STUDIES IN OPTICAL ACTIVITY -
THE ROTATORY POWERS AND
DISPERSIONS OF \( \alpha \)-THIENYL METHYL
AND \( \alpha \)-PHENYLETHYL CARBONOLS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>The Vapour Melting Point</td>
</tr>
<tr>
<td>(2)</td>
<td>The Benzene Solvent</td>
</tr>
<tr>
<td>(3)</td>
<td>The Hexane Solvent</td>
</tr>
<tr>
<td>(4)</td>
<td>Other Solvents</td>
</tr>
<tr>
<td>(5)</td>
<td>Temperature Effects</td>
</tr>
</tbody>
</table>

[Image 0x0 to 617x796]
REPORT TO THE DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

by

I. G. Anderson

of the work carried out at Battersea Polytechnic during the period of a Maintenance Allowance, October 1946 - September 1948, under the supervision of Dr. J. Kenyon, F.R.S.

The results of this investigation have been submitted to the University of London as a thesis for the Ph.D. degree, and this report is presented in the form of a copy thereof.

The author wishes to record his indebtedness to Dr. Kenyon and Dr. M. P. Balfe for their interest and guidance, and also to Dr. G. H. Beaven for the ultraviolet absorption determinations.

39 Demesne Road, Wallington, Surrey.
Abstract of thesis entitled
"Studies on Optical Activity - the rotatory
dispersions and dispersion of 2-Chloromethyl
and α,α-Dimethyl carbine", submitted
in partial fulfillment of the degree of Doctor of Philosophy by
TUCKER, C. A. (A.B., 1947)

Dissipation of α-Chloromethyl
AND α-DIMETHYL CARBOLS.

1. Theories of the nature of optical rotatory power are
reviewed, with special reference to that of Pohl.

2. The preparation of α-Chloromethyl carbine is
described, and the resolution of the bromo salt of its
hydrogen phthalic ester. The rotatory dispersions of the
optically active alcohol and its solutions in various solvents
are recorded, and shown to be simple in the visible spectrum.
The dispersions are discussed in relation to the ultraviolet
absorption of the alcohol and esters, and from regarding
the type of Brin equation that would be required to cover
the complete spectrum, the most likely chromophore
groups in the molecule. Optical data are recorded for the
hydrogen phthalic ester, and α-methoxylation in this
compound has been demonstrated.

3. The preparation of α,α-Dimethyl carbine and a method
for its resolution on the bromo salt of its hydrogen phthalic
ester are described. The rotatory dispersion of the active
alcohol in ethereal solvents has been examined in the visible
spectrum, and found to be simple in all-saturated solvents, but
complex and anomalous in non-polar media. The dispersive
powers of the hydrogen phthalic and acetate esters and of the
α-oxymethyl aromatic are also recorded.

A possible explanation of the dispersion phenomena in different
solvents and the type of Brin equation required to predict
the dispersions are discussed in relation to the ultraviolet
absorption of the alcohol.
# CONTENTS

## Part I. Theoretical Considerations

**Section I. - Optical Rotatory Power**

(1) General Theories
(2) Optical Rotatory Dispersion

**Section II. - Analysis of Optical Rotatory Dispersion Data**

(1) The Davy Equation
(2) The Characteristic Diagram
(3) The Dispersion Ratio
(4) Solvent Effects
(5) Temperature Effects

## Part II. Preparative Work and Discussion

**Section III. - 2 Thiophenyl Cardenol**

(1) Preparation by Oxidation Reaction
(2) Reduction of 2 acetyltiophenes
(3) Resolution
(4) Allyl-oxygen Fission
(5) Rotatory dispersion of (-) 2 thiophenylethyl cardenol
(6) Rotatory dispersion of the hydrogen phthalic ester

**Section IV. - α-Picolinyl Cardenol**

(1) Preparation and Resolution
(2) Rotatory Dispersion of the Cardenol
(3) Solvent Effects
(4) Rotatory Dispersion of Derivatives
(5) General Conclusion

## Part III. Experimental

**Section V. - 2-Thiophenyl Cardenol**

Preparation of α-alcohol
Resolution of α-hydrogen phthalic ester
Allyl-oxygen Fission Reactions
Dispersion Data
Section VI. - d-PEERENREIN CARBIDE

Preparation of dL-alcohol... 69
Epoxidation... 70
Dispersion Data... 74
Optical Activity of Derivatives... 170

The process of various stepsocompounds to make the plane of polarization of a beam of plane polarized light can first observed by Nernst in 1876. Tammann undertook the analysis of molecular dispersion in 1878 and found that the sensitivity of refractive index of an amorphous silicon nitride as a certain condition for optical activity.

