least of the
transition moment $M_x, M_y, M_z$ must not vanish; and it has been
shown (8) that the integral will not vanish only if $M$ has the same
symmetry properties as $q$. That means that the symmetry properties
of $M_x, M_y, M_z$ are those of the coordinates $x, y, z$ respectively, and
therefore it can be read directly from Table 2. In the case of
Raman transition, one of the polarizibility matrix $\alpha_{pq}$ must not
vanish. Any polarizibility integral will not vanish only if $\alpha_{pq}$
has the symmetry properties of the normal coordinates of the
vibration (8). Therefore, $\alpha_{pq}$ will suffer symmetry transformation
which, since they are product of those undergone by the coordinates
$p$ and $q$, can be deduced by multiplying the operators which express
the behavior of the two coordinates $p$ and $q$. This also can be
read directly from Table 2.

For the determination of the normal coordinates of the nodes
of vibrations of mono-substituted benzene use is made of the
symmetry properties discussed above and outlined in Table 2 and also
of the orthogonality principle (8, 29, 52, 59). The orthogonality
of the normal coordinates of the vibrations means that they must
represent independent degrees of freedom. The condition for
orthogonality is that the sum for any two vibrations, over all
the mass-points in the molecule, of the product of the mass of a
point and the scalar product of its displacements in the two
vibrations must vanish. But, since the scalar products contain
the cosine of the angle between the two displacements in the two
TABLE 2. SYMMETRY PROPERTIES OF THE $C_{2v}$ MODEL FOR MONOSUBSTITUTED BENZENE, $C_6H_5X$.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>$C_2^v$</th>
<th>(xy)</th>
<th>(yz)</th>
<th>$a_1$</th>
<th>$a_T$</th>
<th>$a_R$</th>
<th>$a_v$</th>
<th>activity</th>
</tr>
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<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td>I.R. &amp; Ram.</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>Ram.</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>12</td>
<td>$T_x$</td>
<td>$R_x$</td>
<td>10</td>
<td>I.R. &amp; Ram.</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>8</td>
<td>$T_z$</td>
<td>$R_z$</td>
<td>6</td>
<td>I.R. &amp; Ram.</td>
</tr>
<tr>
<td>$\chi$</td>
<td>36</td>
<td>-4</td>
<td>12</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$y$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$z$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Non-degenerate vibrations 30
Doubly-degenerate vibrations 0
Vibrational degrees of freedom 30
Total possible vibrational frequencies 30
Raman active frequencies 30
Infrared active frequencies 27

Ram. = Raman active
I.R. = Infrared active
Inact. = Inactive in Raman and Infrared.
vibrations, the orthogonality condition will be fulfilled by making the angle $90^\circ$ or if that is not possible by making the positive cosines balance the negative cosines, or the parallel displacements balance the antiparallel displacements.

Moreover, extensive use is made of the normal coordinates of benzene given in Figure 1. By the loss of $D_{6h}$ symmetry through substitution of hydrogen by another atom or group, the classes of $D_{6h}$ group merge in fours to form smaller number of new symmetry classes. This is illustrated below:

\[
\begin{align*}
 & C_{2v} & D_{6h} \\
 A_1 & A_{1g}, B_{1u}, E_{2g}, E_{1u} \\
 A_2 & A_{1u}, B_{1g}, E_{1g}, E_{2u} \\
 B_1 & A_{2g}, B_{2u}, E_{2g}, E_{1u} \\
 B_2 & A_{2u}, B_{2g}, E_{1g}, E_{2u}
\end{align*}
\]

However, the mixing of the $D_{6h}$ symmetry classes in the fewor $C_{2v}$ classes is not complete in some cases. For the approximate work presented here the original benzene modes in certain cases are taken to be only modified to a negligible extent. Wherever extensive mixing is suspected, a new normal coordinate diagram is constructed by linear orthogonal combination of the appropriate benzene modes. These modified modes are indicated in Figure 3 by the superscript *. Figure 3 gives all the modes for the vibrations of mono-substituted benzenes.

The approximate nature of the above procedure makes it important to use the measured frequencies (3-11, 12, 13, 16, 18, 19, 23, 24,
fig. 3 contd.
as guides for many of the assignments.

One major criticism for the above work is its complete lack of consideration of the electronic interaction between the benzeno nucleus and the substituent and the neglecting of the mass effect of the substituent. However, it is expected that these two effects will alter mainly the values of the normal frequencies and their intensities, but their effect on the normal coordinates and the symmetry properties can not however be completely ignored since it is well known that certain vibrations which are forbidden in the infrared absorption spectra namely of class \( A_2 \) do appear in the spectra of many monosubstituted benzenes. This is to be expected since the original assumption that the local symmetry of the substituted benzeno is independent of the symmetry of the substituent is not strictly true.

The ability to identify overtones and combinations bands as such adds to the facilities of the assignments of the fundamental frequencies. Since the spectral activity of these bands depends on a similar matrix integral to that presented for the fundamental vibrations, it only remains to point out that in the case of overtones and combinations the class of symmetry of the transition is that for the product \( q^2 \) or \( q_1^1 \) respectively. The symmetry properties of the squares or the products of \( q \)'s can be read directly from Table 2. Table 3 gives the possible overtones and combinations and their spectral activity, it is based mainly on the table given by Bailey, Ingold, Poolo and Wilson (8).
TABLE 3. CLASS SYMMETRY AND ACTIVITY OF OVERTONE AND
COMBINATION MODES OF THE $C_{2v}$ MODEL FOR MONO-
SUBSTITUTED BENZENES.

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2^\neq$</td>
<td>$B_1$</td>
<td>$B_2$</td>
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<tr>
<td>$A_2$</td>
<td>$A_2^\neq$</td>
<td>$A_1$</td>
<td>$B_2$</td>
<td>$B_1$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$B_1$</td>
<td>$B_2$</td>
<td>$A_1$</td>
<td>$A_2^\neq$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$B_2$</td>
<td>$B_1$</td>
<td>$A_2^\neq$</td>
<td>$A_1$</td>
</tr>
</tbody>
</table>

$A_2^\neq$ are forbidden in the infrared spectra.
III. 2 THE INFRARED ABSORPTION SPECTRA OF PHENYL Tin COMPOUNDS.

The infrared absorption spectra of phenyltin compounds of the general formula $\text{Ph}_n\text{SnC}_4\text{H}_{12-n}$ ($n = 1, 2, 3$ and $4$) are given in Tables 4-7 and illustrated in Figures 4 - 14.

The variations in the frequencies and the intensities of the absorption bands with the physical state of the compounds were found to be negligible in almost all cases. The only serious exception to the above observation is the strong band at about $1725 \text{ cm}^{-1}$ which only appears in the spectra of tetraphenyltin and triphenyltin chloride in carbon tetrachloride solutions.

The general pattern of the absorption bands in the region measured (viz. 3500-650 cm$^{-1}$) is very similar in all four compounds. For purpose of comparison and to facilitate the assignments of the fundamental frequencies the best values for the frequencies of the bands are listed together in Table 8. These values are the best experimental values, for example some are the average values for the frequencies as measured in different states and solvents, and others are what was considered to be the best in a particular measurement because of their superior definition.

Assignment of the fundamental frequencies.

Since only a part of the region where the fundamental absorption bands are expected to appear has been investigated, viz. the rock-salt transmission region 3500-650 cm$^{-1}$, and because of the complexity of the molecules an attempt can only be made at a tentative assignment of the frequencies.
### The Infrared Absorption Spectrum of Tetrphenyltin

<table>
<thead>
<tr>
<th>Wavenumbers &amp; Intensities</th>
<th>Solution in CS₂</th>
<th>Solution in OCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>682 cm⁻¹</td>
<td>w</td>
<td>687 cm⁻¹</td>
</tr>
<tr>
<td>710 cm⁻¹</td>
<td>v.s</td>
<td>706 cm⁻¹</td>
</tr>
<tr>
<td>745 cm⁻¹</td>
<td>v.s</td>
<td>739 cm⁻¹</td>
</tr>
<tr>
<td>856 cm⁻¹</td>
<td>w</td>
<td>913 cm⁻¹</td>
</tr>
<tr>
<td>913 cm⁻¹</td>
<td>w</td>
<td>987 cm⁻¹</td>
</tr>
<tr>
<td>978 cm⁻¹</td>
<td>w</td>
<td>998 cm⁻¹</td>
</tr>
<tr>
<td>986 cm⁻¹</td>
<td>m</td>
<td>1013 cm⁻¹</td>
</tr>
<tr>
<td>1025 cm⁻¹</td>
<td>m</td>
<td>1028 cm⁻¹</td>
</tr>
<tr>
<td>1062 cm⁻¹</td>
<td>w(sh)</td>
<td>1065 cm⁻¹</td>
</tr>
<tr>
<td>1075 cm⁻¹</td>
<td>m.s</td>
<td>1075 cm⁻¹</td>
</tr>
<tr>
<td>1153 cm⁻¹</td>
<td>w</td>
<td>1158 cm⁻¹</td>
</tr>
<tr>
<td>1161 cm⁻¹</td>
<td>v.w</td>
<td>1187 cm⁻¹</td>
</tr>
<tr>
<td>1180 cm⁻¹</td>
<td>w</td>
<td>1267 cm⁻¹</td>
</tr>
<tr>
<td>1265 cm⁻¹</td>
<td>w</td>
<td>1304 cm⁻¹</td>
</tr>
<tr>
<td>1306 cm⁻¹</td>
<td>w</td>
<td>1337 cm⁻¹</td>
</tr>
<tr>
<td>1335 cm⁻¹</td>
<td>v.w</td>
<td>1366 cm⁻¹</td>
</tr>
<tr>
<td>1432 cm⁻¹</td>
<td>s</td>
<td>1725 cm⁻¹</td>
</tr>
<tr>
<td>1483 cm⁻¹</td>
<td>m.s</td>
<td>1767 cm⁻¹</td>
</tr>
<tr>
<td>1579 cm⁻¹</td>
<td>w</td>
<td>1822 cm⁻¹</td>
</tr>
<tr>
<td>1644 cm⁻¹</td>
<td>m.w</td>
<td>1900 cm⁻¹</td>
</tr>
<tr>
<td>1693 cm⁻¹</td>
<td>w</td>
<td>1962 cm⁻¹</td>
</tr>
<tr>
<td>1770 cm⁻¹</td>
<td>v.w</td>
<td>1975 cm⁻¹</td>
</tr>
<tr>
<td>1829 cm⁻¹</td>
<td>w</td>
<td>3022 cm⁻¹</td>
</tr>
<tr>
<td>1887 cm⁻¹</td>
<td>w</td>
<td>3061 cm⁻¹</td>
</tr>
<tr>
<td>1906 cm⁻¹</td>
<td>v.w</td>
<td>3125 cm⁻¹</td>
</tr>
</tbody>
</table>

Note: The intensities are relative to the strongest peak, which is set at 100%. The symbols 'w', 'm', 's', 'v.s', 'v.w' indicate the intensity as 'weak', 'medium', 'strong', 'very strong', and 'very very strong', respectively.
### TABLE 5
THE INFRARED ABSORPTION SPECTRUM OF TRIPHENYLITIN CHLORIDE

<table>
<thead>
<tr>
<th>Model w/</th>
<th>solution in CS₂</th>
<th>solution in CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freq. cm⁻¹</td>
<td>relative intensity</td>
<td>freq. cm⁻¹</td>
</tr>
<tr>
<td>680</td>
<td>w</td>
<td>681</td>
</tr>
<tr>
<td>708</td>
<td>v.s.</td>
<td>702</td>
</tr>
<tr>
<td>741</td>
<td>v.s.</td>
<td>736</td>
</tr>
<tr>
<td>881</td>
<td>w</td>
<td>838</td>
</tr>
<tr>
<td>918</td>
<td>w</td>
<td>916</td>
</tr>
<tr>
<td>972</td>
<td>w</td>
<td>971</td>
</tr>
<tr>
<td>987</td>
<td>w(sh)</td>
<td>990</td>
</tr>
<tr>
<td>997</td>
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THE INFRARED ABSORPTION SPECTRUM OF PHENYLITIN TRICHLORIDE

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(for details of concentration of solution and/or path length see the relevant figure of the spectrum)
## Table 8
### Assignment of the Normal Frequencies of Phenyltin Compounds

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Tetraphenyltin
Solvent: carbon disulphide
Molarity: 1.30 x 10^-2
Path length: 0.50 cm

% absorption

FIG. 5
Tetraphenyltin

Solvent: carbon tetrachloride

Molarity $0.6256 \times 10^{-2}$  Path length 0.30 cm

% absorption

FIG. 6
Triphenyltin Chloride
Solvent: carbon disulphide.
Molarity: 0.2736 M

FIG. 8

% absorption

0 20 40 60 80 100

4000 3600 3200 2800 2400 2000 1600 1400 1200 1000 800 600

\( \tilde{v} \text{ cm}^{-1} \)
Triphenyliettin Chloride
Solvent: carbon tetrachloride
Molarity: 3.593 × 10^{-3}
Path length 0.20 cm.

FIG. 9
Diphenyltin Dichloride
Nujol Mull

FIG. 10

% absorption

4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600

$\bar{\nu}$ cm$^{-1}$
Diphenyltin Dichloride
Solvent: carbon disulphide
Molarity: 0.127 M
Path length: 0.30 cm

FIG. 12

% absorption

100
90
80
70
60
50
40
30
20
10
0

4000 4500 5000 5500 6000 6500 7000 7500 8000 8500 9000

$\nu$ cm$^{-1}$
Although in the determination of the normal coordinates of the modes of vibrations of monosubstituted benzenes consideration was given only to the local symmetry of the group $C_{2h}$ without regard to the symmetry properties of the molecule as a whole, in the present case because of the size of the tin atom one would expect very little interaction between the various parts of the molecule.

Assignment of $A_h$ fundamentals

The vibrations of the $A_h$ class preserve all the elements of symmetry of the group $C_{2v}$. There are eleven of them which are derived from three $A_{1g}$, three $E_{2g}$, three $E_{1u}$, and two $E_{2u}$ modes of benzene. They can be roughly divided into the following categories: three C-H stretching modes ($\nu$C-H) i.e. $2^1\nu$, $2^1\nu_{15a}$, and $2^1\nu_{14a}$; one C-Sn stretch $2^2\nu_5$; two C-H in-plane-bending modes ($\delta$C-H) i.e. $2^2\delta_{17a}$ and $2^2\delta_{12a}$; and five C-C stretch and ring vibrations i.e. modes in which the CH group moves as a unit. The latter are $2^2\nu$, $2^2\nu_{6}$, $2^2\nu_{18a}$, and $2^2\nu_{16a}$.

The hydrogen stretching mode and the C-Sn stretch can be considered together since they are obtained from combining the four benzene modes $2^2\nu_{1}$, $2^2\nu_{5}$, $2^2\nu_{14a}$, and $2^2\nu_{15a}$ to give $2^2\nu_{1}$, $2^2\nu_{14a}$, and $2^2\nu_{15a}$ which are purely hydrogen stretching and $2^2\nu_{5}$ which is C-Sn stretch. The assignment of the latter mode will be deferred until later in this section. The assignment of the three $\nu$C-H modes indicated in Table 8 are very uncertain not only because of the limitations of rock-salt optics at that region but also because of the great possibility of overlapping between the fundamentals and the overtones and combinations bands. However, tentatively the band at about 3020 cm$^{-1}$ is assigned to $2^2\nu_{14a}$, and the band at 3060 cm$^{-1}$ to either $2^2\nu_{1}$ or $2^2\nu_{15a}$ or both.
because of the very broad nature of the band. It is very likely that all the other hydrogen stretching nodes of class $B_1$, i.e., $a_{15b}$ and $a_{14b}$, are to be found in this rather broad absorption band.

The $\beta$C-H nodes $a_{12a}$ and $a_{17a}$ correspond to the doubly degenerate benzene vibrations $a_{12}$ and $a_{17}$ belonging to $E_{1u}$ and $E_{2g}$ classes, respectively. They can easily be assigned to the frequencies 1025 and 1190 cm$^{-1}$ because of their similarity to the nodes of monodeuterobenzene (11). The corresponding values for these two modes are 1029 ± 5 and 1177 ± 6 as given by Randle and Whiffen (46) for monosubstituted benzenes.

The symmetrical ring breathing vibration $a_2$ is responsible for the strong Raman line at 991.6 cm$^{-1}$ of benzene (6). The average value found by Randle and Whiffen (46) was 1001 ± 4 cm$^{-1}$ with variable intensity. The bands appearing in all four spectra with remarkable consistency at 997 cm$^{-1}$ is assigned to this mode. However, it has been found (54) that there is some very slight mixing between $a_2$ and $a_6$, the planar trigonal carbon ring bending vibration; to the latter the band at 1013 cm$^{-1}$ is tentatively assigned. Whiffen (54) has calculated the value 1012 cm$^{-1}$ for the benzene molecule.

The vibration portrayed by $a_{18a}$ which consists mainly of stretching and contraction of the carbon ring along the y-axis accommodated almost entirely by the bending of the C-C-C valency angle rather than tension in the C-C bond, has been found to have the frequency 605.6 cm$^{-1}$ in the Raman spectrum of benzene (6), and 601 cm$^{-1}$ in the spectrum of monodeuterobenzene (11). Randle and Whiffen (46) have found this vibration to be very sensitive to the nature of the substituent and for monochalobenzene its frequency varies from 519 cm$^{-1}$ for
fluorobenzene to 270 cm\(^{-1}\) for iodobenzene which places it beyond the range of the region examined. However, the ultraviolet absorption spectra of phenyltin compounds (Section IV 2) indicate a value of about 510 cm\(^{-1}\) for this mode in the first excited state of the molecules.

The benzene frequency of 1596 cm\(^{-1}\) in the Raman spectrum was assigned to the degenerate vibration \(\nu_{16}\) which splits into two components in nonosubstituted benzenes. However, the mode \(\nu_{16a}\) consists mainly of contraction and stretch of the C-C bonds and to it the frequency 1579 cm\(^{-1}\) is assigned. In the case of benzene (6,8) the band has been found to contain an appreciable admixture of the \(\nu_{17}\) normal coordinates.

The remaining \(\nu_{13a}\) C-C stretch is assigned to the band 1482 cm\(^{-1}\) which corresponds to the strong band of benzene at 1485 cm\(^{-1}\) (6). It also agrees with Randle and Whiffen (46) average value of 1499 \(\pm\) 7 cm\(^{-1}\).

Assignment of \(B_1\) fundamentals

The ten \(B_1\) normal coordinates preserve only the symmetry of the plane of the benzene ring \(\sigma(xy)\). They are derived from four \(B_{2g}\), three \(B_{1u}\), one \(A_{2g}\) and two \(B_{2u}\) normal modes of benzene. Two of these modes are hydrogen stretching vibrations \(\nu_{15b}\) and \(\nu_{14b}\); three are hydrogen in-plane bending vibrations \(\nu_3\), \(\nu_{10}\), and \(\nu_{12b}\); one C-Sn bending vibration \(\nu_{17b}\); three C-C stretch \(\nu_{13b}\), \(\nu_{16b}\) and \(\nu_{9}\) and the remaining mode \(\nu_{18b}\) is C-C bending vibration. The two \(\nu_{0}\) C-H vibrations have been dealt with in the preceding section.

The three \(B\) C-H modes \(\nu_3\), \(\nu_{10}\), \(\nu_{12b}\) together with \(\nu_{17b}\) are obtained by linear orthogonal combination of the corresponding benzene modes \(\nu_{3}, \nu_{10}, \nu_{12b}\) and \(\nu_{17b}\). The \(\nu_3\) mode of benzene is
predicted (6, 7, 31) at 1328 cm\(^{-1}\) and is found at 1292 cm\(^{-1}\) in monodeuterobenzene (11) and at 1309 cm\(^{-1}\) in 1:4 dideuterobenzene (10,30).

It is expected that it would be of only moderate intensity and that its frequency would not be greatly affected by substitution. However, Randle and Whiffen (46) assigned the frequency 1248 ± 8 cm\(^{-1}\) to a similar type of node. There are two possible assignments for \(2\gamma_3\), either the moderate band at 1305 cm\(^{-1}\) or the weak band at 1265 cm\(^{-1}\). Assuming that the intensity is enhanced by the polarity of the C-Sn bond and that the effect of the substituent is negligible on the frequency of the vibration one is led to assign \(2\gamma_3\) to 1305 cm\(^{-1}\).

Vibrations \(2\gamma_{10}\) and \(2\gamma_{12b}\) are assigned to 1161 and 1075 cm\(^{-1}\) respectively. They agree with the value 1156 ± 5 and 1072 ± 7 cm\(^{-1}\) given by Randle and Whiffen. The corresponding values for monodeuterobenzene (11) are 1158.2 and 1076 cm\(^{-1}\). Both of these nodes are originated in the degenerate benzene classes \(E_{2g}\) and \(E_{1u}\) and therefore certain amount of mixing is expected between \(2\gamma_{10}\), \(2\gamma_{12b}\) and \(2\gamma_{17a}, 2\gamma_{12a}\) of class \(A_1\).

The expected position of the band corresponding to mode \(2\gamma_{17b}\) lies beyond the range of rock-salt transmission.