References

Fig. I - XIII

The reaction studied for process of epoxidation, so that it is possible of solvents in the reaction product from, related to each in almost equal, the 1 to 50 molar ratio. A useful method of a technique without an experimental system and preparing as well as easily, but relating to the amorphous form, was provided in 1970 by Nelson and Mullen. [1] The eutectic silicon nitride correlating allowed.

\[
\left( \frac{\alpha}{\beta} \right) = \frac{100\alpha}{x} \cdot \frac{1}{x^2}
\]
TWO - THEORETICAL CONSIDERATIONS

I. OPTICAL ROTATORY POWER

(1) General Theory (1, 2)

The power of certain organic compounds to rotate the plane of polarization of a beam of plane polarized light was first observed by Biot in 1815. Pasteur introduced the concept of molecular chirality in 1848, and von Maltz and J. D. B. suggested the presence of an asymmetric carbon atom as a necessary condition for optical activity.

Subsequent work has established that to be optically active, a molecule must possess neither a plane nor centre of symmetry, so that it is capable of existing in two enantiomorphic forms, related as object to mirror image, the two being non-superposable. A striking example of a molecule without an asymmetric carbon atom and possessing an axis of symmetry, but existing in two enantiomorphic forms, was provided in 1935 by Maitland and Mills (3) who resolved diphenyl-dimethyl allene.

The optical rotatory power of a substance is normally recorded as the specific rotatory power, defined as

\[ [\alpha]_\lambda = \frac{100 \alpha}{c \lambda} \]

often also expressed in terms of the molecular rotation, \( \psi \), according to the formula

\[ \psi = \frac{[\alpha]_\lambda \lambda}{100} \]
The first to accept the induction of a rotation
where \( \alpha \) is observed rotation at wavelength \( \lambda \) content of enantiomeric column
\( \lambda \) = \( \frac{\alpha}{\alpha} \) length of the column in dm.
\( \alpha \) = concentration of active solute in g/100 ml. active concentration
\( \lambda \) = density in g/ml.

or the molecular rotatory power.

Equation \( [M]_{\lambda} = \frac{M \alpha}{100} \)

where \( M \) = molecular weight of the solute. The variation of \( \alpha \) with \( \lambda \)
\( \lambda \) is known as the optical rotatory dispersion of a medium. (4)

In 1833 Fresnel (4) interpreted optical rotatory power on the basis of
circular double refraction of two circular vibrations of equal amplitude
but opposite sense, and equivalent to a plane polarised ray. The
velocities of the right and left circularly polarised light are different
in an optically active medium, so that the resultant plane polarised beam
is rotated. Similarly, for light of a wavelength falling within certain
absorption regions of an optically active molecule, there is a difference
in the absorption coefficients for left and right circularly polarised
rays, so that the emergent light is no longer plane, but elliptically
polarised. This phenomenon, known as circular dichroism, was observed
by Cotton (5) in 1889 during a study of the rotatory dispersion of 1,2-
coloured complex salts of tartaric acid in a region of absorption. (5-8)
Cotton also observed that for decreasing wavelengths, the rotatory
dispersion, in passing through the same absorption region, increased to a
maximum, became zero, and increased in the opposite sense to a second
maximum. These phenomena, known as the Cotton effects, occur together
in an "optically active absorption band". All the absorption bands of a
given molecule, however, do not necessarily affect its rotatory power.
Drude was the first to attempt the derivation of a rotatory
dispersion formula, which he based on classical equations of refractive
dispersion, since rotatory precession observed in active absorption bands
are similar in form to the anomalies which occur in refractive dispersion
in a region of absorption. Drude's simplified equation for a region of
transparency has been shown by several workers to represent accurately
in solutions (and) can thus be used to calculate the rotation of light passing through an active substance although Kuhn (6) claimed that the derivation is invalid. The simplified
Drude equation is still the only one in use by the organic chemist.

\[
\alpha \lambda = \frac{K}{\lambda^2 - \lambda_0^2}
\]

where \(\alpha\) = rotation at wavelength \(\lambda\),
\[K = \text{constant}
\]
\[\lambda_0 = \text{the characteristic wavelength of an optically active}
\]

The close relationship between optical rotatory power and certain
in solutions can be represented by the relation that absorption wavelengths having been established, it was evident that the
absorption maxima depend on the size of groups attached to them. An essential feature of a successful theory of optical activity must be the
account for giving rise within a "polarised" field. As such, electronic perturbations giving rise to the absorption bands.