The carbon vibration \(2\gamma_{13b}\) is assigned to the band appearing at 1435 cm\(^{-1}\). It would be expected to appear not very far from \(2\gamma_{13a}\). However, it is quite possible that the combination frequency \((2\gamma_4 + 2\gamma_{11b})\) overlaps this band. The value given by Randle and Whiffen is 1451 ± 12 cm\(^{-1}\) and the corresponding frequency for monodeuterobenzene is 1450 cm\(^{-1}\). The frequency 1606 cm\(^{-1}\) is assigned to the \(2\gamma_{16b}\) mode.

In the spectrum of tetraphenyltin in Nujol mull there appears quite a
broad band extending over this region but all attempts to resolve it have failed. However the band was distinctly resolvable in the spectra of the other compounds. The value quoted by Randle and Whiffen is 1606 ± 7 cm⁻¹. The mode represented by 2g for benzene is best assigned to 1310 cm⁻¹. Randle and Whiffen give the value 1324 cm⁻¹ for monosubstituted benzenes. In the present work the best frequency that can be assigned to 2g is 1334 cm⁻¹.

The carbon vibration 2 18d can, within the approximation of the normal coordinates diagram, be considered as involving the bending of the C-C-C angle with very little or no tension existing in the C-C bonds and the C-H bonds. It would also be expected that the frequencies for the various substituted benzenes would lie very closely together, hence the average value found for monosubstituted benzenes is 620 ± 4 cm⁻¹. Although this lies beyond the range covered in the present work, evidence from the electronic absorption spectra of the phenyltin compounds indicates a value near 640 cm⁻¹ for tetraphenyltin (See Section IV, 2).

Assignment of A2 fundamentals

There are only three A2 normal modes which are derived from one E1g and two E2u nodes of benzene. They preserve only one symmetry element of the molecule namely C2v, and therefore they are theoretically allowed to appear only in the Raman spectra of the compounds. However, the fact that the remainder of the molecule influences its symmetry properties permits the appearance of A2 modes in both the infrared and the Raman spectra of the compounds. These bands would be expected to be rather weak.
Two vibrations in this class are out-of-plane hydrogen bending ($\Phi$ C-H). Apart from the carbon vibration $2^2_{20a}$, the other two modes $2^2_{11a}$ and $2^2_{19a}$ would be expected to show their frequencies in the region examined, particularly below 1000 cm$^{-1}$. To $2^2_{11a}$ the frequency 854 cm$^{-1}$ is assigned. The value for monosubstituted benzenes is 837 ± 10 cm$^{-1}$ (46) and the corresponding value for monodeuterobenzene (11) is 849.9 cm$^{-1}$. The band appearing at 989 cm$^{-1}$ is assigned to $2^2_{19a}$; Randle and Whiffen (46) giving the value 982 ± 6 cm$^{-1}$, whilst the calculated (11) value for monodeuterobenzene is 970 cm$^{-1}$.

Assignment of $D_2$ fundamentals.

The six $D_2$ modes are derived from one $E_{1g}$, one $A_{2u}$, two $B_{2g}$ and two $E_{2u}$ modes of benzene. Apart from $2^2_{20b}$ and $2^2_8$ all the rest can be considered as $\Phi$ C-H vibrations. The frequency of the out-of-plane ring deformation $\Phi$ C-C mode $2^2_{20b}$ lies beyond the rock-salt range. However Randle and Whiffen consider $2^2_{4b}$ as a $\Phi$ C-C mode, an assumption which is not directly supported by the normal coordinates diagram given in the present work. But owing to the complicated nature of the coupling between the out-of-plane bending vibrations, any assignments of the normal coordinates to the individual frequencies of an out-of-plane symmetry class containing as many as six fundamentals must be more than usually arbitrary. However, an aid in the assignments is the study of the combination bands in the region 1650-2000 cm$^{-1}$ which were found to be combinations of out-of-plane C-H bending vibrations.

The frequency corresponding to $2^2_4$ of nonosubstituted benzene with a substituent of infinite mass is calculated (22) to be 723 cm$^{-1}$. 
Therefore, in this case the frequency 739 cm\(^{-1}\) is assigned to that mode. The average value for monosubstituted benzenes is 751 ± 15 cm\(^{-1}\).

The frequency 973 cm\(^{-1}\) is assigned to the trigonally symmetrical vibration \(\nu_7\). Randle and Whiffen give the average value 962 ± 6 cm\(^{-1}\). The corresponding frequencies for nonodeuterobenzene (11) and 1:3:5 trideuterobenzene (9) are 922 and 915 cm\(^{-1}\) respectively.

The mode \(\nu_{llb}\) is assigned the very strong band at 703 cm\(^{-1}\). The average value for monosubstituted benzenes is 699 cm\(^{-1}\). The corresponding value for nonodeuterobenzene (11) is 778 cm\(^{-1}\). The frequencies assigned to modes \(\nu_{19b}\) and \(\nu_{19b}\) for nonodeuterobenzene (11) were 995 and 360 cm\(^{-1}\) respectively. To \(\nu_{19b}\) the frequency 916 cm\(^{-1}\) is assigned.

**Assignment of the summation frequencies.**

The summation bands of the out-of-plane C-H bending fundamentals are of some importance in confirming the assignment of the normal modes of class \(A_2\) and \(B_2\). There are four C-H modes belonging to class \(B_2\) i.e. \(\nu_4\), \(\nu_7\), \(\nu_{11b}\) and \(\nu_{19b}\), and two \(\nu_{lla}\) and \(\nu_{19a}\) to class \(A_2\). Table 3 shows that the overtones and combinations of these two classes belong to either class \(A_1\) or class \(B_1\) and therefore should be of relatively moderate intensity.

Ingold and his coworkers (6) have shown that in the case of benzene the following combinations are quite possible:

\[
\begin{align*}
671 (A_{2u}, \nu_4) + 849 (E_{lg}, \nu_{11}) &= 1520 (E_{lu}) \text{ observed at } 1529 \text{ cm}^{-1}. \\
849 (E_{lg}, \nu_{11}) + 970 (E_{2u}, \nu_{19}) &= 1819 (E_{lu}) \text{ observed at } 1808 \text{ cm}^{-1}. \\
970 (E_{2u}, \nu_{19}) + 985 (B_{2g}, \nu_7) &= 1955 (E_{lu}) \text{ observed at } 1965 \text{ cm}^{-1}.
\end{align*}
\]
The degeneracy of the benzene vibrations is shifted by substitution and Whiffen (53) has found that corresponding to the first of the benzene combinations two strong bands would be expected:

\[ \nu_4(B_2) + \nu_{11a}(A_2) = \alpha (B_1) \quad \text{and} \quad \nu_4(B_2) + \nu_{11b}(B_2) = \beta (A_1) \]

corresponding to the second benzene summation band at 1808 cm\(^{-1}\) there are the following bands

\[ \nu_{11a}(A_2) + \nu_{19a}(A_2) = \delta (B_1), \quad \nu_{11a}(A_2) + \nu_{19b}(B_2) = \delta (B_1), \]

\[ \nu_{11b}(B_2) + \nu_{19a}(A_2) = \xi (B_1), \quad \nu_{11b}(B_2) + \nu_{19b}(B_2) = \xi (A_1), \]

and corresponding to the third summation band at 1965 cm\(^{-1}\) the following bands would be expected:

\[ \nu_{19a}(A_2) + \nu_{7}(B_2) = \eta (B_1), \quad \nu_{19b}(B_2) + \nu_{7}(B_2) = \eta (A_1). \]

Whiffen (53) has investigated only part of the above possible summations. He also considered that the node \(\nu_{11b}\) contains some admixture of mode \(\nu_{19b}\) and concluded that the following summations are possible:

\[ \nu_{11b}(B_2) + \nu_{11a}(A_1) = \kappa (B_1), \quad \nu_{11b}(B_1) + \nu_{11b}(B_2) = \kappa (A_1) \]

\[ \nu_{11b}(B_2) + \nu_{7}(B_2) = \lambda (A_1). \]

However, there are ten more possible summations of these nodes which are indicated in Table 9, where the 21 summations of the six O-H normal nodes are listed together with the observed frequencies. Certain of these bands overlap some of the fundamentals especially in the region 1450-1650 cm\(^{-1}\).

Examination of the summation bands (\(\nu_4 + \nu_{11a}\), \(\nu_4 + \nu_{19b}\), \(\nu_{11b} + \nu_{11a}\), \(\nu_{11b} + \nu_{19b}\) and \(\nu_7 + \nu_{11b}\) together with the fundamentals \(\nu_{16a}\) and \(\nu_{16b}\), all of which are expected in the
**TABLE 9**

**ASSIGNMENT OF THE SUMMATION BANDS OF PHENYL Tin COMPOUNDS**

<table>
<thead>
<tr>
<th>summation band</th>
<th>symmetry class</th>
<th>compounds</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ph₄Sn</td>
<td>Ph₃SnCl</td>
<td>Ph₂SnCl₂</td>
<td>PhSnCl₃</td>
</tr>
<tr>
<td>2² + 2² 7</td>
<td>A₁</td>
<td>1717</td>
<td>1707</td>
<td>1709</td>
<td>1705</td>
</tr>
<tr>
<td>2² + 2² 11b</td>
<td>A₁</td>
<td>1447</td>
<td>1441</td>
<td>1437</td>
<td>1435</td>
</tr>
<tr>
<td>2² + 2² 19b</td>
<td>A₁</td>
<td>1644</td>
<td>1647</td>
<td>1636</td>
<td>1642</td>
</tr>
<tr>
<td>2² + 2² 11a</td>
<td>B₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2² + 2² 19a</td>
<td>B₁</td>
<td>1725</td>
<td>1733</td>
<td>1725</td>
<td>-</td>
</tr>
<tr>
<td>2² + 2² 11b</td>
<td>A₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2² + 2² 19b</td>
<td>A₁</td>
<td>1883</td>
<td>1883</td>
<td>1882</td>
<td>1883</td>
</tr>
<tr>
<td>2² + 2² 11a</td>
<td>B₁</td>
<td>1822</td>
<td>1821</td>
<td>1811</td>
<td>1817</td>
</tr>
<tr>
<td>2² + 2² 19a</td>
<td>B₁</td>
<td>1962</td>
<td>1960</td>
<td>1956</td>
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</tr>
<tr>
<td>2² + 2² 19b</td>
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<td>-</td>
<td>1610</td>
<td>1606</td>
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<tr>
<td>2² + 2² 19a</td>
<td>B₁</td>
<td>1693</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2² + 2² 11a</td>
<td>B₁</td>
<td>-</td>
<td>-</td>
<td>1534</td>
<td>1538</td>
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<tr>
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<td>1561</td>
<td>1555</td>
<td>1553</td>
</tr>
<tr>
<td>2² + 2² 19a</td>
<td>B₁</td>
<td>1750</td>
<td>1758</td>
<td>1757</td>
<td>1750</td>
</tr>
<tr>
<td>2² + 2² 11a</td>
<td>B₁</td>
<td>1769</td>
<td>1773</td>
<td>1768</td>
<td>1772</td>
</tr>
<tr>
<td>2² + 2² 19a</td>
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<td>1900</td>
<td>1904</td>
<td>1903</td>
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<td>2² + 2² 19a</td>
<td>A₁</td>
<td>-</td>
<td>1842</td>
<td>-</td>
<td>1837</td>
</tr>
<tr>
<td>2² + 2² 11a</td>
<td>A₁</td>
<td>1842</td>
<td>1845</td>
<td>1843</td>
<td>1844</td>
</tr>
</tbody>
</table>
The first row corresponding to each summation band indicates the observed frequencies.
region 1550-1650 cm\(^{-1}\), may explain the broadness of the observed absorption band at that region and the difficulty encountered in trying to resolve it into "purer" bands.

No attempts are made at assigning the possible summation bands in the region below 1450 cm\(^{-1}\) since these bands are expected to contain fundamentals which are not investigated in the present work. However the band at 1243 cm\(^{-1}\) may be tentatively assigned to the first overtone of \(\nu_18\) (\(2 \times 640 = 1280\) cm\(^{-1}\)).

Assignment of \(\nu_5'\) mode

The C-Sn stretching frequency which is assigned to \(\nu_5'\) is expected to fall near 1000 cm\(^{-1}\). Young, Servais, Currie and Hunter (61) have examined seven cyclic silicon compounds in which the phenyl group was attached directly to silicon. They found two bands at 1429 and 1110 cm\(^{-1}\) which may be characteristic of the Si-Ph linkage. However Richards and Thompson (48) have also found a band at 1430-1425 cm\(^{-1}\) in six compounds containing the Si-Ph linkage. They have also detected a band near 1123-1110 cm\(^{-1}\) in four of their compounds. In the case of C-Ph linkage, Pinchas and Samuel (43) have found two bands one of medium intensity at about 1185 cm\(^{-1}\) and a weak band at about 1280 cm\(^{-1}\) in thirteen compounds containing the triphenylmethyl group, these bands are assigned to the stretching modes of the C-Ph linkage. It is feasible that the 1185 cm\(^{-1}\) band is due to the symmetric stretch and the 1280 cm\(^{-1}\) band to the asymmetric stretch of the Ph\(_2\)C group. The C-Ph stretching frequency for toluene is given at 1210 cm\(^{-1}\) by Randle and Whiffen (46). Assuming that there is always certain amount of strain in the C-Ph bond in the triphenylmethyl group due to steric effect, the
value for the C-Ph stretch frequency will be better represented by the
toluene value than by the value obtained from triphenylmethyl group.

It would be expected that in the series C-Ph, Si-Ph, Ge-Ph and
Pb-Ph the frequencies of the stretching vibration of the linkage would
fall progressively in that order. Indeed the same behaviour has been
observed in the case of the tetramethylys of carbon, silicon, germanium,
tin and lead (See Part One). Therefore the assignment of the 1429 cm
band to Si-Ph stretch as suggested by Bellamy (16) is rather doubtful.
Furthermore, one may consider the stretching frequency for the diatomic
group C-M depends in the last analysis on the reduced mass of the
diatomic group and the force constant of the bond. Because of the lack
of data on the latter, one can make use of the electronegativity of
the atom as a measure of the force constant (28). As confirmation to
the above suggestion, the frequencies of the Hal-Ph stretch have been
examined. A plot is made in Figure 15a of the logarithm of the
stretching frequency of the Hal-Ph bond against the value of 
\[ 1 + \log \frac{X_M X_{C-M}}{M_{C-M}} \]
where \( X_M \) is the electronegativity of the halogen atom attached to the
phenyl group and \( M_{C-M} \) is the reduced mass of the diatom C-Hal. It
can be clearly seen from the graph that there is a smooth relationship
between the logarithm of the stretching frequency and the value of
\[ 1 + \log \frac{X_C X_M}{M_C M_M} \].
If the same kind of behaviour is expected
in the case of the M-Ph stretching vibrations (where M=C, Si, Ge, Sn or Pb)
as in the case of the halobenzenes (Figure 15a) and the tetramethylys of
group IVB elements (Figure 15b), it would be expected that the Si-Ph
stretching frequency would fall below the C-Ph stretching frequency.
Therefore the value given by Young and coworkers (61) and by Richards
FIG. 15

- (a) ○ Halobenzene
- (c) △ M(CH₃)₄
- (b) △ PhM
and Thompson (48) 1110 cm$^{-1}$ is accepted to be due to the Si-Ph stretch. It is quite possible that the higher frequency at 1429 cm$^{-1}$ is due to a more complicated mode containing the vibrations of other parts of the molecule coupled with the Si-Ph stretch.

The possible frequency to be assigned to $2^2_5$ for phenyltin compounds is that of the weak bands appearing at 1062, 1066 and 1069 cm$^{-1}$ in the spectrum of tetraphenyltin, triphenyltin chloride, and diphenyltin dichloride respectively. This can be assumed to be the symmetrical stretch. Figure 15c offers some support to this assignment. The asymmetrical stretching vibration is expected to show up at higher frequency and the possible bands for this assignment are those appearing at 1161, 1164 and 1171 cm$^{-1}$.

Only one band is expected for phenyltin trichloride and it is expected to show up at higher frequency than that of diphenyltin dichloride as indicated by the series:

$$\text{Ph}_4\text{Sn} \text{ (1062 cm}^{-1}) \text{ } < \text{Ph}_3\text{SnCl} \text{ (1066 cm}^{-1}) \text{ } < \text{Ph}_2\text{SnCl}_2 \text{ (1069 cm}^{-1})$$

However in the spectrum of phenyltin trichloride there is at 1071 cm$^{-1}$ a rather strong band which has been assigned to $2^2_1 2S$ mode, and attempts at detecting a weaker band in that region were unsuccessful. A slight change of slope at about 1069 cm$^{-1}$ was detected but no conclusion can be drawn as to the position of the maximum of the band. However, the value for the frequency of the vibration $2^2_3$ is expected to be very near 1072 cm$^{-1}$. The shoulder at 1090 cm$^{-1}$ is considered to be too high a frequency for this assignment.

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*The value (l) is added to the logarithmic term in order to move the scale to the positive side of the origin of coordinates.*
III. 3. THE INFRARED ABSORPTION SPECTRA OF BENZYL Tin COMPOUNDS

The infrared absorption spectra of tetrabenzyltin and tribenzyltin chloride are given in Tables 10 and 11 and are illustrated in Figures 16 - 21.

No remarkable variations of the absorption spectra of these two compounds were observed with change in their physical state.

The assignment of the normal frequencies for the benzyltin compounds is complicated by the presence of the methylene group whose normal frequencies are expected to overlap some of the fundamentals of the phenyl group. However, the assignment already carried out for the phenyltin compounds and the analytical table on the assignment of the normal frequencies of monosubstituted benzenes presented by Randle and Whiffen ([46]) were found to be of great help in the present case. To facilitate the assignment of the normal frequencies the best values for the frequencies of the absorption bands for tetrabenzyltin and tribenzyltin chloride are listed together in Table 12. The significance of these frequencies is the same as in the case of the phenyltin compounds (Section III 2).

ASSIGNMENT OF THE FUNDAMENTAL FREQUENCIES OF THE PHENYL GROUP

Here again only 24 out of the possible 30 normal vibrations will be assigned. The other six vibrations namely \(^{2}I_{18a},^{2}I_{17b},^{2}I_{18b},^{2}I_{20a},^{2}I_{8},\) and \(^{2}I_{20b},\) lie outside the range of transmission of the rock-salt optics.

Assignment of \(A_{1}\) fundamentals

The hydrogen stretch modes belonging to class \(A_{1}\) and \(B_{1}\) are discussed
### TABLE 10
THE INFRARED ABSORPTION SPECTRUM OF TETRABENZYLITIN

<table>
<thead>
<tr>
<th>mull mull</th>
<th>solid film</th>
<th>solution in CS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq. cm⁻¹ relative intensity</td>
<td>freq. cm⁻¹ relative intensity</td>
<td>freq. cm⁻¹</td>
</tr>
<tr>
<td>707</td>
<td>v.s.</td>
<td>711</td>
</tr>
<tr>
<td>712</td>
<td>v.s.</td>
<td>713</td>
</tr>
<tr>
<td>780</td>
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<td>781</td>
</tr>
<tr>
<td>796</td>
<td>v.w.</td>
<td>797</td>
</tr>
<tr>
<td>842</td>
<td>v.w.</td>
<td>843</td>
</tr>
<tr>
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<td>909</td>
</tr>
<tr>
<td>962</td>
<td>v.s.</td>
<td>963</td>
</tr>
<tr>
<td>978</td>
<td>v.s.</td>
<td>979</td>
</tr>
<tr>
<td>1004</td>
<td>v.w.</td>
<td>1005</td>
</tr>
<tr>
<td>1025</td>
<td>w.(sh)</td>
<td>1026</td>
</tr>
<tr>
<td>1026</td>
<td>m.</td>
<td>1027</td>
</tr>
<tr>
<td>1069</td>
<td>m.</td>
<td>1070</td>
</tr>
<tr>
<td>1147</td>
<td>w.</td>
<td>1148</td>
</tr>
<tr>
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<td>w.</td>
<td>1186</td>
</tr>
<tr>
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<td>w.</td>
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<tr>
<td>1496</td>
<td>m.s.</td>
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</tr>
<tr>
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<td>1551</td>
</tr>
<tr>
<td>1571</td>
<td>w.</td>
<td>1572</td>
</tr>
<tr>
<td>1591</td>
<td>m.(sh)</td>
<td>1592</td>
</tr>
<tr>
<td>1604</td>
<td>m.</td>
<td>1605</td>
</tr>
<tr>
<td>1658</td>
<td>v.w.</td>
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</tr>
<tr>
<td>1675</td>
<td>v.w.</td>
<td>1676</td>
</tr>
<tr>
<td>1750</td>
<td>w.</td>
<td>1751</td>
</tr>
<tr>
<td>1803</td>
<td>w.</td>
<td>1804</td>
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TABLE 10 (Concluded)

<table>
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<tr>
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<th>solid film freq. cm(^{-1})</th>
<th>solution in CS(_2) freq. cm(^{-1})</th>
<th>A%</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative intensity</td>
<td>relative intensity</td>
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<td></td>
</tr>
<tr>
<td>1875 w.</td>
<td>1878 w.</td>
<td>1875</td>
<td>46</td>
</tr>
<tr>
<td>1892 v.w.</td>
<td>1894 v.w.</td>
<td>1892</td>
<td>30</td>
</tr>
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<td>1950 w.</td>
<td>1952 w.</td>
<td>1948</td>
<td>56</td>
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<tr>
<td>1964 v.w.</td>
<td>1980 v.w.</td>
<td>1966</td>
<td>35</td>
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<td>2870</td>
<td>9*</td>
</tr>
<tr>
<td></td>
<td>2951 s.</td>
<td>2943</td>
<td>20*</td>
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<td></td>
<td>3036 s.</td>
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<td>26*</td>
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<td></td>
<td>3061 m(sh)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>3037 m.w. (sh)</td>
<td>3069</td>
<td>19*</td>
</tr>
<tr>
<td></td>
<td>3144 m.w. (sh)</td>
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</table>

For details of concentrations of solutions and path length see the figure of the spectrum.

\* Path length = 0.01 mm
### Table 11

The Infrared Absorption Spectrum of Tribenzylium Chloride

<table>
<thead>
<tr>
<th>Nujol Mull</th>
<th>Solution in CS₂</th>
<th>Solution in CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq. cm⁻¹</td>
<td>relative intensity</td>
<td>freq. cm⁻¹</td>
</tr>
<tr>
<td>700</td>
<td>v.s</td>
<td>702</td>
</tr>
<tr>
<td>710</td>
<td>w(sh)</td>
<td>750</td>
</tr>
<tr>
<td>755</td>
<td>m(sh)</td>
<td>768</td>
</tr>
<tr>
<td>760</td>
<td>v.s</td>
<td>800</td>
</tr>
<tr>
<td>803</td>
<td>n</td>
<td>816</td>
</tr>
<tr>
<td>818</td>
<td>w</td>
<td>842</td>
</tr>
<tr>
<td>848</td>
<td>v.w.</td>
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<tr>
<td>904</td>
<td>w</td>
<td>983</td>
</tr>
<tr>
<td>970</td>
<td>w</td>
<td>996</td>
</tr>
<tr>
<td>997</td>
<td>w</td>
<td>1026</td>
</tr>
<tr>
<td>1028</td>
<td>m.w</td>
<td>1047</td>
</tr>
<tr>
<td>1045</td>
<td>m</td>
<td>1083</td>
</tr>
<tr>
<td>1087</td>
<td>m</td>
<td>1092</td>
</tr>
<tr>
<td>1102</td>
<td>w</td>
<td>1105</td>
</tr>
<tr>
<td>1115</td>
<td>v.w</td>
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<td>1153</td>
<td>v.w</td>
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<td>m.w</td>
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<td>v.w.</td>
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<tr>
<td>1350</td>
<td>v.w.</td>
<td>1354</td>
</tr>
<tr>
<td>1457</td>
<td>s</td>
<td>1492</td>
</tr>
<tr>
<td>1488</td>
<td>m.s</td>
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<tr>
<td>1721</td>
<td>62</td>
<td>1746</td>
</tr>
</tbody>
</table>

* indicates strong band; ** indicates medium band; *** indicates weak band.
TABLE II (Concluded)

<table>
<thead>
<tr>
<th>Mijol null</th>
<th>solution in CS₂</th>
<th>solution in CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq. cm⁻¹</td>
<td>freq. cm⁻¹</td>
<td>freq. cm⁻¹</td>
</tr>
<tr>
<td>relative</td>
<td>A%</td>
<td>A%</td>
</tr>
<tr>
<td>intensity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1801 v.w</td>
<td>1804 25</td>
<td>1809 22</td>
</tr>
<tr>
<td>1871</td>
<td>1875 20</td>
<td></td>
</tr>
<tr>
<td>1883</td>
<td>1883 17</td>
<td></td>
</tr>
<tr>
<td>1946</td>
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<td>1958</td>
<td>1958 16</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>2046</td>
<td>2827 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2832 10</td>
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</tr>
<tr>
<td></td>
<td>2935 40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2930 58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2967 18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2965 34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3034 65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3032 85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3070 62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3072 82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3141 15</td>
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</tr>
</tbody>
</table>

for details of the concentration of solutions and path length see the figure of the spectrum.

* Path length = 0.10 cm. All others were measured with path length = 0.30 cm.
FIG. 17

Tetrahydrocannabinol
Solid Film

% absorption
Tetrabengyttin
Solvent: carbon disulphide
Molarity: $7.725 \times 10^{-2}$
Tribenyltin Chloride
Solvent: carbon disulphide
Molarity: $3.24 \times 10^{-3}$
Tribenzylltin Chloride
Solvent: carbon tetrachloride
Molarity: $3.891 \times 10^{-2}$
Path length: 0.30 cm

FIG. 21
### Table 12

**Assignment of the Fundamental Frequencies of Benzyltin Compounds**

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Frequency</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrabenzyltin</td>
<td>tribenzyltin chloride</td>
<td>assignment</td>
</tr>
<tr>
<td>709</td>
<td>701</td>
<td>$\gamma$ C-H, $\omega_{11b}$</td>
</tr>
<tr>
<td>710</td>
<td>710</td>
<td>$\gamma_{(CH_2)}$</td>
</tr>
<tr>
<td>752</td>
<td>764</td>
<td>$\gamma$ C-H, $\omega_4$</td>
</tr>
<tr>
<td>780</td>
<td>801</td>
<td>$\delta$ C-H, $\omega_{1n}$</td>
</tr>
<tr>
<td>796</td>
<td>817</td>
<td>$\delta$ C-H, $\omega_{19n}$</td>
</tr>
<tr>
<td>907</td>
<td>903</td>
<td>$\gamma$ C-H, $\omega_7$</td>
</tr>
<tr>
<td>946</td>
<td>975</td>
<td>$\gamma$ C-H, $\omega_{19n}$</td>
</tr>
<tr>
<td>962</td>
<td>983</td>
<td>ring vibration, $\omega_{2}$</td>
</tr>
<tr>
<td>978</td>
<td>997</td>
<td>ring vibration, $\omega_{2}$</td>
</tr>
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<td>1006</td>
<td>1028</td>
<td>$\beta$ C-H, $\omega_{12n}$</td>
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<tr>
<td>1016</td>
<td>1047</td>
<td>$\beta$ C-H, $\omega_{12b}$</td>
</tr>
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<td>1087</td>
<td>$\beta$ C-H, $\omega_{12b}$</td>
</tr>
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<td>$\beta$ C-H, $\omega_{12b}$</td>
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<td>$\beta$ C-H, $\omega_{10}$</td>
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<td>1152</td>
<td>1155</td>
<td>$\beta$ C-H, $\omega_{17n}$</td>
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<td>$\nu$ C-CH$_2$, $\omega_5$</td>
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<td>1209</td>
<td>$\omega$ (CH$_2$)</td>
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<tr>
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<td>1250</td>
<td>$\beta$ O-H, $\omega_3$</td>
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<td>1296</td>
<td>$\beta$ O-H, $\omega_3$</td>
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<td>$\omega$ (CH$_2$)</td>
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<td>$\beta$ O-H, $\omega_3$</td>
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<tr>
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<td>assignment</td>
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<td>1392</td>
<td>$^2_4 + ^2_4$</td>
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</tr>
<tr>
<td>3144</td>
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<td>$^2_4 + ^2_4$</td>
</tr>
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</table>
together. There are five such modes, three from class $A_1$ viz. $^2_1$, $^2_{14a}$, and $^2_{15a}$ and two from class $B_1$ viz. $^2_{15b}$ and $^2_{14b}$. The same difficulty is encountered here for the identification of these modes as in the case of the phenyltin compounds. The strong band at 3033 cm$^{-1}$ is assigned to $^2_{14a}$ while the moderate band at 3061 cm$^{-1}$ is assigned to $^2_{15a}$. The strong broad band at 3071 cm$^{-1}$ is assigned to modes $^2_1$ and $^2_{14b}$ which are expected to lie very near each other. The high frequency band at 3142 cm$^{-1}$ is assigned to the remaining mode $^2_{15b}$. The above assignment should be considered quite tentative.

The C-H modes $^2_{12a}$ and $^2_{17a}$ are assigned to the bands appearing at 1027 and 1183 cm$^{-1}$ respectively, which are in excellent agreement with the average frequencies for monosubstituted benzenes 1029 ± 5 and 1177 ± 6 cm$^{-1}$ (46).

Slight mixing is expected between the two ring vibrations, the totally symmetrical mode $^2_2$ and the planar trigonal mode $^2_6$. The band at 1000 cm$^{-1}$ is assigned to the former while the band at 1016 cm$^{-1}$ is assigned to $^2_6$ which agrees with the calculated value of 1012 cm$^{-1}$ for benzene.

The band near 1575 cm$^{-1}$ corresponds to the degenerate benzene vibration $^2_{16}$ which is Raman active. One member of the pair of the degenerate vibration namely $^2_{16a}$ consists of contraction and stretch of the C-C bonds and is therefore assigned to the above frequency. The remaining mode $^2_{13a}$ is assigned to the moderately strong band near 1493 cm$^{-1}$.
Assignment of B\textsubscript{1} fundamentals.

The two $^2$C-H modes $^2_{14b}$ and $^2_{15b}$ have already been discussed.

The three $^2$C-H modes $^2_{23}$, $^2_{10}$, and $^2_{12b}$ are assigned to the bands near 1311, 1158 and 1067 cm\(^{-1}\) respectively. Apart from the assignment of the 1311 cm\(^{-1}\) band the other two are in good agreement with the values quoted by Randle and Whiffen for monosubstituted benzene. The reason for the assignment of the 1311 cm\(^{-1}\) band to mode $^2_{23}$ is the same as that given for the phenyltin compounds (Section III 2).

The assignment of the carbon vibrations $^2_{9}$, $^2_{13b}$, $^2_{16b}$, and $^2_{18b}$ is very similar to the assignment for the phenyltin compounds. Thus $^2_{9}$, $^2_{13b}$, and $^2_{16b}$ are assigned to the bands appearing at 1331, 1457 and 1603 cm\(^{-1}\) respectively. The last mentioned band i.e. at 1603 cm\(^{-1}\) is much better defined than the corresponding, rather broad, band of the phenyltin compounds.

Assignment of A\textsubscript{2} fundamentals.

The two $^2$C-H modes $^2_{11a}$ and $^2_{19a}$ are assigned to the weak bands at 843 and 985 cm\(^{-1}\) respectively. Some mixing is expected between these two vibrations which may account for the fact that the former is lower in frequency and the latter is of higher frequency than the corresponding frequencies for the phenyltin compounds.

Assignment of B\textsubscript{2} fundamentals.

Four of the six modes lie in the region measured in the present work. They are all $^2$C-H vibrations and are expected to be of higher intensity than the A\textsubscript{2} vibrations.

The strong band near 705 cm\(^{-1}\) is assigned to node $^2_{11b}$. The next
strong band at 764 cm\(^{-1}\) is assigned to mode $\text{a}^2_4$. It is interesting to compare the value of the $\text{a}^2_4$ mode for the phenyltin and the benzyltin compounds. The value for the phenyltin compounds lie near 739 cm\(^{-1}\) which is at the lower end of the average value quoted by Randle and Whiffen (46) viz. 751 ± 15 cm\(^{-1}\) while the value for the benzyltin compounds lies near the higher end of that average.

The remaining two modes $\text{a}^2_7$ and $\text{a}^2_{19b}$ are assigned to the bands near 976 and 905 cm\(^{-1}\) respectively.

Assignment of the summation bands.

The summation bands of the out-of-plane C-H vibrations provide further confirmation for the assignments of the fundamentals. These bands are expected to appear in the range 1450-2000 cm\(^{-1}\). They are in general very similar to the summation bands of the phenyltin compounds which have already been discussed in details in Section III 2. The assignment of the observed frequencies is given in Table 12.

The assignment of mode $\text{a}^2_5$.

The assignment of the mode $\text{a}^2_5$ for the two compounds investigated is rather tentative. The corresponding frequency for toluene (46) is 1210 cm\(^{-1}\). The substitution of a heavy atom, such as tin, on the methyl carbon would be expected to lower the frequency of the C-C stretch. However, as has already been discussed in Section III 2, the triphenylmethyl group has two absorption bands at 1185 and 1280 cm\(^{-1}\) characteristic of the C-Ph stretch vibration. The only possible candidate for the assignment to mode $\text{a}^2_5$ is the band near 1211 cm\(^{-1}\).
There are six normal vibrations associated with the methylene group (52). The two νC-H modes, symmetrical $\nu_3$ and asymmetrical $\nu_a$ vibrations, are assigned to the band at 2872 cm$^{-1}$ and to the bands near 2940 cm$^{-1}$ respectively. They agree quite well with the two bands of benzyl alcohol (52) i.e. 2874 and 2937 cm$^{-1}$, but are rather high with respect to the frequencies of diphenylmethane (52) i.e. 2844 and 2912 cm$^{-1}$ and with the frequencies 2851 and 2923 cm$^{-1}$ of polystyrene (36).

The other four modes are C-H bending vibrations which may be classified as rocking (νr), wagging (ω), twisting and scissoring (νs) modes (48a). The $\nu_2$(CH$_2$) vibration have been found to lie near 1460 cm$^{-1}$ in a number of alkyl substituted benzenes (52). However the band at 1457 cm$^{-1}$ which has been assigned to the C-C mode $\nu_3$ is quite strong and its strength may be partly due to the $\nu_2$(CH$_2$) vibration. This assignment can only be considered as tentative since Francis (27a) has shown that the scissoring vibration of the methylene group is quite sensitive to the type of atom or group to which it is attached.

The rocking mode $\nu_r$(CH$_2$) in a number of aliphatic compounds is found near 720 cm$^{-1}$. However, it has been found (18a) to be highly sensitive to coupling with the vibrations of the neighbouring groups, and therefore its assignment to the band at 710 cm$^{-1}$ can only be quite tentative. The wagging mode ω(CH$_2$) is expected (52) to give rise to a weak band near 1300 cm$^{-1}$. The band at 1296 cm$^{-1}$ is therefore assigned to ω(CH$_2$).
INTRODUCTION

Although the strict symmetry of p-substituted benzenes with different substituents is that of Group $C_2v$, the normal coordinates of the modes of vibrations can best be dealt with on the basis of the molecular symmetry of Group $D_{2h}(V_h)$ (29, 46, 59). The coordinate axes of p-substituted benzene may be fixed so that the $y$-axis passes through the unique 1:4 positions and the $z$-axis is perpendicular to the plane of the molecule and the origin of the coordinates is the geometric centre of the benzene hexagon which lies in the $xy$-plane with the $x$-axis bisecting the $C_2-C_3$ bond. A model of $V_h$ symmetry will have the following elements of symmetry:

- $E$, the identity element;
- $C_2^x$, 2-fold axis of symmetry along the $z$-axis;
- $C_2^y$, 2-fold axis of symmetry along the $y$-axis;
- $C_2^x$, 2-fold axis of symmetry along the $x$-axis;
- $\sigma_{xy}$, a plane of symmetry, the plane of the molecule;
- $\sigma_{xz}$, a plane of symmetry in the $xz$-plane containing the 2-fold axes $C_2^x$ and $C_2^x$;
- $\sigma_{yz}$, a plane of symmetry in the $yz$-plane containing the 2-fold axes $C_2^y$ and $C_2^y$;
- $i$, a centre of symmetry, the geometric centre of the molecule.

Since there is no symmetry axis of higher order than two, all the possible vibrational degrees of freedom are therefore non-degenerate and there are thirty different modes of vibrations. These vibrations are
designated as:

- \( A \) symmetrical to \( C_2, C_{\infty}, C_2^* \)
- \( B_1 \) symmetrical to \( C_2^* \) only
- \( B_2 \) symmetrical to \( C_{\infty} \) only
- \( B_3 \) symmetrical to \( C_{\infty} \) only
- \( g \) symmetrical to \( i \)
- \( u \) antisymmetrical to \( i \)

There are eight symmetry classes which are related to the symmetry classes of the benzene model \( D_{6h} \) and the monosubstituted benzenes model \( C_{2v} \) as outlined below:

\[
\begin{array}{ccc}
D_{6h} & V_h & C_{2v} \\
A_{1g}, E_{2g} & A_g & A_1 \\
B_{1u}, B_{1u} & B_{2u} & \\
A_{1u}, E_{2u} & A_u & A_2 \\
B_{1g}, E_{1g} & B_{2g} & \\
A_{2g}, E_{2g} & B_{1g} & B_1 \\
B_{2u}, E_{1u} & B_{3u} & \\
A_{2u}, E_{2u} & B_{1u} & B_2 \\
B_{2g}, E_{1g} & B_{3g} & \\
\end{array}
\]

For \( p \)-substituted benzenes with identical substituents there are 15 Raman active modes (those which are symmetrical with respect to the centre of symmetry) and 15 Raman inactive modes (antisymmetrical with respect to \( i \)). Of these 13 are infrared active and the remaining two which belong to class \( A_u \) are infrared inactive. However for the compounds investigated here this distinction is no longer valid for in reality the molecules have no centre of symmetry. The approximation of the symmetry
of the molecules to $V_h$ model is quite useful however in the assignment of the fundamental frequencies. It makes it possible to construct the normal coordinates of the $\pi$-substituted benzenes irrespective of the nature of the substituents, directly from the normal coordinates of benzene. Because of the mixing expected between the benzene classes which are merging together in the $V_h$ symmetry classes in the manner indicated above, it is expected that in certain cases new normal coordinates diagrams would have to be constructed. These new modes will be indicated when the assignment of the normal frequencies is attempted.

The method outlined in Section III 1 to determine the symmetry properties of model $C_{2v}$ is used here to find the symmetry properties of model $V_h$ for $\pi$-substituted benzenes. The number of normal vibrations per class symmetry thus determined is given below:

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The normal coordinates for the normal modes of vibrations $1:4$ dideutero benzene given by Ingold and his co-workers (10) have been used, with certain modification, in the presentation of the normal coordinates for $\pi$-substituted benzenes. Use is also made of the values of the average frequencies for the normal modes of $\pi$-substituted benzenes presented by Randle and Whiffen (46).
The spectra of tetra-\(\alpha\)-tolyltin and tetrakis-\(\alpha\)-chlorophenyltin have been determined in various solvents and in suspension in Nujol. No significant difference was found between the measurements in different states and solvents (see Tables 13 and 14 and Figures 22 - 27).

**Assignment of the fundamental frequencies of the phenyl group:**

Assignment of \(A_g\) fundamentals.

There are six modes derived from \(2A^1g\) and \(4E^2g\) modes of benzene. They can be divided into two hydrogen and three carbon vibrations and one vibration of the \(M-C\) diatom (where \(M\) represents the substituent atom or group).

Two of the three carbon modes are similar to the corresponding benzene vibrations, they are \(2^2_{16a}\) and \(2^2_{18a}\). The \(2\sigma-C-C\) mode, \(2^2_{16a}\), is expected near 1600 cm\(^{-1}\). The weak band near 1628 cm\(^{-1}\) in the spectrum of tetra-\(\alpha\)-tolyltin is assigned tentatively to this mode. The average value for this mode is 1620 ± 8 cm\(^{-1}\) for \(\alpha\)-substituted benzenes (46). The third carbon vibration \(2^2_{18a}\) is expected to fall beyond the spectral range investigated (10).

The \(\beta-C-H\) vibration, \(\delta^2_{17a}\), is similar to that of benzene and its frequency is expected near 1179 ± 7 cm\(^{-1}\). The moderately intense band near 1187 cm\(^{-1}\) in the spectrum of tetrakis-\(\alpha\)-chlorophenyltin and the band near 1191 cm\(^{-1}\) in the spectrum of tetra-\(\alpha\)-tolyltin are assigned to \(2^2_{17a}\) mode.

The remaining two modes \(2^2_{1}\) and \(2^2_{15a}\) in this class are expected to undergo extensive mixing with modes \(2^2_{5}\) and \(2^2_{14a}\) of class \(B_{2u}\). The fact that the strict symmetry of the molecules is that of \(C_{2v}\) makes such mixing possible; for as has been discussed earlier both \(A_g\) class and
<table>
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<th>soln. in CHCl₃</th>
<th>Assignment</th>
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For details of path length and concentration of solutions see the figure of the spectrum.
## Table 14

The Infrared Absorption Spectrum of Tetraakis-\( \text{p-CH}_3 \text{C}_{6} \text{H}_4 \text{Sn} \text{Sn})\text{Cl}_2\text{Sn} \text{SnCl}_3\text{SnCl}_2\text{Cl}

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**TABLE 14 (concluded)**
Figure 23

Tetra-p-tolyltin

Solvent: carbon disulphide

Saturated solution, Path length: 0.10 cm.
Temp. polystyrene
Solvent: chloroform
Saturated solution
Path length: 0.2 cm

FIG. 24
Tetrakis-p-chlorophenyltin
Solvent: carbon disulphide
Molarity: $3.76 \times 10^{-2}$
Path length: 0.30 cm

% absorption

FIG. 26
Tetraakis-p-chlorophenyltin
Solvent: carbon tetrachloride
Molarity: \(1.018 \times 10^{-2}\)
Path Length: 0.30 cm

FIG. 27
B_{2u} class of Group V_{h} merge together to form A_{1} class of Group C_{2v}.