Born and Osamu, independently, in 1916, advanced the theory of
which the rotatory power arises from the characteristic properties
coupled resonators within a molecule giving rise to the rotatory power.
Dyson and others, after a study made to a major extent
Both considered the molecule as consisting of several units, held firmly
of the equivalent nuclei. Even the total of these rotations become together, but each capable of displacement in the electric field of
polarised light. Each of these displacements or polarisations then
results in a field of force which acts on all the other units of the
molecule, so that the total effect is one of coupled forces, all due
to the incident polarised light, and all interacting with it. Four
molecules are required for the description of 4 given
non-linearly coupled electrons, as present in an asymmetric carbon atom,
could produce this effect, but uncoupled electrons would contribute nothing to the rotary power of a molecule. Born’s calculations, however, resulted in equations so complex as to be useless for practical purposes, but the idea of coupled oscillators dominates all subsequent theories.

De Hevesy (1927) and Boys (1931) attempted to derive dispersion equations on the basis of a model consisting of four groups tetrahedrally arranged around a central atom. Calculating the mean polarisabilities of the groups from their known atomic refractivities both theories resulted in complex formulae involving interatomic distances, and coupling between the groups. Weak absorption bands in the near ultra-violet region of the spectrum have little influence on ordinary refractivity, but are known to have a profound effect on rotary power. Both theories fail to account for this. Long, however, considered that the de Hevesy-Boys model was qualitatively correct, but pointed out that smaller units than the atoms or groups employed by them are required to account for rotation anomalies within an “optically active” absorption region. In his model, it becomes interdependent, and requires a new theory.

Kuhn (9) in 1939 published a review of the fundamental phenomena of optical activity, and developed a theory based on a simple model consisting of a pair of rectilinear harmonic oscillators, with different characteristic frequencies, at right angles, and separated by a distance (d). To satisfy Fresnel’s concept of optical activity, (i.e. a different response to left and right circularly polarised light), Kuhn showed that the resonators must be interdependent, i.e. coupled, and derived an expression for the rotary contribution of a given
absorption band, which reduced, in a region outside the band, to a single
Drude type term. The total rotation of the molecule would be the sum of
the contributions of all the bands

\[ \alpha = \frac{a_m}{\lambda^2 \lambda_m n^2} \]

where \( a_m \) is the characteristic constant of an absorption band at
wavelength \( \lambda_m \). This expression differs from the earlier Drude
equation only in that Kuhn was able to show that

\[ a_m = 0 \]

a most important development, indicating that the contributions of
individual active bands vary in sign. Kuhn also related the rotatory
contribution of an active band to its refractive contribution, by the
anisotropy factor, which could be obtained from the circular dichroism
of the band. Only weak absorption bands could have a high anisotropy
factor, and thereby a large rotatory contribution.

Then a group with a definite absorption band is introduced into an
optically active molecule, the band does not invariably contribute to the
rotatory power. If, however, the electronic excitation responsible for
the band is coupled, it becomes anisotropic, and acquires a rotatory
contribution. Such a group is called a chromophoric group, and its
anisotropy is defined by Kuhn as induced anisotropy. Then a band
becomes anisotropic, furthermore, it influences the induced anisotropy
of all the bands with which it is coupled, and this effect Kuhn termed
"vicious function". It is in this way that Kuhn is able to account for
the optical rotation associated with an absorption band due to a formally
symmetrical group (such as carbonyl) in an unsymmetrical molecule (such
as eserine). The percentage contribution of each such band would be a
(1) A useful mixing power is a small distribution of arbitrary
measure of the vicinal motion of the other groups in a molecule. The
frequency of the vibration responsible for a chromophoric absorption
band is termed the characteristic frequency, and the characteristic
frequency corresponding to each active band should theoretically appear
as a term in the dispersion equation required for a given molecule.