Besides, the difference of masses of the two substituents (Cl and Sn in one case and CH\textsubscript{3} and Sn in the other case) makes it quite likely that the amplitude of their vibrations is so different as to exclude any extensive coupling. Therefore, the mixing of these four modes gives rise to the following modified normal coordinates for the vibrations which can be easily identified as

two \nu^{C-H} modes \nu_{1}', \nu_{14a}' and two \nu^{C-M} modes. Modes \nu_{5}' and \nu_{15a}' are expected to undergo some slight coupling which increases as the masses of the two substituents approach equality. Thus more coupling is expected between \nu_{5}' and \nu_{15a}' in tetrakis-\textgamma-chlorophenyltin than in tetra-\textgamma-tolyltin. In the extreme case where complete coupling takes place, modes \nu_{5}' and \nu_{15a}' may be modified to give:
The two bands near 3024 and 3069 cm\(^{-1}\) in the spectrum of tetrakis-\(\beta\)-chlorophenyltin are assigned to \(2\nu_{14a}\) and \(2\nu_{1}\) respectively. In the spectrum of tetra-\(\beta\)-tolyltin, the bands at 3032 and 3057 cm\(^{-1}\) are assigned to these modes respectively. The above assignment is guided by the frequencies of the corresponding vibrations of the phenyltin and the benzyltin compounds (Section III 2 and III 3).

The Sn-C stretching vibration, mode \(\nu_{5}\), is assigned to the strong band at 1061 cm\(^{-1}\) in the spectrum of tetrakis-\(\beta\)-chlorophenyltin and to the strong band at 1076 cm\(^{-1}\) in the spectrum of tetra-\(\beta\)-tolyltin. The values assigned to \(\nu_{C-Sn}\) in the phenyltin compounds were in the range of 1062-1069 cm\(^{-1}\).

The assignment of \(\nu_{15a}\) to the bands at 1094 cm\(^{-1}\) and 1216 cm\(^{-1}\) for \(\nu_{C-Cl}\) and \(\nu_{C-CH_3}\) respectively is confirmed by the values for chlorobenzene (1083 cm\(^{-1}\)) (55) and for toluene (1210 cm\(^{-1}\)) (46). Both these frequencies indicate certain amount of coupling between \(\nu_{5}\) and \(\nu_{15a}\) in the manner indicated by the extreme case of modes \(\nu_{5}\) and \(\nu_{15a}\), and that there is more coupling in tetrakis-\(\beta\)-chlorophenyltin than in tetra-\(\beta\)-tolyltin, in accordance with expectations.

Similar mixing takes place between mode \(\nu_{2}\) of class \(A_g\) and \(\nu_{6}\) of class \(B_{2u}\) to give the following trigonally symmetrical modes \(\nu_{2}\) and \(\nu_{6}\):

![Diagram showing trigonally symmetrical modes \(\nu_{2}\) and \(\nu_{6}\)](image-url)
Mode $\nu_2$ involves the motion of the tin atom, which is assumed to be attached to C1, and therefore the corresponding frequency is expected to fall below 650 cm\(^{-1}\). Mode $\nu_6$ which involves the motion of the chlorine atom in tetrakis-p-chlorophenyltin and the methyl group in tetra-p-tolylltin can be assigned to the strong bands at 730 cm\(^{-1}\) and 796 cm\(^{-1}\) respectively. The corresponding values for chlorobenzene and toluene are 701 and 786 cm\(^{-1}\).

Assignment of $D_{1g}$ fundamentals.

There are five normal modes in this class derived from 1 $A_{2g}$ and 4 $E_{2g}$ modes of benzene. The three $E_{2g}$-like modes $\nu_{15b}$, $\nu_{16b}$, and $\nu_{18b}$ are unmodified benzene modes.

Mode $\nu_{15b}$ is a C-H vibration which is assigned to the band at 3109 cm\(^{-1}\) in the spectrum of tetra-p-tolylltin. The poor resolving power of rock-salt optics at that region may be responsible for the failure to observe any similar band in the spectrum of tetrakis-p-chlorophenyltin.

Mode $\nu_{16b}$ constitutes a carbon stretching vibration. The average value found for p-substituted benzenes is 1571 ± 11 cm\(^{-1}\). The bands at 1573 cm\(^{-1}\) and at 1600 cm\(^{-1}\) of tetrakis-p-chlorophenyltin and of tetra-p-tolylltin respectively are assigned to this mode.

Mode $\nu_{18b}$ which is a carbon deformation vibration is expected (46) at 644 ± 8 cm\(^{-1}\) in p-substituted benzenes. No band near 650 cm\(^{-1}\) was detected in either spectra.
The remaining two modes are derived from the orthogonal combination of \( ^2 \) and \( ^2 \) modes of benzene to give \( ^{22} \) and \( ^{17b} \).

The latter mode involves C-M in-the-plane bending vibration and is therefore expected to fall outside the spectral range covered. The former mode is expected to have a weak band near 1309 cm\(^{-1} \). The bands near 1310 and 1309 cm\(^{-1} \) in the spectra of tetrakis-\( \delta \)-chlorophenyltin and tetra-\( \delta \)-tolyltin respectively are assigned to mode \( ^{22} \).

Assignment of \( B_{2g} \) fundamentals.

There is only one normal vibration in this class which is derived from the \( \delta \) C-H mode \( ^{11a} \) of benzene. The mode is expected to have a very weak band near 850 cm\(^{-1} \). The weak band at 842 cm\(^{-1} \) and at 845 cm\(^{-1} \) in the spectra of tetrakis-\( \delta \)-chlorophenyltin and tetra-\( \delta \)-tolyltin are therefore assigned to this mode.

Assignment of \( B_{3g} \) fundamentals.

The three modes of this class are all \( \delta \) C-H vibrations which are derived from 2 \( B_{2g} \) and 1 \( E_{1g} \) modes of benzene. One of the two \( B_{2g} \) -like modes viz. \( \nu_6 \) is similar to that of benzene. The frequency of the
vibration is however expected outside the range studied (10).

The remaining $B_{2g}$-like mode mixes with the $E_{1g}$ mode to give $\nu_7$ and $\nu_{11b}$.

The frequency of the latter mode is expected to fall below 650 cm\(^{-1}\).

The former mode is assigned to frequency 947 cm\(^{-1}\) and to 962 cm\(^{-1}\) of tetrakis-$p$-chlorophenyltin and of tetra-$p$-tolyltin respectively. The average value for $p$-substituted benzenes is 961 ± 12 cm\(^{-1}\).

**Assignment of $A_u$ fundamentals.**

There are two modes, $\nu_{19a}$ and $\nu_{20a}$, which are derived from class $E_{2u}$ of benzene. They are both forbidden in a molecule obeying strictly $V_h$ symmetry; but in the present case the vibrations are expected to show weak bands. Ingold and co-workers have calculated the frequencies 970 and 405 cm\(^{-1}\) for these two modes respectively for 1:4 dideuterobenzene. The average value found for $p$-substituted benzenes is 961 ± 12 cm\(^{-1}\) for $\nu_{19a}$. The band near 964 cm\(^{-1}\) of tetra-$p$-tolyltin is assigned to this mode. For tetrakis-$p$-chlorophenyltin the band at 970 cm\(^{-1}\) is assigned.
Assignment $B_{2u}$ fundamentals.

The three normal modes of this class namely $\nu_4$, $\nu_{19b}$ and $\nu_{20b}$ are derived from 1 $A_{2u}$ and 2 $E_{2u}$ classes of benzene. Apart from mode $\nu_{20b}$, the other two modes are expected to interact considerably and to give rise to two new modes $\nu_4$ and $\nu_{19b}$.

Only the frequency of mode $\nu_4$ is expected within the spectral range studied. The average value found for $\pi$-substituted benzenes is $817 \pm 13$ cm$^{-1}$. The bands at 804 cm$^{-1}$ and at 803 cm$^{-1}$ of tetraakis-$\pi$-chlorophenyltin and of tetra-$\pi$-tolyltin respectively are assigned to this mode.

Assignment of $B_{2u}$ fundamentals.

There are five modes in this class derived from 2 $B_{1u}$ and 3 $E_{1u}$ modes of benzene. While the two $\nu$-$C$-$H$-like modes derived from class $B_{1u}$ and class $E_{1u}$ are expected to interact together with the two $\nu$-$C$-$H$-like modes of class $A_y$, as well as node $\nu_6$, as discussed earlier, the $\beta$-$C$-$H$ node $\nu_{12a}$ and the carbon vibration $\nu_{13a}$ are left almost unaffected by substitution. They resemble the corresponding
benzene nodes.

The $\nu_{C-C}$ mode $\nu_{13a}$ is assigned to the frequencies 1533 and 1501 cm$^{-1}$ of moderately strong intensities of tetrakis-$p$-chlorophenyltin and tetra-$p$-tolytlin respectively. The average value of $p$-substituted benzenes is $1512 \pm 12$ cm$^{-1}$.

The $\beta_0$-H mode, $\nu_{12a}$, is assigned to the frequencies 1015 and 1020 cm$^{-1}$ of tetrakis-$p$-chlorophenyltin and tetra-$p$-tolytlin respectively. The average value for $p$-substituted benzenes is $1018 \pm 10$ cm$^{-1}$.

Assignment of $B_{3u}$ fundamentals.

The five $B_{3u}$ modes are derived from 2 $B_{2u}$ and 3 $E_{1u}$ modes of benzene. They can be divided into 1 $\nu$-C-H vibration i.e. $\nu_{14b}$, 2 $\beta$-H-like vibrations i.e. $\nu_{10}$ and $\nu_{12b}$, and two vibrations ( $\nu$-C-C) i.e $\nu_9$ and $\nu_{13b}$.

The $\nu$-C-H mode, $\nu_{14b}$, is assigned to the broad band at 3069 and 3057 cm$^{-1}$ of tetrakis-$p$-chlorophenyltin and tetra-$p$-tolytlin.

The two $\beta$-H-like modes are derived from the orthogonal combination of modes $\nu_{10}$ and $\nu_{12b}$ of benzene to give modes $\nu_{10}$ and $\nu_{12b}$:
The former mode is assigned to frequencies 1130 and 1117 cm\(^{-1}\) of tetrakis-\(p\)-chlorophenyltin and tetra-\(p\)-tolyltin respectively. The average frequency found for \(p\)-substituted benzenes is 1125 \(\pm\) 10 cm\(^{-1}\). Mode \(v_{12b}\) is expected with a frequency below 650 cm\(^{-1}\).

The \(\nu\)-C-O vibrations \(\nu_{9}\) and \(\nu_{13b}\) are assigned to frequencies 1324 and 1483 cm\(^{-1}\) of tetrakis-\(p\)-chlorophenyltin. The corresponding frequencies for tetra-\(p\)-tolyltin are 1321 and 1457 cm\(^{-1}\) respectively.

Assignment of the summation frequencies

The summation bands characteristic of aromatic compounds appearing in the region 2000-1600 cm\(^{-1}\) are due to the \(C-H\) out-of-plane normal frequencies appearing between 1000 and 650 cm\(^{-1}\). Whiffen has found that the following combinations are expected to have moderate intensities and to be responsible for the absorption pattern observed in aromatic compounds in the region 2000-1600 cm\(^{-1}\);

\[
\begin{align*}
\nu_{4} + \nu_{11a} \\
\nu_{4} + \nu_{7} \\
\nu_{11a} + \nu_{19a} \\
\nu_{7} + \nu_{19a}
\end{align*}
\]

The assignment of these combination bands is indicated in Tables 10 -11.

The strong band at 1725 cm\(^{-1}\) in the spectrum of tetra-\(p\)-tolyltin in carbon tetrachloride solution appears to be anomalous. It is of higher intensity than that expected for a combination band and its position rules out the possibility that it might be a fundamental.

The assignment of the summation bands expected in the region \(<1600\text{cm}^{-1}\) could not be attempted since not all of the fundamentals below 1000 cm\(^{-1}\) are known.
There are four prominent methyl modes expected in the spectral region studied:

- Two methyl C-H stretch and two deformation vibrations i.e. $\nu_s(CH_3)$, $\nu_a(CH_3)$, $\beta_a(CH_3)$ and $\beta_s(CH_3)$ respectively (52).

The bands at 2876 and 2931 cm$^{-1}$ of the spectrum of tetra-2-tolyltin are assigned to $\nu_s(CH_3)$ and $\nu_a(CH_3)$ respectively. The agreement of the present assignment with that for toluene and 1:4 dimethylbenzene is quite good (52).

The methyl deformation vibrations are expected (52) to fall near 1454 and 1391 cm$^{-1}$. The bands appearing at 1454 and 1391 cm$^{-1}$ are assigned to $\beta_a(CH_3)$ and $\beta_s(CH_3)$ respectively.
III. 5. THE InFRARED ABSORPTION SPECTRA OF TRIETHYLTIN PHENOXIDE AND N-TRIETHYLTIN PHTHALIMIDE.

The infrared absorption spectra of triethyltin phenoxide was measured in order to investigate the variation in the phenyl frequencies in the series: PhSn, PhOCH₂Sn, PhOSn. In the case of N:triethyltin phthalimide the interest is focussed on the effect at attaching a heavy atom (i.e. tin) to the nitrogen atom on the carbonyl frequencies.

The spectra of the two compounds were measured in the region 4000-650 cm⁻¹. They are given in Tables 15 and 16 and in Figures 28-30.

Triethyltin phenoxide and N:triethyltin phthalimide belong to the same symmetry group viz: C₂ᵥ. However, some variations are expected in the frequencies of the two compounds. Therefore the assignment of the phenyl frequencies will be carried out separately for the two compounds.

ASSIGNMENT OF THE PHENYL FREQUENCIES FOR TRIETHYLTIN PHENOXIDE.

The frequencies of the νC-H mode viz, ν₁, ν₁₅a, ν₁₄a of class A₁ and ν₁₅b, ν₁₄b of class B₁ are expected in the region 3100-3000 cm⁻¹. However the very strong νC-H bands of the ethyl group together with the possible summation bands which are expected in this region have confused the picture of the spectrum. But the two moderate bands at 3025 and 3066 cm⁻¹ can be easily located. These two bands are assigned tentatively to the above phenyl modes with the exception of ν₁₅b which is expected to have a frequency greater than 3100 cm⁻¹.

The C-H in-the-plane bending modes ν₁₂a, ν₁₇a of class A₁ and ν₁₀, ν₁₂b of class B₁ are all assigned to frequencies in the region 1300-1000 cm⁻¹ in good agreement with the phenyltin and the benzyltin compounds. Modes ν₁₂a, ν₁₇a, ν₁₀, ν₁₂b are assigned to frequencies
## Table 15

**The Infrared Absorption Spectrum of Triethyltin Phenoxide**

<table>
<thead>
<tr>
<th>Capillary Film</th>
<th>0.001 cm lig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq. cm(^{-1})</td>
<td>freq. cm(^{-1})</td>
</tr>
<tr>
<td>r.i.</td>
<td>%</td>
</tr>
</tbody>
</table>

<p>| 675 | m.s | 671 | 95 | C-O-H, (\nu_{11b}) |
| 699 | m.s | 677 | 96 | C-O-H, (\nu_{7}) |
| 767 | m.s | 698 | 98 | CH(_3) rocking |
| 800 | w | 766 | 100 | sym. stretch (C-Sn-C) |
| 831 | m(sh) | 766 | 100 | asym. stretch (C-Sn-C) |
| 835 | m | 699 | 70 | CH(_3) rocking |
| 844 | m(sh) | 831 | 96 | |
| 849 | m.s | 836 | 100 | |
| 883 | w | 836 | 100 | |
| 912 | w | 883 | 71 | |
| 951 | w | 887 | 69 | |
| 962 | w | 878 | 70 | |
| 1001 | m(sh) | 956 | 78 | |
| 1003 | m(sh) | 963 | 79 | |
| 1009 | m(sh) | 975 | 57(sh) | |
| 1012 | m | 1002 | 97 | |
| 1016 | m | 1009 | 93 | |
| 1021 | m | 1013 | 95 | |
| 1074 | m.w | 1016 | 96 | |
| 1115 | w | 1022 | 97 | |
| 1155 | w | 1072 | 85 | |
| 1169 | n | 1115 | 30 | |
| 1194 | n | 1156 | 66 | |
| 1198 | m.w | 1167 | 98 | |
| 1240 | m.s | 1197 | 91 | |
| 1261 | m.s(sh) | | | |</p>
<table>
<thead>
<tr>
<th>capillary film</th>
<th>0.001 cm li</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq.$\text{cm}^{-1}$</td>
<td>freq.$\text{cm}^{-1}$</td>
</tr>
<tr>
<td>r.i.</td>
<td>%</td>
</tr>
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<td>s</td>
</tr>
<tr>
<td>1283</td>
<td>m.s</td>
</tr>
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<td>w</td>
</tr>
<tr>
<td>1329</td>
<td>w</td>
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<td>w(sh)</td>
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<tr>
<td>2863</td>
<td>m.s</td>
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<td>2885</td>
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<td>2927</td>
<td>s</td>
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<td>capillary film</td>
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<tr>
<td>---------------</td>
<td>-------------</td>
</tr>
<tr>
<td>freq. cm⁻¹</td>
<td>freq. cm⁻¹</td>
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<tr>
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<td>s</td>
</tr>
<tr>
<td>2985</td>
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<tr>
<td>2998</td>
<td>m(sh)</td>
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<tr>
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<td>m(w)</td>
</tr>
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<td>3066</td>
<td>m(w)</td>
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<tr>
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<td>48</td>
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<tr>
<td>3337</td>
<td>37</td>
</tr>
<tr>
<td>3586</td>
<td>28</td>
</tr>
</tbody>
</table>

\( ^2a_{3}(CH_3) \)

\( \nu C-H, \nu_{14a}, \nu_{15a} \)

\( \nu C-H, \nu_{1}, \nu_{14b} \)
### Table 16

**The Infrared Absorption Spectrum of N-Triethyltin Phthalimide**

<table>
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<th>soln. in CS₂</th>
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</thead>
<tbody>
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<td>freq. cm⁻¹</td>
</tr>
<tr>
<td>r.i.</td>
<td>A%</td>
</tr>
</tbody>
</table>

<p>| 666  | m(sh) | 660 | 65 | ν_C-H, ν₁₁b |
| 673  | m     | 666 | 70 | (CH₂)       |
| 687  | m     | 977 | 74 |           |
| 698  | m(sh) | 688 | 70 |           |
| 704  | w     | 698 | 38 |           |
| 711  | w     | 698 | 38 |           |
| 728  | s     | 731 | 98 |           |
| 760  | v.w   | 731 | 98 |           |
| 769  | w     | 731 | 98 |           |
| 784  | w     | 731 | 98 |           |
| 803  | m.w   | 731 | 98 |           |
| 821  | w     | 824 | 19 | CH₃ rocking |
| 832  | v.w   | 824 | 19 |           |
| 844  | v.w   | 824 | 19 |           |
| 848  | v.w   | 824 | 19 |           |
| 859  | m     | 854 | 33 | ν_C-H, ν₁₁a |
| 889  | w     | 854 | 33 |           |
| 963  | w     | 854 | 33 |           |
| 969  | m.w   | 854 | 33 |           |
| 975  | m.w   | 854 | 33 |           |
| 988  | w     | 854 | 33 |           |
| 997  | w     | 854 | 33 |           |
| 1016 | m     | 1003| 23 | C₅H₅ skeletal vibration |
| 1022 | m     | 1003| 23 | ring vibration, ν₂ |
| 1029 | m(sh) | 1003| 23 | ring vibration, ν₆ |
| 1022 | m     | 1003| 23 |           |
| 1029 | m(sh) | 1003| 23 |           |</p>
<table>
<thead>
<tr>
<th>freq. cm(^{-1})</th>
<th>Assignment</th>
<th>Assignment</th>
<th>Assignment</th>
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<tbody>
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<td>solid film</td>
<td>soln. in CS(_2)</td>
<td>Assignment</td>
<td>Assignment</td>
</tr>
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<td>freq. cm(^{-1})</td>
<td>r.i.</td>
<td>freq. cm(^{-1})</td>
<td>A%</td>
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<td>1032 m</td>
<td>1032</td>
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<td>(\beta) C-H, (\tilde{v}_{12a})</td>
</tr>
<tr>
<td>1044 w</td>
<td>1049</td>
<td>24</td>
<td>(\beta) C-H, (\tilde{v}_{12b})</td>
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<tr>
<td>1064 m, w</td>
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<td>skeletal vibration of heterocyclic ring</td>
</tr>
<tr>
<td>1082 w</td>
<td>1084</td>
<td>29</td>
<td>((\omega_{10}) C-H, (\tilde{v}_{10}))</td>
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<tr>
<td>1113 s</td>
<td>1106</td>
<td>100</td>
<td>(\beta) C-H, (\tilde{v}_{17a})</td>
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<td>(\tilde{v}<em>{16b}) C-O, (\tilde{v}</em>{16b})</td>
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<tr>
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<td>1346</td>
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<td>(\delta(CH_{2}))</td>
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<tr>
<td>1366 m</td>
<td>1359</td>
<td>94</td>
<td>(\delta(CH_{2}))</td>
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<tr>
<td>1372 m</td>
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<td>CH(_2) wagging</td>
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<td>1474</td>
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<td>CH(_2) wagging</td>
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### TABLE 16 (Concluded)

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</table>

Soln. concentration 0.8165 M; path length 0.200 cm.
Triethyltin Phenoxide

liquid

FIG. 28
N:Triethyltinphthalamide
Solid film.

FIG. 29
NiTriethylnaphthalimide
Solute: carbon disulphide
Molarity: $0.8165 \times 10^{-2}$
Pathlength: 0.20 cm
1021, 1168, 1155 and 1073 cm\(^{-1}\) respectively. Mode \(v_3\) is expected to have a weak band near 1300 cm\(^{-1}\). It is assigned tentatively to the weak inflexion at 1310 cm\(^{-1}\).

There are five \(\text{C-C}\) modes viz. \(v_{13a}^\prime\), \(v_{16a}^\prime\), of class \(A_1\) and \(v_{13b}^\prime\), \(v_{16b}^\prime\) of class \(B_1\). Modes \(v_9\), \(v_{13a}^\prime\), \(v_{13b}^\prime\), and \(v_{16b}^\prime\) are assigned to frequencies 1327, 1487, 1457 and 1595 cm\(^{-1}\) respectively. The assignment to the remaining mode, \(v_{16a}^\prime\), is not possible for it is expected to have a weak band near 1588 cm\(^{-1}\) which region is overshadowed by the very strong band at 1595 cm\(^{-1}\).

The two ring vibrations \(v_2\) and \(v_6\) of class \(A_1\) are assigned to the bands at 1003 and 1013 cm\(^{-1}\) respectively. This assignment is rather tentative since there are quite a number of other lines of comparable intensity in the same region. The frequencies of the other two ring vibrations are expected to fall below 650 cm\(^{-1}\).

The assignment of mode \(v_5\) and \(v_7\) will be considered after the assignment of the ethyl frequencies.

The \(\text{C-H}\) modes \(v_{11a}^\prime\), \(v_{19a}^\prime\) of class \(A_2\) and \(v_4\), \(v_7\), \(v_{11b}^\prime\), \(v_{19b}^\prime\) of class \(B_2\) are assigned to frequencies below 1000 cm\(^{-1}\) in agreement with the expected values for monosubstituted benzenes. Modes \(v_{11a}^\prime\) and \(v_{19b}^\prime\) are expected to have weak bands near 837 and 908 cm\(^{-1}\). However both of these regions are populated with strong absorption bands and therefore only very tentative assignment can be made. The inflexion at 944 cm\(^{-1}\) is assigned to \(v_{11a}^\prime\) and the weak band at 912 cm\(^{-1}\) is assigned to \(v_{19b}^\prime\).

Modes \(v_4\) and \(v_{11b}^\prime\) are assigned to the very strong bands at 767 and 699 cm\(^{-1}\) respectively. The corresponding frequencies for the phenyltin compounds are 742-736 cm\(^{-1}\) and 708-699 cm\(^{-1}\) and for the benzyltin compounds 764 cm\(^{-1}\) and 709-701 cm\(^{-1}\).
The regaining modes $^2_7$ and $^2_{19a}$ are assigned to frequencies 962 and 975 cm$^{-1}$ respectively. The average values for monosubstituted benzenes are 962 and 982 cm$^{-1}$.

The frequencies of modes $^2_8$ and of the two out-of-plane ring deformation vibrations $^2_{20a}$ and $^2_{20b}$ are expected to fall outside the range studied.

**ASSIGNMENT OF THE PHENYL FREQUENCIES FOR N:TRIETHYLTIN PHTHALIMIDE.**

Although the symmetry properties of ortho-substituted benzenes with two identical substituents, as in the case of N:triethyltin phthalimide, is that of model $C_{2v}$, the normal coordinates of the modes of vibrations of the molecule is expected to be different from those of monosubstituted benzenes. Therefore in the present case although the same numbers will be used for the normal modes their normal coordinates are expected to be different. However, not enough data are available for the construction of the normal coordinates of ortho-substituted benzenes. In general, the modes involving the vibration of the substituents will be expected, in the extreme case, to suffer such modifications as to uncouple the vibrations of the substituents from the vibrations of the rest of the benzene molecule.

The strong absorption bands of the $^2$C-H modes of the ethyl group have almost overshadowed the $^2$C-H bands of ortho-substituted benzenes. Only two weak bands appear at 3065 and 3075 cm$^{-1}$. The former band is assigned tentatively to $^2_{15a}$ and the latter to $^2_1$ and $^2_{14b}$.

The $^2$C-H modes $^2_{12a}$ and $^2_{17a}$ are assigned to frequencies 1032 and 1167 cm$^{-1}$. Modes $^2_3$, $^2_{10}$, $^2_{12b}$ are assigned respectively
to the bands at 1243, 1149 and 1070 cm\(^{-1}\). Randle and Whiffen quote only one \(\beta\) C-H frequency belonging to class \(B_1\) namely 1126 \(\pm\) 12 cm\(^{-1}\).

Four of the five \(\nu\) C-C modes \(\alpha_{13a}\) of class \(A_1\) and \(\alpha_{9}, \alpha_{13b}\) and \(\alpha_{16b}\) of class \(B_1\) are assigned to the following frequencies: 1474, 1348, 1436 and 1608 cm\(^{-1}\). The average values for \(\beta\)-substituted benzenes are 1490, 1315, 1445 and 1606 cm\(^{-1}\) which are in good agreement with the above assignment. The remaining \(\nu\) C-C mode, \(\alpha_{16a}\), could not be assigned with any certainty. It is expected to have a frequency near 1579 cm\(^{-1}\) and this region falls at the low frequency side of the rather broad band at 1608 cm\(^{-1}\) which overlaps this particular band.

The two ring vibrations \(\gamma_2\) and \(\gamma_6\) of class \(A_1\) are assigned tentatively to the bands at 1000 and 1031 cm\(^{-1}\). This assignment agrees with the assignment of the phenyltin and the benzyltin compounds.

The C-H out-of-plane vibrations of class \(A_2\) are assigned to frequencies 856 and 970 cm\(^{-1}\). Those of class \(B_2\) can only be assigned partially to modes 728 and 963 cm\(^{-1}\). The former is probably derived from mode \(\gamma_4\) of monosubstituted benzene. The average values for \(\beta\)-substituted benzenes are 751 \(\pm\) 7 and 934 \(\pm\) 11 cm\(^{-1}\). The assignment of mode \(\gamma_{11b}\) to the medium band at 698 cm\(^{-1}\) is highly tentative.

**ASSIGNMENT OF THE ETHYL FREQUENCIES**

An attempt has been made at a tentative assignment of the normal vibrations of the ethyl group.

There are two \(\nu\) C-H modes for the methyl groups (symmetrical and asymmetrical stretch) which are assigned to frequencies 2885 and 2960 cm\(^{-1}\) of triethylditin phenoxide and to frequencies 2887 and 2956 cm\(^{-1}\) of triethylditin phthalimide.
The symmetrical and asymmetrical $\nu$ C-H vibrations of the methylene group are assigned to frequencies 2863 and 2927 cm$^{-1}$ of triethyltin phenoxide and to frequencies 2866 and 2928 cm$^{-1}$ of N:triethyltin phthalimide.

The C-H deformation modes of the methyl group are expected at 1380 cm$^{-1}$ (symmetrical $\beta$ C-H) and 1450 cm$^{-1}$ (asymmetrical $\beta$ C-H). The bands at 1379 and 1457 cm$^{-1}$ in the spectrum of triethyltin phenoxide are assigned to $\beta$$_s$ C-H and $\beta$$_a$ C-H respectively. The corresponding frequencies for N:triethyltin phthalimide are 1375 and 1459 cm$^{-1}$ respectively.

The scissoring mode $\delta$ (CH$_2$) of the methylene group is expected at 1470 cm$^{-1}$. In the spectrum of triethyltin phenoxide the band at 1463 cm$^{-1}$ is partly assigned to this mode. For N:triethyltin phthalimide the band at 1457 cm$^{-1}$ is attributed to $\delta$ (CH$_2$).

The methylene rocking vibrations, $\gamma$$_r$(CH$_2$), is expected near 720 cm$^{-1}$. It could only be traced in the spectrum of N:triethyltin phthalimide as a weak band at 711 cm$^{-1}$.

The wagging mode of methylene is expected to have a frequency of about 1300 cm$^{-1}$. It has been assigned to the strong band at 1302 cm$^{-1}$ in the spectrum of N:triethyltin phthalimide. The band at 1320 cm$^{-1}$ in the spectrum of triethyltin phenoxide may belong to the same mode.

As to the skeletal vibrations, theoretical calculations (18a) indicate a Raman active C-C stretch for the ethyl group just below 1000 cm$^{-1}$. In the spectrum of N:triethyltin phthalimide there are two possible bands for the assignment, a medium weak band at 964 cm$^{-1}$ and a weak inflexion at 988 cm$^{-1}$. The C-C stretch may be tentatively assigned
to the weak inflexion at 983 cm\(^{-1}\) on the account that it is theoretically forbidden in the infrared absorption spectrum of the compound. No such band was identified in the spectrum of triethyltin phenoxide.

**ASSIGNMENT OF THE C-O VIBRATIONS OF TRIETHYL Tin PHENOXIDE**

The assignment of the Ph-O stretching vibration portrayed by mode \( \nu^s \) is rather tentative because of the absence of sufficient data on the infrared absorption spectra of the phenoxydes. However, it has been found (52) that in the case of alkyl phenoxydes a strong band is expected in a range 1200-1270 cm\(^{-1}\). The band is usually assigned to the asymmetrical vibration:

\[
\begin{array}{c}
\text{O} \\
\text{R} \quad \text{R'}
\end{array}
\]

which in the present case would involve the stretching of the O-Sn bond. Because of the heaviness of the tin atom it is very unlikely that the amplitude of the O-Sn stretching vibration will be comparable to that of the C-O stretch and therefore the C-O and O-Sn bonds will very probably perform two separate vibrations which may slightly interact with each other. Hence, the remarkably strong band at 1265 cm\(^{-1}\) is assigned to the C-O stretching vibration as illustrated in mode \( \nu^s \).

Two very moderately strong bands in the region below 1000 cm\(^{-1}\) have been left unassigned (viz. 850 and 836 cm\(^{-1}\)). Their relatively high intensity casts some doubt on considering them as summation bands
and therefore they must be assumed to be fundamental bands. Although
the mass of the tin atom is great compared with that of the carbon and
the oxygen atoms which are attached to it, it seems possible that the
triatom O.Sn.C may show some characteristic frequencies similar to those
of the triatom Si.O.C. Such vibrations as would be considered possible
must involve mainly the motion of the carbon and the oxygen atom. This
assumption will make it possible to visualize two types of vibration: a
symmetrical stretching mode and an asymmetrical stretching mode of the
C-Sn and O-Sn bonds thus:

\[
\begin{array}{c}
\text{Sym} \\
\text{O} \quad \text{Sn} \quad \text{C} \\
\end{array}
\]

\[
\begin{array}{c}
\text{asym} \\
\text{O} \quad \text{Sn} \quad \text{C} \\
\end{array}
\]

The symmetrical stretching vibration can therefore be assigned to 836 cm\(^{-1}\)
and the asymmetrical stretch to 850 cm\(^{-1}\).

**Assignment of the O-O Frequencies of N:Triethyltin Phthalimide**

The infrared absorption spectrum of phthalimide (16, 20, 52) indicates
the presence of three bands at 1748, 1698 and 1653 cm\(^{-1}\) in the region
where the carbonyl stretching frequency is expected (16, 25, 52). However
the infrared absorption spectrum of N:triethyltin phthalimide shows a
prominently strong band at 1677 cm\(^{-1}\) in the solid state and 1687 cm\(^{-1}\) in
carbon disulphide solution. On either side of this band there is a
moderate band, one on the high frequency side at 1744 cm\(^{-1}\) (solid state), 1748 cm\(^{-1}\) (\(CS_2\) solution), and one on the low frequency side at 1627 cm\(^{-1}\) (solid state), 1630 cm\(^{-1}\) (\(CS_2\) solution). The general behaviour of these bands is in accord with the expectation of decreasing frequency in passing from the solution to the solid state (16, 52).

Acceptance of the possibility of coupling between the stretching vibrations of the two carbonyl groups leads to the assignment of the high frequency band, at about 1746 cm\(^{-1}\), to the asymmetric stretch (i.e. \(\nu_{as}C=O\)) and the strong band at 1687-1677 cm\(^{-1}\) to the symmetric stretch (i.e. \(\nu_sC=O\)). The fact that the frequencies of the carbonyl absorption are lower in N:triethyltin phthalimide than in the parent compound, phthalimide, indicates that the single bond character of the carbonyl bond is enhanced together with the double bond character of the C-N bond. This argument is further supported by the fact that the triethyltin group is strongly electron releasing. The general picture for the interaction of all these effects is:
Thus, the third moderate band at 1630-1627 cm\(^{-1}\) may be assigned to the stretching vibration of the carbon-nitrogen bond. The C=N stretching vibrations usually occur between 1680 and 1630 cm\(^{-1}\) (16,52) and they can be identified easily since they are stronger than C=O bands but weaker than C=O bands. In conjugated and aromatic systems the frequency of the C=N is usually depressed considerably (52).

There remain unassigned two strong bands at 1120 and 1113 cm\(^{-1}\) in the solid phase spectrum of N-triethyltin phthalimide. The corresponding frequency in the solution spectrum is 1106 cm\(^{-1}\). These and other unassigned moderate bands in the region 1600-1000 may be assumed to arise from the skeletal vibrations of the heterocyclic five numbered ring (16).
III. 6. GENERAL DISCUSSION ON THE INFRARED ABSORPTION SPECTRA OF ORGANOTIN COMPOUNDS:

Now that the results of the infrared absorption spectra have been presented this is an appropriate point to consider in some detail the effect of the tin atom on the normal frequencies of the phenyl group. Two points have to be born in mind in the following discussion - the first is that only part of the normal frequencies has been assigned and that the assignment can only be considered as tentative. The second and more important point is concerned with the fact that any attempt at theoretical interpretation of the phenyl frequencies in molecules as complicated as those studied in the present work can only be highly qualitative in most cases but may in a few cases be semi-quantitative.

The limit of the resolving power of rock-salt optics in the region \(3000 \text{ cm}^{-1}\) makes it impracticable to correlate the frequencies of the C-H stretching vibrations with the effect of the substitution of the tin atom in the benzene molecule. However, it seems that by comparison with the corresponding frequencies of alkyl substituted benzenes the frequencies of the \(\nu^C-H\) modes are within the expected range for hydrocarbons (46).

As for the C-C stretching vibrations the same generalization seems to be applicable. In general, on the one hand the frequencies of the \(\nu^13_{a}\) and \(\nu^13_{b}\) modes are for the phenyltin compounds on the low side of the average frequencies for the hydrocarbons. On the other hand the frequencies of mode \(\nu^9\) are on the high side of the average value and of modes \(\nu^16_{a}\) and \(\nu^16_{b}\) they are within the range of the average value for hydrocarbons. For the benzyltin compounds, the frequencies
of modes \( \nu_9, \nu_{13a}, \nu_{13b}, \text{ and } \nu_{16b} \) are all within the range of the average frequencies for the hydrocarbons; the frequencies of mode \( \nu_{16a} \) are on the low side of the average. The values of tetra-\( \beta \)-tolyltin and tetraldehyde-\( \beta \)-chlorophenyltin lie on opposite sides of the average frequencies of \( \beta \)-substituted benzenes (46). Thus the frequencies of modes \( \nu_9, \nu_{13a}, \nu_{13b}, \text{ and } \nu_{16a} \) are higher and of mode \( \nu_{16b} \) is lower in tetraldehyde-\( \beta \)-chlorophenyltin than in tetra-\( \beta \)-tolyltin. The frequencies of the triethyltin compounds are all normal.

The two ring vibrations \( \nu_2 \) and \( \nu_6 \) give very consistent values in all the monosubstituted benzenes examined; the average values are 999 cm\(^{-1}\) and 1031 cm\(^{-1}\) for modes \( \nu_2 \) and \( \nu_6 \) respectively.

The two groups of vibrations that were found to be sensitive to the nature of the substituent are: the bending modes \( \gamma \text{C-H} \) and \( \beta \text{C-H} \). Bell, Thompson, and Vago (15) and Cole and Thompson (22) have calculated, on the basis of a simple theory, the normal coordinates of the out-of-plane bending vibrations and the dipole moment of the C-H linkage in substituted benzenes. Their values for the electric dipole moments of the C-H linkage varies greatly according to the nature of the substituent e.g., for the halobenzenes the following values were obtained (22): fluorobenzene (1.1 D), chlorobenzene (2.2 D), bromobenzene (1.4 D).

Margoshes and Fassel (40) and Kross, Fassel, and Margoshes (35) have investigated in great detail the out-of-plane C-H bending vibrations in the region 625-900 cm\(^{-1}\) for substituted benzenes. Margoshes and Fassel (40) have found that in the compounds \( \text{Ph}_n \text{M} \), where \( n \) is the valence of the substituent atom M, the frequency of the absorption line lying
between 725-820 cm\(^{-1}\) decreases linearly with the reduced mass of the diatomic group M-C. However, Kross, Fassel and Margoshes (35) have also found that in certain monosubstituted and \(\sigma\)-substituted benzenes the frequency of one of the out-of-plane C-H bending vibrations falls above the characteristic frequency range assigned to that vibration. They explained their experimental observations on electrical grounds, pointing out that these substituents are in general electrophilic in nature and therefore they tend to deplete the aromatic nucleus of \(\pi\)-electronic charge thus hindering the carbon bonding orbital from following the out-of-plane movement of the hydrogen atom which results in higher bending frequencies because the vibrations occur with greater difficulty as orbital overlap decreases (37).

That the pure mechanical picture of the C-H out-of-plane bending modes is inadequate is illustrated by the calculations of Bell and co-workers (14, 15) and of Cole and Thompson (22) who assumed a substituent of infinite mass and found the values 739 and 723 cm\(^{-1}\) respectively for the vibrational mode in which all the remaining hydrogen atoms move out of the plane of the carbon ring in phase, a mode approximately similar to mode \(\nu_4\) for benzene. The average value for monosubstituted benzenes is 751 ± 15 cm\(^{-1}\). That there are electrical factors involved in determining the out-of-plane vibrations of the C-H linkage have been demonstrated quite clearly by the work of Kross, Fassel and Margoshes (35).

The present work has shown that for the phenyltin compounds, where the tin atom is directly attached to the phenyl group, the frequencies of the C-H out-of-plane vibration (\(\nu_4\)) fall at the low side of the
average frequency of hydrocarbons, whilst for the benzyltin compounds
and triethyltin phenoxides the frequencies are on the high side of the
average value. These frequencies fall along the series:
\[ \text{Et}_3\text{SnOPh} \rightarrow \text{Bz}_3\text{SnCl} \rightarrow \text{Bz}_4\text{Sn} \rightarrow \text{Ph}_4\text{Sn} \rightarrow \text{Ph}_3\text{SnCl} = \text{PhSnCl}_3 \rightarrow \text{Ph}_2\text{SnCl}_2 \]

The fact that all the phenyltin compounds show an overall decrease
in the frequency may be accounted for by the mass effect. But the
variation within the homologous series \( \text{Ph}_n\text{SnCl}_{4-n} \) can only be accounted
for by the electrical factors. It seems that among all the electrical
effect (inductive, mesomeric and field effects) the field effect is the
most likely factor in influencing the C-H out-of-plane vibrations to the
greatest extent.

A simple electrostatic model has been constructed to illustrate
the argument of the previous paragraph. Consider that the substituent
M is the negative end of the Ph-M dipole and that the hydrogen atom is
the positive end of the H-C dipole. The negative field of the
substituent M will stiffen the movement of the positively charged
hydrogen atoms at the ortho-positions out of the plane of the benzene
nucleus and thus increase the frequency of the vibration. Let the
relative electric charges on the substituent M and the hydrogen atom
be \( e_M^- \) and \( e_H^+ \); the force of interaction between these two charges
along the direction of motion of the hydrogen atom will be given by:

\[ F = -\frac{e_H^+ e_M^-}{r^2} \cdot \frac{\delta}{r} \quad \ldots (1) \]

where \( r \) is the M-H distance and \( \delta \) is the displacement of the H
atom out of the plane of the carbon hexagon.

The corresponding increment \( h' \) in the force constant of the vibration due to the negative electric field of M will therefore be given by:

\[
h' = \frac{e^+ e^-}{r^2} \quad \ldots \ldots (2)
\]

The frequency of the vibration of the unperturbed benzene molecule is given by:

\[
f = \frac{2}{\pi} \sqrt{\frac{h}{m}} \quad \ldots \ldots (3)
\]

where \( \omega_0 \) is the frequency of the unperturbed molecule and \( h \) is the unperturbed force constant, and \( m_{\text{C-H}} \) is the reduced mass of the diatomic group C-H.

The additional force constant \( h' \) will act in addition to the force constant \( h \) to give for the frequency of the perturbed molecule:

\[
4 \pi^2 \omega^2 = \frac{h + h'}{m_{\text{C-H}}} \quad \ldots \ldots (4)
\]

The additional force constant \( h' \) may be obtained by combining
equation (3) and (4) to give:

\[ 4 \pi^2 \left( z^2 - z_o^2 \right) = \frac{h'}{m_{C-H}} \]  \hspace{1cm} \ldots \ldots (5) \]

in which \((h')\) can be expanded in term of the more accurate form of equation (2') which can be expressed as a polynomial in \((r)\):

\[ h = e_+^H e_-^M \left[ \frac{A}{r^3} + \frac{B}{r^4} + \frac{C}{r^5} + \ldots \ldots \right] \] \hspace{1cm} \ldots (2')

where \(A, B, C, \ldots\) are constants which can be evaluated empirically to fit the experimental results.