Experimental correlation between values for the dispersion
constants \( \lambda_i^2 \) calculated from rotational dispersion data, and actual
absorption bands, measured directly, is available for a limited number
of compounds. The majority of optically active organic compounds only
sharply absorb in the region of the spectrum below 2,000\( \AA \), which is
difficult to reach experimentally. By employing compounds containing
chromophoric groups with an absorption band in the near ultraviolet,
direct comparison is possible. Richard and Hunter (8) found for
\( \Delta \)-napthyl nitrate that the rotary dispersion was controlled by a
dispersion constant corresponding to \( 3000 \AA \); direct measurement of the
absorption characteristics revealed a mid-max at 3000\( \AA \). Lacey et al
(10, 11) found that the rotary dispersion of cinnamic acids gave a
value of 4750\( \AA \) for the controlling bend, with a "real" band at 4675\( \AA \).

Similarly, dispersion data of chromophoric aldehydes have been related to
the characteristic aldehyde band at 1680\( \AA \), and Hunt (6) related the
dispersion of the chromophoric of \( \alpha \)-naphthyl propionic acid to the aldehyde
band at 2000\( \AA \). These results give strong support to the theoretical
methods used in deriving the dispersion formula.

The principal conclusions drawn from Laha's theory and review may
be summarized as follows.
(1) Optical rotatory power is a small disturbance of ordinary light with two linearly polarized light vibrations and it is due to 

refraction, produced by coupled forces between the various substituents 

of para-rotatable molecules. Buhl's formula may be 

in a diatomic molecule,

\[ \theta = \frac{\pi L}{\lambda} \left( n_2 - n_1 \right) \]

where \( \theta \) is the angle of rotation, \( n_2 \) and \( n_1 \) being the refractive 

indices for left and right circularly polarized light.

(2) Greater optical activity is associated with weak than with 

strong absorption bands, 

only for molecules in simple rather than a fixed-distance matrix. Buhl's 

(3) The rotatory power of a compound in the visible spectrum is 

influenced by other molecules of the matrix which is 

chiefly governed by the nearest absorption bands, since the partial 

intensity of the rotation has a matrix, but for weak, 

bands the rotations of bands in the Schumann region are not all of the same sign, 

excess of positive is due to weak \( \xi^2 - \xi \) while negative has the 

and tend to cancel one another in a distant part of the spectrum, 

positive rotation of an anisotropic 

(4) An anisotropic absorption band contributes to the rotatory 

in many cases through (2) and similar, weak as \( \xi^2 - \xi \) for 

power of a molecule by its induced anisotropy, and also by vicinal action 

with a non-rotatable molecule in the electronic transitions 

on other bands. Vicinal action appears to be mainly due to strong bands 

of vibration and absorption, if planar form, and are able to absorb in 

the Schumann region, which make little direct contribution. 

The action of a complex of crystals rotated by ordinary energy 

Apart from the significant qualitative agreement between Buhl's 

in a molecule. However, as \( \xi^2 - \xi \) in a region of these radicals, 

theory and experimental results, and the derivation of a Buhl type 

identity between the angles double of optical activity and angle of 

rotatory dispersion equation for a region of transparency, Buhl's 

experimental data and theory for these two equations. One may 

equations for dispersion within an absorbing region represent 

as a direct and indirect way to re-establish the optical 

experimental data are closely than any earlier attempts. Calculations 

for each \( \xi^2 - \xi \) of the band \( \xi^2 - \xi \) on \( \xi - \xi \), values of 

of values of \( \xi - \xi \), the distance between Buhl's coupled resonators, 

closer rather than between their non-rotatable molecules, 

however, have yielded values which bear no relation to known molecular 

forces, provide a potential method of theoretical physics and 

dimensions (15). 

molecules and the formulae derived exactly at any infinite 

molecular standards that they are of little value to the laboratories
Born (13), in 1926, reformulated his theory using a model of the Boys type, with four vibrators arranged tetrahedrally, and forming two pairs of weakly anisotropic resonators. Born's formula was too complex for everyday use, but his model bears close resemblance to the spiroamine formula:

$$\alpha = \frac{\lambda}{c}$$

where

- \(\alpha\) is the angle between the vibrators,
- \(\lambda\) is the wavelength of the light,
- \(c\) is the velocity of light.

Optically active substances such as spiroamine, as found that he was resolved by Pope and Stranski (14), where the -\(\text{CH}_3\) and -\(\text{H}\) groups form two pairs of resonators at right angles, and a fixed distance apart. Born's formula gives a value for the rotatory power of this molecule which is of the correct order of magnitude, but no more. Born also obtained the important result arrived by Ehrn, \(\alpha \approx 2\), which accounts for the pronounced rotatory effect of weak absorption bands.

In recent years Ishimoto (15) and Condon, Syring et al (16) have applied wave-mechanical calculations to the electronic transitions associated with absorption of polarised light, and are able to calculate the order of magnitude of partial rotations provided by specific groups in a molecule. Kinemann et al (17) in a review of these methods, classify perturbations capable of virtual action and correlate much experimental data with the aid of these new equations. Thus they calculate that virtual action in 3-methylcyclopentene is responsible for about 3% of the total (i.e., observed) rotatory power. The detailed mathematical treatment of these wave-mechanical conceptions, however, requires a profound knowledge of theoretical physics and mathematics and the formulae derived contain so many fundamental molecular constants that they are of little value in the laboratory.
(11) Optical Rotation Dispersion

The effect of the wavelength of light on rotatory power was first examined and in the dispersion of light and of rotatory power recorded by Biot, who found that nearly all the optically active compounds the optical rotation of which is constant in diameter then known obeyed a law of inverse squares in rotatory power with frequency variation, and an additional dispersion

\[ \frac{\Delta \theta}{\lambda} = \frac{\Delta \theta}{\lambda^2} \]

This fact led to the conclusion that simple dispersion is always to be expected; Tartaric acid was found to be an exception. Biot then divided the known substances into two classes, (1) those which obeyed the inverse square law, and (2) those which did not obey the law, due to the presence of two substances, one of which in the second group, could be experimentally prepared to produce a dispersion that did not obey the inverse square law by superposing two "orthodox" substances, (a) of lower and (b) of higher order of rotatory power, in equal proportions. With this assumption, it was possible to classify all substances with rotatory power into two classes, (a) those which obeyed the inverse square law, and (b) those which did not. It was further pointed out that these two classes were of equal and opposite rotatory power. Toluenepic? (13), by the analysis of the former substance, showed that only one type of rotatory power, namely, of the former type was possible with two asymmetric compounds of opposite sign contained within the same molecule. Of these two, Lecoq concluded, the order of priority is that of the former. However, later and more accurate measurements of rotatory power have shown that this statement is not entirely true, since it has been shown that many substances of Biot's orthodox class cannot be represented by Biot's equation, which is essentially an equation of the second degree. Such a simple expression as the inverse square law, and Biot, by the initial assumption of the constant or of the inverse square law, published his dispersion formula in 1849. Later it was found that the assumptions of a straight line in the medium were correct. This formula is still valid in a region of transparency, which he discovered, but that this region should be referred to is not immediately apparent from the equation. It is a single line with all possible solutions leading to an identical expression.

Lecoq's conclusion is still valid, but the final formula would hold for a single line only.

Lecoq has been largely responsible for the wide application of the formula, and his work has been a valuable contribution to the study of rotatory power. He has shown that the dispersion of rotatory power is a function of the frequency of light, and that the rotatory power of a compound is the result of the rotatory power of its constituent parts. This has been confirmed by later work on the rotatory power of compounds of different sign, and it has been shown that the rotatory power of a compound is the sum of the rotatory power of its constituent parts.
constant "K" of each term \( \frac{K}{\lambda^2 - \lambda_0^2} \) they defined as the "rotatory power constant" and \( \lambda_0 \) as the "dispersion constant". Furthermore, extending Arrhenius of the Arrhenius plane (21). Arrhenius of this type are the earlier nomenclature, in that a normal dispersion exhibited an increase constant of the type "rotatory power" in rotatory power with decreasing wavelength, and on anomalous dispersion the introduction of a denominator group into a molecule and we did not, it was now evident that simple dispersion must always be normal.

Lorenz and Weller (22) recognize that this group will always require a normal dispersion, however, might be either simple or complex, in that it might have a relatively active. Lorenz and Weller (22) recognize that right require either one or two Drude terms to express it adequately.

Division of rotatory dispersion data into "simple" and "complex" is an arbitrary, and the "first (they were) arbitrary means of the theoretical method of classifying experimental results, since theoretically the Drude expression represents a series of terms, each attributable to a separate electronic transition. Lorenz and Weller (22) point out that even in the case of the simplest asymmetric molecule, the whole rotatory power could be divided into two terms in the expression \( \lambda_0 \). A term, \( \lambda_0 \), cannot be developed by one electronic transition corresponding to the wavelength range of the dispersion constant of a single Drude term. Largely due to the magnitude of the rotatory power also is expressed as a set of general discussion of observed rotations, and the order of accuracy of polarimetry, however, lower terms have been added to the invariable formulas which two terms are adequate to express experimental data with precision.

Furthermore, as Rabin has pointed out, rotatory dispersion in the visible range dispersion data is not usually considered, because a species which is generally controlled by the nearest one or two active absorption bands. It may frequently occur that the contribution of a subsequent term is too small to be detected, or that two active absorption bands occur close together, so that the actual rotation data will fit a single Drude term, also in solution. The separation of dispersion phenomena into rotatory with a dispersion constant representing the mean of the two bands.

Lorenz and Weller (22) cite the remarkable example of tert-butyl \( \mu \) -amylase.

In the figure 2, we consider only two absorption bands. These illustrations are the "where the partial rotations of high frequency associated with the three of the butyl group is of the rotation of the first butyl asymmetric carbon atoms of the \( \text{[CH}_3 \text{]}_4 \text{C} \) chain.
can be represented by a single low frequency term with the characteristic frequency of the aldehyde group (21).\(^{2}\). Dispersions of this type are described by Lowry as “pseudo-simple”.

The introduction of a chromophoric group into a molecule does not imply that each absorption frequency of the grouping will become coupled and hence optically active. Leverre and Pothier (2), reviewing the general effect of chromophores on rotatory power, have concluded, for example, that the first (long wave) absorption band of the hydroxyl group in aliphatic alcohols at ca. 1600\(^{2}\) is inactive.

Lowry (1) refers to the discrepancy between the calculated and observed values for the band of an optically active absorption band, and points out that it is always in the direction \(\lambda_{\text{calc.}} > \lambda_{\text{obs.}}\), and may be as great as 15\(^{2}\). This discrepancy can be accounted for, since the selective absorption is superposed on a curve of general absorption tending towards a very high maximum in the inaccessible Schumann region.

Experimental examination of a dispersion in the neighborhood of a given absorption band is not usually possible, suitable apparatus being available in only a few laboratories. Indeed, no rotatory dispersion measurements appear to have been made in the Schumann region, so that the anomalies of the Cotton effect for the majority of compounds have so far defied investigation. The correlation of absorption phenomena and rotatory dispersion thus depends mainly on the observation of rotation complexities in the visible and near ultra-violet regions. These complexities are the result of the relative signs and contributions of the partial rotations controlling the dispersion in a region of transparency, can be fitted to a Drake expression, and are quite different in character from the
anomalies of the Cotton effect. There are three possible causes of anomalous dispersion in a region of transparency:

1. Partial rotations due to two different molecular species.
2. Partial rotations having their origin in two asymmetric centres within the same molecule.
3. Partial rotations associated with one asymmetric centre, one of which is due to induced chirality in a chiral compound.

II. ANALYSIS OF MEASURED DISPERSION DATA

1. The Brule Equation

The Brule equation is similar to (1). Calculation of the constants of a two term Brule expression will be unnecessary unless the dispersion is so great that such is required to fit the experimental data, should be capable of yielding values for \( \lambda_1 \) and \( \lambda_2 \). At least one of these (\( \lambda_1 \)) should correspond to a real absorption band, but the other (\( \lambda_2 \)) may represent a weighted mean of all the active bands of shorter wavelength than \( \lambda_1 \).

Preliminary analysis of experimental rotatory dispersion data is usually carried out by recording the results graphically, plotting \( \theta \lambda \) against \( \lambda^2 \) (\( \theta \lambda = \) angle of rotation at wavelength \( \lambda \)). A simple dispersion results in a straight line, intersecting the \( \lambda^2 \) axis at \( \lambda_0^2 \), and corresponding to a single Brule term.

For a single term equation \( \theta \lambda = \frac{\lambda^2 - \lambda_0^2}{K} \), the equation (2) can be written

\[
\frac{1}{\theta \lambda} = \frac{\lambda^2 - \lambda_0^2}{K}.
\]
If the resulting graph deviates from a straight line, the dispersion is complex.

Algebraic analysis of the two-term Drude expression shows that for combinations of the constants $\mu_1$, $\mu_2$, $\lambda_1$, $