From equations (2') and (5) an expression for the frequency of the perturbed vibration can be obtained:

\[ 4 \pi^2 \left( z^2 - z_o^2 \right) = \frac{e_+^H e_-^M}{m_{C-H}} \left[ \frac{A}{r^3} + \frac{B}{r^4} + \frac{C}{r^5} + \ldots \ldots \right] \]

\[ \therefore \quad z^2 = z_o^2 + \frac{e_+^H}{4 \pi^2 m_{C-H}} \cdot \frac{e_-^M}{r^3} \left[ A + \frac{B}{r} + \frac{C}{r^2} + \ldots \ldots \right] \] \hspace{1cm} \ldots (6)

As a first approximation the correction terms \(\left( \frac{B}{r} + \frac{C}{r^2} + \ldots \ldots \right)\) may be neglected and a linear plot would be expected between \(z^2\) and \(\frac{e_-^M}{r^3}\).

The value of the constant \(A\) may be evaluated directly from the above plot.

The values of the electrical charges \(e_+^H\) and \(e_-^M\) can be evaluated from the data on the bond dipole moments (49). The value used for the C-H dipole is that given by Cole and Thompson (22) (viz. 0.57 D) and the C-H bond length is taken to be 1.08 Å. The value of the electric charge...
can then be calculated from the relationship:

\[ \mu_{M-C} = \alpha \frac{1}{r_{M-C}} \]

where \( \mu_{M-C} \) is the bond dipole moment and \( r_{M-C} \) is the interatomic distance.

The distance between the substituent atom M and the ortho-hydrogen is calculated trigonometrically from the M-C, C-C and C-H bond lengths and from the angles MCC and HOC which are assumed to be equal to 120° each. The C-C bond length is taken as 1.39 Å. The values for the M-C bond lengths were taken as far as possible from data on the phenyl substituted compounds M-Ph.

The values of \( \frac{e^+}{r^3} \) and of \( \frac{e^-}{r^3} \) are given in Table 17 for a number of monosubstituted benzenes. Figure 31 shows quite clearly that there is a linear relationship between the square of the wave number and the values of \( \frac{e^-}{r^3} \). Further consideration of the graph shows that the intercept on the ordinate axis is 522 cm\(^{-1}\), which if equation (6) is true should be equal to \( 2v^2 \), the square of the frequency of the unperturbed benzene molecule. The value of \( 2v_0 \) thus obtained is 723 cm\(^{-1}\), which is significantly in excellent agreement with the value calculated by Cole and Thompson assuming a substituent of infinite mass and neglecting all electrical effects. This agreement lends further confirmation to the electrostatic picture so far developed. The slope of the experimental line should be approximately equal to \( \left( \frac{e^+}{4\pi^2} \frac{A}{4} \right) \) if the terms in B and C are neglected. The value of \( A \) thus obtained is equal to 7950. Equation (6) can now be written in the simplified form:

\[ 2v^2 = \frac{2}{20} + \frac{7950 e^+}{4\pi^2} \frac{e^-}{r^3} \]

\[ 4\pi \frac{m_{C-H}}{2} \]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>$\nu$ (c) cm$^{-1}$</th>
<th>$\nu$ x 10$^{-2}$</th>
<th>$r_{M-O}$</th>
<th>$\mu_{M-O}$</th>
<th>$\mu_{M-O}$ (e)</th>
<th>$e_M \times 10^{10}$ esu</th>
<th>$(e_M/r^3) \times 10^{-11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH$_3$</td>
<td>O-C</td>
<td>734</td>
<td>5388</td>
<td>1.54</td>
<td>2.95</td>
<td>0.40</td>
<td>0.260</td>
<td>10.12</td>
</tr>
<tr>
<td>PhNH$_2$</td>
<td>N-C</td>
<td>755</td>
<td>5700</td>
<td>1.47</td>
<td>2.88</td>
<td>1.53</td>
<td>1.041</td>
<td>43.57</td>
</tr>
<tr>
<td>Ph$_2$O</td>
<td>O-C</td>
<td>750</td>
<td>5625</td>
<td>1.43</td>
<td>2.85</td>
<td>1.14</td>
<td>0.797</td>
<td>34.43</td>
</tr>
<tr>
<td>Ph$_2$S</td>
<td>S-C</td>
<td>738</td>
<td>5446</td>
<td>1.82</td>
<td>3.21</td>
<td>1.0</td>
<td>0.549</td>
<td>16.6</td>
</tr>
<tr>
<td>PhCl</td>
<td>Cl-C</td>
<td>742</td>
<td>5506</td>
<td>1.76</td>
<td>3.15</td>
<td>1.56</td>
<td>0.886</td>
<td>28.3</td>
</tr>
<tr>
<td>PhBr</td>
<td>Br-C</td>
<td>736</td>
<td>5417</td>
<td>1.939</td>
<td>3.32</td>
<td>1.48</td>
<td>0.763</td>
<td>20.8</td>
</tr>
<tr>
<td>PhI</td>
<td>I-C</td>
<td>731</td>
<td>5344</td>
<td>2.324</td>
<td>3.70</td>
<td>1.29</td>
<td>0.555</td>
<td>11.0</td>
</tr>
<tr>
<td>Ph$_3$Pb</td>
<td>Pb-C</td>
<td>727</td>
<td>5285</td>
<td>2.39</td>
<td>3.74</td>
<td>0.79</td>
<td>0.331</td>
<td>6.33</td>
</tr>
</tbody>
</table>

(a) From T.L. Cottrell (23a).
(b) From G. Giacomello (27a).
(c) From M. Margoles and V.A. Fassel (40).
(d) From A.R.H. Cole and H.W. Thompson (22).
(e) From J.W. Smith (49).
(f) Calculated from the dipole moments of triethylphenyllcad and ethyltriphenyllcad.
FIG. 31
A system of dipole moments can now be evaluated from equation (7). These dipole moments are expected to approximate to the bond dipole moments for simple substituent e.g., an atom or simple group such as OH. For the more complicated substituents especially those containing highly polar groups, such as C=O, NO₂ etc., the dipole moments thus calculated would be expected to approximate to the group dipole moments. Table 18 contains the calculated dipole moments from the frequency of the \( \gamma \) C-H vibration \( \nu_4' \) for monosubstituted benzenes. They compare favourably with the bond dipole moments for simple molecules and with the group dipole moments for the more complicated molecules (49).

The behaviour of the \( \gamma \) C-H vibrations in the compounds \( \text{Ph}_n \text{SnCl}_2 \)-n with variation in the number of phenyl groups is indicated in Figure 32 for modes \( \nu_4' \) and \( \nu_{11b} \). The fall in the frequencies of both modes in going from \( \text{Ph}_4 \text{Sn} \) to \( \text{Ph}_2 \text{SnCl}_2 \) indicates clearly that the Sn-C dipole moment decreases in that order. However, for phenyltin trichloride the frequency is greater than that for diphenyltin dichloride and therefore the Sn-C dipole moment is greater in the former compound than in the latter. An attempt will be made at explaining the above behaviour after the \( \beta \) C-H vibrations have been discussed.

The \( \gamma \) C-H frequencies of mode \( \nu_4 \) of the benzyltin compounds are higher than the corresponding frequencies for toluene (734 cm\(^{-1}\)), ethylbenzene (747 cm\(^{-1}\)) and benzyl alcohol (747 cm\(^{-1}\)). The increase in frequency from 764 cm\(^{-1}\) for tetrabenzyltin to 768 cm\(^{-1}\) for tribenzyltin chloride may be attributed to the increase in hyperconjugation between the methylene group and the tin atom caused by the increase in the electronegativity of the tin atom due to the negative inductive effect
<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>$a^2$ (cm$^{-2}$)</th>
<th>$r_{\text{N-H}}$</th>
<th>$e^{-10}$ esu</th>
<th>$l_{\text{M-C}}$</th>
<th>$\mu_{\text{M-C}}$</th>
<th>Group moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCHO</td>
<td>C-C</td>
<td>743</td>
<td>2.95</td>
<td>0.827</td>
<td>1.54</td>
<td>1.27</td>
<td>2.92</td>
</tr>
<tr>
<td>PhCOCl</td>
<td>C-C</td>
<td>779</td>
<td>&quot;</td>
<td>1.889</td>
<td>&quot;</td>
<td>2.91</td>
<td>3.32</td>
</tr>
<tr>
<td>PhCOOH</td>
<td>C-C</td>
<td>808</td>
<td>&quot;</td>
<td>2.924</td>
<td>&quot;</td>
<td>4.50</td>
<td></td>
</tr>
<tr>
<td>PhON</td>
<td>O-O</td>
<td>763</td>
<td>&quot;</td>
<td>1.336</td>
<td>&quot;</td>
<td>2.06</td>
<td>3.8</td>
</tr>
<tr>
<td>PhN(CH$_3$)$_2$</td>
<td>N-C</td>
<td>753</td>
<td>2.88</td>
<td>0.926</td>
<td>1.47</td>
<td>1.56</td>
<td>1.58</td>
</tr>
<tr>
<td>Ph$_3$N</td>
<td>N-C</td>
<td>750</td>
<td>&quot;</td>
<td>0.832</td>
<td>&quot;</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>PhNH$_3$Cl$^-$</td>
<td>N-C</td>
<td>741</td>
<td>&quot;</td>
<td>0.552</td>
<td>&quot;</td>
<td>0.811</td>
<td></td>
</tr>
<tr>
<td>PhNO$_2$</td>
<td>N-C</td>
<td>794</td>
<td>&quot;</td>
<td>2.251</td>
<td>&quot;</td>
<td>3.31</td>
<td>3.93</td>
</tr>
<tr>
<td>PhOH</td>
<td>O-C</td>
<td>753</td>
<td>2.85</td>
<td>0.897</td>
<td>1.43</td>
<td>1.28</td>
<td>1.45</td>
</tr>
<tr>
<td>PhOCH$_3$</td>
<td>O-C</td>
<td>758</td>
<td>&quot;</td>
<td>1.051</td>
<td>&quot;</td>
<td>1.50</td>
<td>1.30</td>
</tr>
<tr>
<td>PhF</td>
<td>F-C</td>
<td>754</td>
<td>2.76</td>
<td>0.847</td>
<td>1.36</td>
<td>1.15</td>
<td>1.5</td>
</tr>
<tr>
<td>Ph$_4$Si</td>
<td>Si-Si</td>
<td>740</td>
<td>3.26</td>
<td>0.755</td>
<td>1.88$^{(a)}$</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>Ph$_3$P</td>
<td>P-C</td>
<td>745</td>
<td>2.97</td>
<td>0.740</td>
<td>1.565</td>
<td>1.16</td>
<td>1.39</td>
</tr>
<tr>
<td>PhSO$_2$Cl</td>
<td>S-C</td>
<td>754</td>
<td>3.21</td>
<td>0.928</td>
<td>1.82</td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td>PhSO$_2$Na $\text{(a)}$</td>
<td>S-C</td>
<td>757</td>
<td>&quot;</td>
<td>1.019</td>
<td>&quot;</td>
<td>1.85</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE 18 (Concluded)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>bond</th>
<th>(\nu_{\text{cm}^{-1}})</th>
<th>(\mathbf{\mathbf{r}}_{\text{M-H}})</th>
<th>(\mathbf{g}_{\text{A}}\times 10^{10}) esu</th>
<th>(\mathbf{\mathbf{1}}_{\text{M-C}})</th>
<th>(\mathbf{\mathbf{M}}_{\text{M-C}})</th>
<th>Group moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₄Ge</td>
<td>Ge-C</td>
<td>735</td>
<td>3.36</td>
<td>0.581</td>
<td>1.98</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>Ph₄Sn</td>
<td>Sn-C</td>
<td>(b) 739</td>
<td>3.58</td>
<td>0.790</td>
<td>2.07 (d)</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>Ph₂SnCl₂</td>
<td>Sn-C</td>
<td>(b) 736</td>
<td>&quot;</td>
<td>0.642</td>
<td>&quot;</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>Ph₂SnCl₃</td>
<td>Sn-C</td>
<td>(b) 734</td>
<td>&quot;</td>
<td>0.544</td>
<td>&quot;</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>Ph₂Hg</td>
<td>Hg-C</td>
<td>732</td>
<td>3.60</td>
<td>0.535</td>
<td>2.234</td>
<td>1.20</td>
<td></td>
</tr>
</tbody>
</table>

(a) From M. Margoshes and V.A. Fassel (40).

(b) The present work.

(c) From T. L. Cottrell (23a).

(d) From G. Giacomello (27a).

(e) From J. W. Smith (49).
FIG. 32

\[ \bar{\nu} \text{ cm}^{-1} \]

- \( \bar{\nu}_4 \)
- \( \bar{\nu}_4 \) soln.
- \( \bar{\nu}_4 \) mull
- \( \bar{\nu}_4 \) soln.

(a) \( \bar{\nu}_4 \)

(b) \( \bar{\nu}_4 \)

No. of Phenyl Groups
of chlorine. The overall increase in the frequencies of the benzyltin compounds may be explained on the basis of increased hyperconjugative effect of the methylene group thus increasing the CH$_2$ -C bond dipole moment.

The corresponding frequency for triethyltin phenoxide viz. 767 cm$^{-1}$ is almost identical with that for tribenzyltin chloride. The corresponding value for phenol (753 cm$^{-1}$), for diphenylether (750 cm$^{-1}$) and for anisole (758 cm$^{-1}$) are all lower than that for triethyltin phenoxide. The above experimental observation may indicate that although the ethyl group is electron releasing yet the empty outermost d-orbitals of tin are still active in depleting electronic charges from centres of high electronic concentration such as the two lone pairs of electrons on the oxygen atom. The oxygen atom is made therefore more electron attracting for the electronic clouds of the phenyl group, thus increasing the frequency of the C-H vibration.

The frequencies of the C-H vibration for the series Ph$_4$M where M is C, Si, Ge, Sn or Pb give the following values for the bond dipole moments, excluding the case of tetraphenyl methane because of the great steric strain in the Ph-C bonds: $\mu_{\text{CH}}$, $\mu_{\text{C-M}}$

<table>
<thead>
<tr>
<th>$\text{Ph}_4\text{M}$</th>
<th>$\mu_{\text{CH}}$</th>
<th>$\mu_{\text{C-M}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_4$C</td>
<td>755 cm$^{-1}$</td>
<td>-</td>
</tr>
<tr>
<td>Ph$_4$Si</td>
<td>740 cm$^{-1}$</td>
<td>1.42 D</td>
</tr>
<tr>
<td>Ph$_4$Ge</td>
<td>735</td>
<td>1.15</td>
</tr>
<tr>
<td>Ph$_4$Sn</td>
<td>739</td>
<td>1.64</td>
</tr>
<tr>
<td>Ph$_4$Pb</td>
<td>727</td>
<td>(0.79)</td>
</tr>
</tbody>
</table>

* Determined by vector analysis from the dipole moments of triphenyl ethylead and phenyltriethylleadt

** Electrostatic electronegativities of Allred and Rochow (1, 2)
The values of the bond dipole moments follow the same trend as the difference in the electronegativities of carbon and the element M, as shown above. The values of electronegativities used were those derived by Allred and Rochow (1, 2) from electrostatic attraction.

Kross and Fassel (34) have investigated the frequencies of the $\beta$C-H mode ($\nu_{12b}$) for monosubstituted benzene in the region 1045-1185 cm$^{-1}$. Their results have shown that the vibration in this region is sensitive to the nature of the substituent. Thus for the halobenzenes there is a linear relationship between the frequency ($\nu$ cm$^{-1}$) and the extra-ionic energy of the bond C-Hal. For the other compounds a relationship was found between the frequency and the square of the electronegativity of the substituent atom. In the present work the values of the frequencies of mode $\nu_{12b}$ for the phenyltin compounds fall near 1075 cm$^{-1}$ with very little variation in the different compounds and therefore no conclusion can be derived as to the variation in the properties of the tin atom upon increasing the number of the chlorine atoms attached to it. However, for the benzyltin compounds and triethyltin phenoxide the frequencies show a considerable drop to 1067 and 1064 cm$^{-1}$ respectively.

The frequencies of modes $\nu_{3}$ and $\nu_{12a}$ behave in a similar fashion. Whilst the frequencies of modes $\nu_{17a}$ and $\nu_{10}$ both show considerable variation with the number of chlorine atoms in the molecule Ph$_n$SnCl$_{4-n}$, as illustrated in Figure 33. Assuming that Kross and Fassel relationship still holds for these two $\beta$C-H modes, one can conclude from Figure 33 that the electronegativities of the tin atom decreases in the order:

$$\text{Ph}_4\text{Sn} < \text{Ph}_3\text{SnCl} < \text{Ph}_2\text{SnCl}_2 < \text{PhSnCl}_3$$

Further support for the above conclusion is forthcoming from the results
FIG. 33

\[ v \text{ cm}^{-1} \]

\[ 1200 \]

\[ 1180 \]

\[ 1160 \]

\[ n = \text{of phenyl groups} \]

\[ v_{17a} \]

\[ \Delta \text{soln.} \]

\[ + \text{mull} \]

\[ v_{10} \]

\[ \circ \text{soln.} \]

\[ \square \text{mull} \]
of the ultraviolet absorption spectra of the phenyltin compounds (Part Four).

A possible explanation of the above trend in the electronegativity of tin is that as the number of the chlorine atoms in the molecule increases the electron withdrawing power (-I effect) of the chlorine atoms depletes electronic charges from the tin atom and causes it to contract. This contraction of the electronically poor tin decreases the diffused character of the outermost d-orbitals and enhances their ability for accommodating acquired electronic charges.

Referring back to the \( \delta C-H \) vibrations, one is now in a position to explain the trend observed in the frequencies of these vibrations in the phenyltin compounds. The conclusion arrived at in the previous paragraph may be qualified in the following way. It seems that the effect of the enhancement of the outermost d-orbitals to act as electron acceptors lags behind the rate of disappearance of the phenyl groups which act as the source of these electronic charges, and hence the overall decrease in the electronic charge on the tin atom (\( e_{\text{M}} \)) as measured by the \( \delta C-H \) frequency. However, in the compound phenyltin trichloride the balance between the inductive effect of the chlorine atom and the mesomeric effect of the phenyl group has been upset in favour of the latter and therefore greater electronic charge would be expected to reside on the tin atom of that compound.

The fact that no such behaviour is exhibited by the \( p C-H \) frequencies may be explained by the theory of "orbital following" (37) as applied by Kross, Fassel and Margoshes (35). Thus, whilst the \( \delta C-H \) vibrations require the movement of the carbon bonding orbital to follow the movement
of the hydrogen atom out of the plane of the carbon ring and therefore...

the condition of the $\pi$-electronic clouds are of prime importance; on the other hand the in-the-plane vibrations of the hydrogen atom require no such consideration of the condition of the $\pi$-electronic clouds and therefore they are only affected by the electrical nature of the substituent as measured by their electronegativities.

In the assignment of the phenyl frequencies reference was constantly made to the average frequencies found for hydrocarbons. The fact that no considerable variations were found leads to the conclusion that the tin atom seems to be large enough to prevent any interaction between groups or atoms attached to it. For if there were any interaction between such atoms and groups, one would expect a considerable variation in the spectra of the compounds of the series $\text{Ph}_4\text{SnCl}_{4-n}$. Such variations would also be expected from Group Theory considerations, since the actual symmetry of the molecules would not be $C_{2v}$ but $T$, $C_{3v}$, $C_{2v}$, and $C_{3v}$ for $\text{Ph}_4\text{Sn}$, $\text{Ph}_3\text{SnCl}$, $\text{Ph}_2\text{SnCl}_2$ and $\text{PhSnCl}_3$ respectively. Besides, the number of atoms (vibrating mass points) will obviously be different for different compounds of the series and therefore the number of possible normal vibrations will differ vastly. The absence of such interaction is also manifest in the homologous series $(\text{CH}_3)_n\text{SnCl}_{4-n}$ and is supported by electric dipole moments data (Part One).
REFERENCES:


PART FOUR

THE ULTRAVIOLET ABSORPTION SPECTRA OF ORGANOTIN COMPOUNDS
IV. I. THE ULTRAVIOLET ABSORPTION SPECTRA OF ORGANOTIN COMPOUNDS

IV. I. General Introduction

The study of the ultraviolet absorption spectra of aryltin compounds and especially of the homologous series $\text{Ph}_n \text{SnCl}_{4-n}$ has been carried out in order to investigate the nature of the C-Sn and the Cl-Sn bonds and the extent of electronic interaction between the tin atom and the phenyl group and between tin and chlorine.

Previous work on the ultraviolet spectra of organotin compounds have tetramethyltin (31), tetraethyltin, triethyltin chloride, diethyltin dichloride (25), tetraphenyltin (21), triethylphenyltin (2) and methyltin triiodide (1). Tetramethyltin (31) and the ethyltin compounds (25) have been reported to show dissociation limits in the ultraviolet region of the spectra in polar solvent but the measurement by Bowden and Braude (2) of the ultraviolet spectrum of triethylphenyltin indicated no photo-decomposition. However, Milazzo (21) had concluded from his work on the tetraphenyls of silicon, tin and lead that the transition to the second excited state of these molecules was accompanied by dissociation. In the present work no indication of photo-decomposition of phenyltin compounds was obtained in cyclohexane and chloroform solutions.

Since an attempt has been made at a tentative assignment of some of the vibrational fine structures of the phenyl absorption band (namely the B-band), the underlying theory of the electronic spectra of substituted benzenes will be outlined briefly.

The concept that the electronic motion could be separated from the nuclear motion makes it possible to formulate a simple theory for the
electronic excitation of molecules and atoms. The freedom of motion of the electrons of a system (molecular or atomic) is dependent on the nature of the potential field in which the electrons move. Although the potential field of non-linear molecule is rather complicated, a great amount of information can be obtained from the symmetry properties of the field. The potential field of a molecule will have the same symmetry properties as the geometric arrangement of the nuclei in the molecule (9). Accordingly, the electrons of the molecule will move in a field which has the symmetry properties of that particular molecule, e.g. the electrons of the benzene molecule will move in a field which has the symmetry of the regular hexagon. The electronic wave function of the molecule will therefore be transferred in definite ways when the symmetry operations are performed, thus making it possible to classify these wave functions and their electronic states on the basis of symmetry properties (9, 32).

Such classification is most easily stated in terms of Group Theory to which detailed reference was made in Part Three. It may be stated at this stage that the wave functions of a molecule transform according to, or belong to, definite representations of the symmetry group of that molecule (9). Thus for every group there would be expected one totally symmetrical representation so that the wave function of this type is symmetrical to every operation of the group. The total wave function of the ground state of a stable molecule belongs to this representation (32). Similarly, the wave function of any other possible electronically excited state of the molecule would be expected to belong to one of the symmetry classes of the group. It has also been shown that the energy
states themselves follow the behaviour of the wave function to which they belong and therefore they can be classified in the same way \((9, 32)\).

As to the selection rule \((9, 32)\) it is required that for an electronic transition to take place between any two states with wave function \(\psi_i^e\) and \(\psi_j^e\) that the integral or matrix elements:

\[
\int \psi_i^e M \quad \psi_j^e \quad d\tau
\]  

shall be different from zero. In the above integral, \(M\) is a component of the dipole moment \(\mathbf{M}\) and \(d\tau\) is the volume element of the electrons involved in the transition. The above condition can be fulfilled only if the integrals transform in a totally symmetrical manner. Since it has been assumed that the ground state of the stable molecule is totally symmetrical it is necessary, in order that the above integral shall have the representation of the totally symmetrical class, for the product \(M_j \quad \psi_j^e\) to be totally symmetrical. This last condition can be met if \(M\) and \(\psi_j^e\) both belong to the same symmetry class.

The above rule could be extended to include vibrations excited simultaneously with the electronic transition. In this case it is necessary to multiply the electronic wave function \(\psi^e\) by the appropriate vibrational wave function \(\psi^v\) so that the resultant integral is not zero i.e.

\[
\int \psi_i^e \quad \psi_1^v \quad \psi_2^v \quad \cdots M_j \quad \psi_j^e \quad \psi_1^v \quad \psi_2^v \quad \cdots d\tau \neq 0
\]  

where \(\psi_1^v\) and \(\psi_2^v\) are the vibrational wave functions for the ground state and the excited state to which the molecule is transferred respectively.
Before dealing with the case of substituted benzene which is of interest in the present work, reference has to be made to the molecular orbitals of benzene and their energies. The molecular orbitals of benzene have been derived \((5, 6, 8, 13, 2k, 28, 22, 27)\) from the six \(\pi\) electrons of the carbon ring; the other electrons with the six carbon nuclei are supposed to constitute a smoothed-out potential field of six \(C\) ions in the \(sp^2\) valence state. The hydrogen atoms were ignored. The six molecular orbitals obtained are: \(\Pi_1, \Pi_2, \Pi_3, \Pi_4, \Pi_5, \Pi_6\), listed in the order of increasing energy with the exception that \(\Pi_2\) and \(\Pi_3\) and that \(\Pi_4\) and \(\Pi_5\) are two degenerate pairs. The ground state of the molecule has the configuration: \(\Pi_1^2 \Pi_2^2 \Pi_3^2\) which belongs to class \(A_{1g}\). The first excited state is expected to be four fold degenerate. However the introduction of electron repulsion into the theory eliminates some of the degeneracy giving two non-degenerate states of symmetry \(B_{2u}\) and \(B_{1u}\) and a doubly degenerate state of symmetry \(E_{1u}\). The \(B_{2u}\) state has the configuration:

\[
\Pi_1^2 \Pi_2^2 \Pi_3^2 \Pi_5^2 \Pi_1 \Pi_2 \Pi_3 \Pi_4
\]

The three benzene absorption bands at about 2600, 2000 and 1800 \(\AA\) are assigned \((30)\) to the electronic transitions \(A_{1g} \rightarrow B_{2u}, A_{1g} \rightarrow B_{1u}\) and \(A_{1g} \rightarrow E_{1u}\) respectively. With the exception of the latter transition the first two are forbidden by selection rule \((1)\). However, for the transition \(A_{1g} \rightarrow B_{2u}\), it has been shown that simultaneous transition to a vibrational level of class \(E_{2g}\) makes the total symmetry \(E_{1u}\) \[\text{where } B_{2u} \text{ (electronic) } \times \ E_{2g} \text{ (vibrational) } = E_{1u}\].
and therefore the transition is allowed with a component of the dipole moment transferring like $E_{1u}$ (See Table 1 of Part Three). However the absorption band due to such a transition is rather weak.

It has been shown (32) that with respect to one of the symmetry operations namely that corresponding to the plane of symmetry $\sigma_v$ which passes through the 1:4 positions, the following orbitals $\pi_1, \pi_3, \pi_5$ and $\pi_6$ are symmetrical while $\pi_2$ and $\pi_4$ are antisymmetrical. It has also been found that the anti-symmetrical orbitals $\pi_2$ and $\pi_4$ cannot contain the atomic orbitals of carbon atoms 1 and 4 and therefore substitution on carbon atoms 1 and 4 does not change the energy of the antisymmetric orbitals.

In monosubstituted benzenes, most substituents shift the 2600 Å band of benzene (B-band) to longer wave length and intensify it. This shift and intensification is usually produced through the operation of the inductive effect and/or the resonance effect (20, 26, 32). The latter effect is considered to be generally responsible for the major changes in the B-band. For monosubstituted benzene here are seven molecular orbitals $\pi_1, \pi_2, \pi_3, \pi_4, \pi_5, \pi_6, \pi_7$. Molecular orbitals $\pi_2$ and $\pi_4$ are similar to those of benzene, as explained in the previous paragraph. The remaining five orbitals which are called "symmetrical orbitals" do interact and produce most of the changes associated with substitution on benzene (32).

The configuration of the ground state of monosubstituted benzene is: $\pi_1^2 \pi_2^2 \pi_3^2 \pi_5^2$. The frequency of the $A_{1g} \rightarrow B_{2u}$ -like transition is given by $E_5 - E_3$ (32) where $E_5$ and $E_3$ are the energies of the molecular orbital $\pi_3$ and $\pi_5$. It has been found that the energies of the
symmetrical orbitals and especially the energy of $\pi_7$ are rather sensitive to the electronegativity difference between the substituent and carbon, and that the frequency shift of the B-band was found to decrease as the ionization energy of the substituent increases. However, the resonance effect has been found (2, 26, 32) to lower the ionization energy of the monosubstituted benzene by raising the energy of the highest occupied orbital viz. $\pi^*$. Thus the resonance effect would be expected to shift the B-band towards the red end of the spectrum.

Since the strict symmetry of the monosubstituted benzene is that of point group $C_2v$, the $A_1 \rightarrow B_2$ transition of benzene will correspond to $A_1 \rightarrow B_1$ transition for monosubstituted benzene. In this case the above transition is completely allowed in the absorption spectra. However, the symmetry of the six $p$ $\pi$-electrons is still approximately similar to that for the carbon ring and therefore the intensity of the $A_1 \rightarrow B_1$ band would be expected to depend on the degree of polarization (32) (and therefore the degree of distortion of the symmetry) of the $\pi$-electrons (32). The greater the distortion the greater the intensity of the B-band.

Such distortion of the symmetry of the $\pi$-electrons orbitals can be obtained either by the resonance effect, as in the case of aniline (28) or by a strong inductive effect, as in the case of fluorobenzene (26). The maximum interaction between the substituent and the ring is obtained when the $p$ $\pi$-orbitals of the benzene ring and the $p$-orbital of the substituent are parallel (3, 24). Thus in monosubstituted benzene simultaneously excited vibrations need no longer be of $E_2g$ type as in the case of benzene.
The case of \( p \)-substituted benzenes with two different substituents is very similar to that discussed for monosubstituted benzenes. However, two points are worth mentioning at this stage. The first is that for a weakly resonating substituents the wave length shift is nearly additive as would be expected from simple perturbation theory. The other point is that the intensity of the B-band is vectorially additive \((29, 32)\).

In the following discussions the designations of the symmetry classes of the electronic states for the benzene molecule as well as those of the vibrational modes were used for simplicity sake. A distinction is made between the designations of the electronic states and the vibrational modes by using Capital letters for the former and small letters for the latter to avoid any possible confusion.
IV. 2. THE ULTRAVIOLET ABSORPTION SPECTRA OF PHENYL Tin COMPOUNDS

The ultraviolet absorption spectra of the homologues $\text{Ph}_n\text{SnCl}_{4-n}$ ($n=4,3,2,1$ and 0) are illustrated in Figures 1, 2, 3, 4, and 5 respectively. In the spectra of the phenyl compounds, the B-band and the K-band have both suffered bathochromic shifts. The B-band has only undergone a slight shift towards the red end of the spectra and it shows a considerable degree of vibrational fine structure. The K-band, on the other hand, has undergone considerable shift especially in chloroform, and it also shows a number of vibrational fine structures.

The effect of using chloroform as a polar solvent on the position and the contour of the bands follows usual trends (12). However, it is interesting to note the rather drastic change in the shape of the spectrum of phenyltin trichloride (figure 4) between cyclohexane solution and chloroform solution. This may be due to some photo-chemical interaction between chloroform and phenyltin trichloride, similar to that reported by Razuvaev and Fetyukova (23) between unsymmetrical alkyl-aryl tin compounds and chloroform.

The band appearing at the longer wave length (2900Å) in the spectra of phenyltin chlorides may be attributed to the electronic transition of the Sn-Cl bond from the ground state to the first excited state. This assignment is supported by comparison with the ultraviolet absorption spectrum of tin tetrachloride (figure 5) which has a band of high absorptivity starting at 3000Å. The very low absorptivity $\sim 30$ and the limited solubility of the phenyltin compounds in cyclohexane make a fuller investigation of this region rather difficult (see IV 3). However
FIG. 2

Triphenyllum Chloride
- chloroform soln.
- cyclohexane soln.

\[
\log \varepsilon
\]

\[\lambda \text{ m}u\]

200 400 600 800 1000
FIG. 4

Phenytoin Trichloride
--- chloroform soln.
--- cyclohexane soln.

log ε

λµ  200  20  40  60  80  300  40  80
the possibility that this band arises from the absorption of the photo-decomposition products of the solute can not be ruled out completely.

The analysis of the ultraviolet absorption spectra of the phenyltin compounds is based on the analysis of the ultraviolet spectra of the tetraphenyls of silicon, tin, and lead in chloroformic and ethanolic solutions undertaken by Milazzo (21). Milazzo’s spectrum for tetraphenylin tin in chloroform is in substantial agreement with the present work. Further support for the analysis is given by the infrared absorption spectra of the phenyltin compounds (see Section III 2).

That the B-band is due to the electronic transition of the phenyl group from the ground state ($A_{1g}$) to a stable excited state ($B_{2u}$) is indicated by the behaviour of the band in changing from non-polar solvent to polar solvent, where the change in the polarity of the solvent molecules has little effect on the position of the band. Further support for this assignment is forthcoming from the fact that the shape of the band is similar not only in the homologous series Ph$_n$SnCl$_{4-n}$ but also in the tetraphenyls of carbon (11), silicon, tin and lead (21).

The analysis of the vibrational fine structures of the B-band for all the members of the series is set out in Tables 1 and 2.

Milazzo (21) attributed the fourth band at 37760 cm$^{-1}$ in the spectrum of tetraphenylin tin in chloroform, to the 0→0 transition i.e. transition from the vibrationless ground state $A_{1g}$ to the vibrationless excited state $B_{2u}$ which transition is allowed in substituted benzene (20). The present work supplies further evidence for the confirmation of this assignment; and by referring the vibrational absorption bands to this frequency for the different molecules examined the correlation is completed.
TABLE 1

Vibrational Fine Structures of the B-band
(Cyclohexane solutions)

<table>
<thead>
<tr>
<th>Band</th>
<th>( \nu ) cm(^{-1} )</th>
<th>( \Delta \nu ) cm(^{-1} )</th>
<th>( \epsilon )</th>
<th>( \nu ) cm(^{-1} )</th>
<th>( \Delta \nu ) cm(^{-1} )</th>
<th>( \epsilon )</th>
<th>( \nu ) cm(^{-1} )</th>
<th>( \Delta \nu ) cm(^{-1} )</th>
<th>( \epsilon )</th>
<th>( \nu ) cm(^{-1} )</th>
<th>( \Delta \nu ) cm(^{-1} )</th>
<th>( \epsilon )</th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>910</td>
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<td>37040</td>
<td>980</td>
<td>510</td>
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TABLE 2

Vibrational Fine Structures of the B-band

(Chloroform solutions)

<table>
<thead>
<tr>
<th>Band</th>
<th>Ph₄Sn</th>
<th>Ph₃Sn Cl</th>
<th>Ph₂SnCl₂</th>
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<td>Δν</td>
<td>e</td>
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<tr>
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<td>36650</td>
<td>1100</td>
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<td>660</td>
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</tr>
<tr>
<td>9</td>
<td></td>
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</tr>
</tbody>
</table>

* From G. Milazzo (21)
The third band at 37100 cm\(^{-1}\) corresponding to \(\Delta \nu \approx 600\) cm\(^{-1}\) appears in the chloroformic solution of triphenyltin chlorides only. It corresponds to the 606 cm\(^{-1}\) Raman shift associated with the unsymmetrical breathing vibration \(\nu_{18b}\) of Class \((e_{2g})\) of the benzene ring (16).

The second band at 37040 cm\(^{-1}\) only appears in the spectra of phenyltin trichloride and diphenyltin dichloride and in the chloroform solution of triphenyltin chloride; however, Milazzo reported a similar band at 36650 cm\(^{-1}\) for the chloroform solution of tetraphenyltin, but of much lower absorptivity. It can be assigned to the phenyl skeletal vibration of the symmetrical breathing mode \(\nu_{2s}\) of class \(\alpha_{1g}\) (16, 32).

The first band, appearing at 36230 cm\(^{-1}\) of \(\Delta \nu = 1790\) cm\(^{-1}\) in the cyclohexane solution of phenyltin trichloride only, may be considered arising from the absorption of two quanta of the \(\nu_{2s}\) vibration, i.e., a first harmonic of the second band.

Band number 6, 7, 8 and 9 correspond to the \(0 \rightarrow 1, 0 \rightarrow 2, 0 \rightarrow 3, \text{ and } 0 \rightarrow 4\) progression arising from transition from the vibrationless ground state to the first, second, third and fourth vibrational levels of the \(\alpha_{1g}\) type in the \(B_{2u}\) excited state of the benzene nucleus.

The band appearing at 38250 cm\(^{-1}\) in the cyclohexane solution of tetraphenyltin, triphenyltin chloride and diphenyltin dichloride of \(\Delta \nu = 510\) cm\(^{-1}\) corresponds to the transition from the vibrationless ground state \(A_{1g}\) to the first vibrational level of the \(e_{2g}\) type (mode \(\nu_{18a}\)) in the excited state of the benzene nucleus, which vibrational level in the first excited electronic state has \(\Delta \bar{\nu} = 520\) cm\(^{-1}\) (32).
The K-band may be considered to arise from the electronic transition of the phenyl group to the second excited state, i.e., $A_{1g} \rightarrow B_{1u}$ transition (32). Milazzo (21) failing to observe any vibrational fine structures in this band concluded that this transition was accompanied by dissociation of the tetraphenyl compounds of silicon, tin and lead. However, the solvents used by Milazzo were both polar, viz. chloroform and ethanol, it is quite possible that because of the greater solvent effect on the K-band the fine structures of the band have been smoothed out. The fact that in cyclohexane, a non-polar solvent, the vibrational fine structures are abound points to the absence at least in non polar solvents of any considerable photo-dissociation of the solute. Analysis of the K-band is made quite difficult because of the greater perturbation of the vibrational levels of the phenyl group in the second excited state (32).
IV. 3. THE ULTRAVIOLET ABSORPTION SPECTRA OF BENZYL Tin COMPOUNDS

The ultraviolet absorption spectra of tetrabenzyltin and tribenzyltin chloride are presented in Figures 6 and 7 respectively.

In the spectrum of tetrabenzyltin, the B-band ($\lambda_{\text{max}} =$ 2650 Å in cyclohexane solution and $\lambda_{\text{max}} =$ 2655 Å in chloroform solution) and the K-band ($\lambda_{\text{max}} =$ 2078 Å in cyclohexane solution) have both suffered bathochromic shifts compared with the position of the corresponding bands of benzene. Both of these bands, and especially the B-band, possess some vibrational fine structures. The general contour of the spectrum is strikingly similar to that of tetraphenyltin in the region 2000-2800 Å. The remarkable shallow band extending from 2800 to 3400 Å in the spectrum of tetrabenzyltin have all the characteristics of an R-band (12). The maximum absorptivity of this band has the values 84.1 at 2900 Å. A similar band but extending from 2800 to 3000 Å has been observed in the spectrum of tetraphenyltin in cyclohexane solution with maximum absorptivity of 37.9 at 2830 Å.

In the previous section (IV.2) the bands observed at about 2900 Å in all the phenyltin compounds were assigned in the case of the chlorides to the transition of the Sn-Cl bond from the ground state of the first excited state. However, the low absorptivity of these bands compared with the very high absorptivity in the same region of tin tetrachloride coupled with the fact that both tetraphenyltin and tetrabenzyltin show similar bands of comparable intensity at the same region casts some doubt on the validity of the previous assignment. A more favourable assignment of the 2900 Å band is to the electronic excitation of the
FIG. 7

Tribengytytin Chlorid

- chloroform soln.
- cyclohexane soln.

$\log \varepsilon$

$\lambda \mu$m
Sn-C bond

The B-band is assigned, on similar grounds to that for the phenyltin compounds, to the electronic transition $A_{1g} \rightarrow B_{2u}$ of the phenyl group. The band at 2650 $\AA$ in the spectrum of tetrabenzyltin is assigned to the 0→0 transition and this band is used as the origin to all the other vibrational fine structures of the B-band (Table 3).

The first band appearing at 37240 cm$^{-1}$ in the cyclohexane solution and at 37170 cm$^{-1}$ in the chloroform solution with $\Delta \bar{v} = 500$ cm$^{-1}$ is assigned to the transition of the phenyl group from the ground state with one quantum of the vibrational mode $\omega_{18a}$ of class $e_{2g}$ to the vibrationless excited state.

The third band with $\Delta \bar{v} = 865$ cm$^{-1}$ is assigned to the transition of the phenyl group from the vibrationless ground state to the first excited state gaining one quantum of the vibrational mode $\omega_2$ of class $a_{1g}$.

The band appearing at 38980 cm$^{-1}$ with $\Delta \bar{v} = 1240$ cm$^{-1}$ in the cyclohexane solution spectrum only is assigned to the transition of the phenyl group from the vibrationless ground state to the first excited state gaining two quanta of the vibrational energy one of mode $\omega_2$ and the other of mode $\omega_{18a}$.

The fifth band at 39220 cm$^{-1}$ is assigned to the transition from the vibrationless ground state of the phenyl group to the first excited state gaining three quanta of the $18a$ mode.

The bands at 39370, 40320 and 41140 cm$^{-1}$ are assigned to the 0→2, 0→3, and 0→4 progression arising from the transition from the vibrationless ground state to the second, third and fourth vibrational levels of the $\omega_2$ mode in the $B_{2u}$ excited state of the benzene.
TABLE 3
The vibrational fine structures of the
B-band of tetrabenzyltin

<table>
<thead>
<tr>
<th>Band</th>
<th>cyclohexane solution</th>
<th>chloroform solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ [Å]</td>
<td>$v$ [cm$^{-1}$]</td>
</tr>
<tr>
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<tr>
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<td>265.0</td>
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</tr>
<tr>
<td>3</td>
<td>259.0</td>
<td>38610</td>
</tr>
<tr>
<td>4</td>
<td>256.5</td>
<td>38980</td>
</tr>
<tr>
<td>5</td>
<td>255.0</td>
<td>39220</td>
</tr>
<tr>
<td>6</td>
<td>254.0</td>
<td>39370</td>
</tr>
<tr>
<td>7</td>
<td>249.4</td>
<td>40090</td>
</tr>
<tr>
<td>8</td>
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<td>40320</td>
</tr>
<tr>
<td>9</td>
<td>242.5</td>
<td>41240</td>
</tr>
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</table>
nucleus.

The K-band is assigned to the electronic transition $A_{1g} \rightarrow E_{lu}$. The position of the $\lambda_{max}$ of the band (viz. $2078 \AA$) is lower than that for tetraphenyltin ($2110 \AA$) indicating a possible shielding by the methylene group of the interaction between the $\pi$-electronic clouds of the phenyl group and the outermost empty d-orbital of the tin atom.

The spectrum of tribenzyltin chloride is strikingly different from the spectra of tetrabenzyltin and that of triphenyltin chloride both in cyclohexane and chloroform solutions. The absence of any well defined vibrational fine structures from the B-band and its hypsochromic shift to $2474 \AA$ coupled with the increase in the absorptivity to a value of $48340$ (cf. tetrabenzyltin $1256$ at $2590 \AA$) indicate a probable photo-decomposition with a possible limit at $2100 \AA$. 
IV. 4. THE ULTRAVIOLET ABSORPTION SPECTRA OF TETRA-\(\mu\)-TOLYLtin AND TETRAKIS-\(\mu\)-CHLOROPHENYLtin

The ultraviolet absorption spectra of tetra-\(\mu\)-tolyltin and tetrakis-\(\mu\)-chlorophenyltin are given in Figures 8 and 9 respectively.

In general the spectra of these two compounds are similar. They both show four absorption bands within the range 2000-4000 \(\AA\). A very weak band starts at 3500 \(\AA\) with absorptivity of less than 10. A medium weak band extends from about 2900 \(\AA\) to about 3400 \(\AA\) of absorptivity approximately 100. A moderately strong band covers the region 2450-2800 \(\AA\) with absorptivity of over 1000. Finally, a very strong band starts at about 2450 \(\AA\) and covers the remainder of the quartz optics transmission range. Furthermore, tetra-\(\mu\)-tolyltin shows signs of even a further band possibly of \(\lambda_{max}\) just below 2000 \(\AA\).

There can be little doubt that the two strong bands (2450-2800 \(\AA\) and 2000-2400 \(\AA\)) are due to the electronic transitions of the phenyl group \(A_{1g} \rightarrow B_{2u}\) and \(A_{1g} \rightarrow B_{1u}\) respectively. The former band corresponds to a B-band and the latter to a K-band.

Since the band extending over the range 2900-3400 \(\AA\) has already been indentified as due to the electronic excitation of the Sn-C bond, there seems to be no reason for doubting this assignment in the present case.

There remains the question of the very weak band at the long wave length end of the measured region. No indication could be obtained as to its origin but the suggestion that it may arise from electronic transition between multiplet states of the ground state of the molecule.
as a whole or some part of it is quite plausible.

The assignment of the vibrational fine structures of the B-band for the two compounds will now be carried out separately. These structures are indicated in Tables 4 and 5 for the two compounds respectively.

Tetra-p-tolyltin:

The band appearing at 2685 and 2690 Å in the spectrum of tetra-p-tolyltin in cyclohexane and chloroform solutions respectively, is assigned to the $0 \rightarrow 0$ transition.

The first band with $\Delta \bar{\nu} = 480 \text{ cm}^{-1}$ is assigned to the transition from the ground state to the first excited state with the loss of one quantum of vibration belonging to mode \( \nu_{18a} \) of class \( e_{2g} \).

The bands number 3, 7, 9 and 10 are assigned to the $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$ and $0 \rightarrow 4$ progression arising from the electronic transition from the vibrationless ground state to the first, second, third and fourth vibrational levels of mode \( \nu_{2} \) of the first excited state of the benzene nucleus.

Band number 4 is assigned to the electronic excitation from the vibrationless ground state to the first excited state gaining two quanta of the vibrational mode \( \nu_{18a} \). Band number 6 is similar to the above band with the additional gain of a further quantum of the same vibration.

The band appearing at 38530 cm$^{-1}$ is due to the electronic transition from the ground state to the first excited state gaining two quanta of vibrations one of mode \( \nu_{2} \) and the other of mode \( \nu_{18a} \). The band at 39060 cm$^{-1}$ is similar to the above band with the additional gain of a further quantum of mode \( \nu_{18a} \).
### TABLE 4

The Vibrational Fine Structures of the B-band of Tetra-\(p\)-tolyltin

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<th>Band</th>
<th>cyclohexane solution</th>
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</table>
Tetrakis-p-chlorophenyltin:

The B-band of this compound contains fewer vibrational fine structures than tetra-p-tolyltin.

The band appearing at 36830 cm\(^{-1}\) is assigned to the \(0 \rightarrow 0\) transition. Only three members of the progression were observed, they are \(0 \rightarrow 1\), \(0 \rightarrow 2\), and \(0 \rightarrow 3\) which are assigned to bands number 3, 4 and 6 respectively.

The first band at 36360 cm\(^{-1}\) with \(\Delta v = 470\) cm\(^{-1}\) is assigned to the electronic transition from the ground state of the substituted benzene ring to the first excited state with the loss of one quantum of vibration \(\nu\)\(^{18a}\).

Band number 5 which only appears in the spectrum of the compound in chloroform solution is assigned to the excitation of the substituted benzene ring to the first electronic state with the gain of two quanta, one of mode \(\nu_2\) and the second of mode \(\nu_1\)\(^{18a}\).

The absorption maxima of these two compounds show considerable bathochromic shifts compared with the other aryltin compounds examined here. \(\lambda_{\text{max}}\) of the tetra-p-tolyltin in cyclohexane solution appears at 2260 Å and that of tetrakis-p-chlorophenyltin appears at 2338 Å. The former is shifted to 2350 Å in chloroform solution while the latter is only shifted to 2370 Å in chloroform.
TABLE 5

The Vibrational Fine structures of the B-band of Tetraakis-2-chlorophenyltin

<table>
<thead>
<tr>
<th>Band</th>
<th>cyclohexane solution</th>
<th></th>
<th></th>
<th></th>
<th>chloroform solution</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ (nm)</td>
<td>$\vec{E}$ (cm$^{-1}$)</td>
<td>$\Delta \vec{E}$</td>
<td>$\epsilon$</td>
<td>$\lambda$ (nm)</td>
<td>$\vec{E}$ (cm$^{-1}$)</td>
<td>$\Delta \vec{E}$</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>1</td>
<td>275.0</td>
<td>36360</td>
<td>470</td>
<td>1044</td>
<td>271.5</td>
<td>36830</td>
<td>0</td>
<td>1283</td>
</tr>
<tr>
<td>2</td>
<td>271.5</td>
<td>36830</td>
<td>0</td>
<td>1283</td>
<td>271.5</td>
<td>36830</td>
<td>0</td>
<td>1137</td>
</tr>
<tr>
<td>3</td>
<td>265.5</td>
<td>37670</td>
<td>840</td>
<td>1893</td>
<td>265.5</td>
<td>37670</td>
<td>840</td>
<td>1544</td>
</tr>
<tr>
<td>4</td>
<td>259.5</td>
<td>38530</td>
<td>1700</td>
<td>1770</td>
<td>260.0</td>
<td>38460</td>
<td>1630</td>
<td>1347</td>
</tr>
<tr>
<td>5</td>
<td>259.0</td>
<td>39370</td>
<td>2540</td>
<td></td>
<td>259.0</td>
<td>38610</td>
<td>1780</td>
<td>1367</td>
</tr>
</tbody>
</table>
IV. 5. THE ULTRAVIOLET ABSORPTION SPECTRUM OF TRIETHYLTIN PHENOXIDE AND N-TRIETHYLTIN PHTHALIMIDE

The ultraviolet absorption spectra of triethyltin phenoxyde and N:triethyltin phthalimidse are given in Figures 10 and 11 respectively. There is little in common between the spectra of these two compounds and therefore they will be discussed separately.

Triethyltin phenoxyde:

Whilst the K-band has suffered some bathochromic shift compared with the spectrum of phenol (9a, 12, 32), the B-band is almost identical for the two compounds. Furthermore, the spectrum of the compound shows some shift in the K-band from $\lambda_{\text{max}}$ at 2210 $\AA$ for cyclohexane solution to 2360 $\AA$ for chloroform solution.

The fine structures of the B-band could be assigned to the vibrational levels of the molecule (Table 6). The band at 36690 cm$^{-1}$ is assigned to the 0$\rightarrow$0 transition of the phenyl group in agreement with the assignment for phenol.

Band number 5 with $\Delta\tilde{\nu}=980$ cm$^{-1}$ is assigned to the electronic transition from the vibrationless ground state to the first excited state gaining a quantum of the vibrational mode $\nu_2$. The band at 35590 cm$^{-1}$ with $\Delta\tilde{\nu}=970$ cm$^{-1}$ is assigned to the transition from the ground state with one quantum of the vibrational mode $\nu_2$ to the vibrationless excited state. The band at 34800 cm$^{-1}$ with $\Delta\tilde{\nu}=1850$ cm$^{-1}$ is the first harmonic of band number 2.

The band at 36090 cm$^{-1}$ with $\Delta\tilde{\nu}=660$ cm$^{-1}$ is assigned to the electronic excitation of the phenyl group from the ground state with one quantum of the vibrational mode $18a$ to the vibrationless first
The Vibrational Fine Structures of the B-band of Triethyltin Phenoxide

<table>
<thead>
<tr>
<th>band</th>
<th>cylohexane solution</th>
<th>chloroform solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ (nm)</td>
<td>$\bar{\nu}$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>287.0</td>
<td>34840</td>
</tr>
<tr>
<td>2</td>
<td>281.0</td>
<td>35590</td>
</tr>
<tr>
<td>3</td>
<td>277.5</td>
<td>36030</td>
</tr>
<tr>
<td>4</td>
<td>272.5</td>
<td>36690</td>
</tr>
<tr>
<td>5</td>
<td>265.5</td>
<td>37670</td>
</tr>
</tbody>
</table>
excited state.

**N:** Triethyltin phthalimide:

Besides the K-band and the B-band, there appears a medium weak band extending from 3050 $\AA$ up to 3400 $\AA$ and a very weak band between 3500-4000 $\AA$. The moderate band with $\lambda_{\text{max}}$ at about 3080 $\AA$ with absorptivity of about 264 in cyclohexane solution may be assigned to the R-band of the molecule due to the electronic excitation of the imide group -N(CO)$_2$ (9a).

The B-band extending from 2550 $\AA$ to 3050 $\AA$ with $\lambda_{\text{max}}$ at 2875 $\AA$ and absorptivity of 1530 in cyclohexane solution and $\lambda_{\text{max}}$ at 2930 $\AA$ and absorptivity 1994 in chloroform solution agrees well with the values found for phthalimide (15a) namely $\lambda_{\text{max}}$ 2900 $\AA$ and absorptivity 2200 in alcoholic solution. No assignment of vibrational structures of the band is attempted because of the diffuse nature of the band and the absence of well defined fine structures.

The K-band has suffered a considerable shift in chloroform solution. $\lambda_{\text{max}}$ has shifted from 2150 $\AA$ with absorptivity of 42220 to 2360 $\AA$ with absorptivity of 10540. The corresponding values for phthalimide (15a) are $\lambda_{\text{max}}$ 2200 $\AA$ and absorptivity 34500.
IV. 6. GENERAL DISCUSSION ON THE ULTRAVIOLET ABSORPTION SPECTRA OF ORGANOTIN COMPOUNDS

The fact that the tin atom has an empty d-orbital in the ultimate electronic orbit coupled with its high nuclear charge (z=50) relative to its size (r=1.40Å) facilitates the formation of dπ-pπ dative bond between the tin atom and a donor group or atom such as phenyl, chlorine, etc. In the case where such group or atom (X) is already bonded to tin, it has been shown from studies of overlap integrals involving d-orbitals, by Craig, Maccoll, Nyholm, Orgel and Sutton (7), that the Sn-X bond would be expected to have a bond order higher than one. Giacometta (10) has determined the M-C\text{ar} bond length of the compounds Ph\textsubscript{4}M (M=Si, Sn & Pb), and comparison of his results with the theoretical single and double bond lengths shows clearly that the Si-C\text{ar} bond and the Sn-C\text{ar} bond have some double bond character. The work of Chatt and Williams (4) on the thermodynamic dissociation constants of the acids p-R\textsubscript{3}MC\textsubscript{6}H\textsubscript{4}COOH (M=Si, Ge and Sn) shows that resonance between the substituted benzene ring and the metal atom (M) is possible and suggested that the following unperturbed electronic structures (i-iv) contribute to the actual state of the molecules:

![Diagram](image-url)
The present work fully supports the above theory as can be seen from inspection of Figure 12 where $\lambda_{max}$ is plotted against the number of phenyl groups ($n$) in the molecule in accordance with Lewis and Calvin equation (17):

$$\lambda = k \cdot n.$$  

However it is remarkable that the decrease in $\lambda_{max}$ is not uniform throughout the series which indicates the possible participation of chlorine in the resonance not separately but in conjunction with the phenyl group, thus:

\[
\begin{align*}
\text{Sn} & \equiv \text{CCl} \\
\text{Cl}^- & \equiv \\
\end{align*}
\]

Further support for the participation of structure (v) in the determination of the actual state of the phenyltin chlorides is given by the values of the oscillator strength listed in Table 7. The oscillator strengths ($f$) were calculated by measuring the area under the B-band between 2800A and 2400A for the cyclohexane solutions and using the following formula (19):

$$f = 4.31 \times 10^{-9} \int \varepsilon \, d\varepsilon$$

The fact that diphenyltin dichloride has the lowest $f$-value points to the possibility that while the decrease in the number of the phenyl groups...
FIG 12

Graph showing a linear relationship between \( \lambda_{max} \) and the number of phenyl groups. The x-axis represents the number of phenyl groups, and the y-axis represents \( \lambda_{max} \) values. The graph exhibits an upward trend, indicating an increase in \( \lambda_{max} \) as the number of phenyl groups increases.
### Table 7

Oscillator Strengths of $\text{Ph}_n\text{SnCl}_{n-4}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Area under curve</th>
<th>$f$-value</th>
<th>$f$-value/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraphenylnitine</td>
<td>$380 \times 10^4$</td>
<td>$1.6 \times 10^{-2}$</td>
<td>$0.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Triphenyltin chloride</td>
<td>$330 \times 10^4$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>$0.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>Diphenyltin dichloride</td>
<td>$300 \times 10^4$</td>
<td>$1.3 \times 10^{-2}$</td>
<td>$0.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Phenyltin trichloride</td>
<td>$320 \times 10^4$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>$1.4 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
lowers the number of the oscillating units \((n)\), or in the language of the resonance theory the number of unperturbed electronic structures of type \((i-iv)\), the ability of chlorine to interact with the phenyl group, as in the case of structure \(v\), counteracts this trend and provides a point of inflexion at diphenyltin dichloride. However, the \(f\)-value for phenyltin trichloride can only be accepted with certain reservation since the B-band can not be considered as arising solely from the electronic transition of the phenyl group, due to the possible overlapping of the absorption band of the Sn-Cl bond.

A plot of the absorptivity \(\varepsilon\) (molecular extinction coefficient) for the centre of the B-band (i.e. for the \(0 \rightarrow 0\) transition) against the number of the phenyl groups in the molecules is given in Figure 13. It is interesting to observe the effect of the solvent on the absorptivity. Thus for the B-band, the first two members of the series show an increase in \(\varepsilon\) while the other two compounds have lower \(\varepsilon\) in the chloroform solutions than in the cyclohexane solutions. The absorptivity at \(\lambda_{\text{max}}\) of the K-band shows an all round decrease of a factor of 10. Taking these two facts together the extent of the molecular association between chloroform and the members of the homologous series may be arranged in the following descending order:

\[
\text{PhSnCl}_3 \quad \text{Ph}_2\text{SnCl}_2 \quad \text{Ph}_3\text{SnCl} \quad \text{Ph}_4\text{Sn}
\]

Matsen (20, 26) has shown that the bathochromic shift of the B-band of monosubstituted benzene is related to the ionization potential of the substituent atom or group and in turn to the extent of the resonance between the substituent and the benzene nucleus. For the homologous series \(\text{Ph}_n\text{SnCl}_{4-n}\), the resonance effect can, therefore, be arranged in
FIG. 13

\[ \begin{align*}
\text{cyclohexane soln.} & \quad \varepsilon_{\text{max}} \text{ of } E_{\text{band}} \\
\text{chloroform soln.} & \quad \varepsilon_{\text{max}} \text{ of } K_{\text{band}}
\end{align*} \]

\[ \begin{align*}
\text{multiply } \varepsilon \text{ by 100} \\
\text{multiply } \varepsilon \text{ by 10}
\end{align*} \]

\( \text{Na of Phenyl Groups} \)
the following ascending order:

\[
\text{PhSnCl}_3, \Delta \tilde{\nu} = 80 \text{ cm}^{-1} < \text{Ph}_2\text{SnCl}_2, \Delta \tilde{\nu} = 150 \text{ cm}^{-1} < \text{Ph}_3\text{SnCl}, \Delta \tilde{\nu} = 220 \text{ cm}^{-1} < \text{Ph}_4\text{Sn}, \Delta \tilde{\nu} = 360 \text{ cm}^{-1}
\]

However, if the f-values, which are a measure of intensity of the band, are divided by the number of phenyl groups in the molecules as in the fourth column of Table 7 (11), it will be apparent that these values will be in contradiction with the order of the bathochromic shifts. This apparent contradiction arises from the fact that while the frequency of the absorption band is a "resonance effect" the intensity of the band is an "inductive effect". Therefore the inductive effect, and hence the electronegativity of the tin atom, will be expected to fall in the following order:

\[
\text{PhSnCl}_3 \succ \text{Ph}_2\text{SnCl}_2 \succ \text{Ph}_3\text{SnCl} \succ \text{Ph}_4\text{Sn},
\]

which agrees with the order of molecular association between chloroform and the phenyltin compounds.

Hence, it can be concluded that in the phenyltin compounds both resonance and inductive effects are active and as the number of the chlorine atoms in the molecule increases their effect on the tin atom is such as to enhance its electronegativity which in turn will facilitate the resonance between the \( \pi \)-orbital of the benzene nucleus and the empty d-orbital of the tin atom. Illustratively, the combined resonance and inductive effect may be represented as follows:
which shows a possible mechanism for the participation of form (v) in the actual structure of the molecule.

The above findings are in complete accord with the conclusions arrived at from the infrared absorption spectra of the phenyltin compounds (Part Three, section III.6)

In the cyclohexane solutions the 0→0 band of tetraphenyltin and tetrabenzyltin are identical in both frequency and absorptivity. However in the chloroform solution very little difference in the frequencies of the two compounds was observed, the absorptivities were found to differ thus \( \varepsilon_{\text{max}} \) for tetrabenzyltin is 1070 compared with the value of 1245 for tetraphenyltin. Comparison of the frequency of tetrabenzyltin viz 37740 cm\(^{-1}\), with that of some alkyl substituted benzenes (32) (e.g. toluene 37480 cm\(^{-1}\) ethylbenzene 37530 cm\(^{-1}\)) shows that some hypsochromic shift with respect to these compounds is exhibited. Such a shift seems to indicate that the tin has somehow deactivated the methylene group, possibly by influencing the extent of its hyperconjugative effect, an assumption which has some support from the infrared absorption spectrum of the compound.

The slight fall in the frequency of the 0→0 band of triethyltin phenoxide compared with that for phenol (12, 21a, 32) is so small as to be of no considerable significance. However a considerable difference is observed with the corresponding values for anisole (12, 21a)

\[
\begin{align*}
\text{triethyltin phenoxide} & \quad 36690 \text{ cm}^{-1} & \quad 1611 \\
\text{phenol} & \quad 36630 & \quad 2050 \\
\text{anisole} & \quad 37740 & \quad 2300
\end{align*}
\]

The difference in the frequencies of anisole and triethyltin phenoxide
may be explained on the basis that whilst the methyl group is electron releasing the triethyltin group seems to be electron attracting and therefore it would be expected to provide through the empty outermost d-orbital of tin an extension of the conjugation of the \( \pi \)-electrons of the phenyl group.

The spectra of tetra-\( \rho \)-tolyldtin and tetrakis-\( \rho \)-chlorophenyltin are rather instructive. It has been pointed out in the Introduction to Part IV that the frequency shift of the B-band in \( \rho \)-substituted benzene is approximately additive for the two substituents. In the case of tetra-\( \rho \)-tolyldtin the bathochromic shift observed is 860 cm\(^{-1}\) which compares well with the sum of the shifts obtained in toluene (32) and tetraphenyltin (620 + 360 = 980 cm\(^{-1}\)). For tetrakis-\( \rho \)-chlorophenyltin the relative agreement is even better \( \Delta \tilde{\nu} \) (obsd) = 1270 cm\(^{-1}\); \( \Delta \tilde{\nu} \) (cald) = 1047 + 360 = 1407 cm\(^{-1}\) (1a, 30a). It seems that the only conclusion possible from the above experimental observation is that there is some electronic interaction between the two substituents (Sn and Cl in one case and Sn and \((\text{CH}_3)\) in the other case)
REFERENCES:

21. C. Milazzo, Gazz. chim. ital., 1941, 71, 73.

Additional references: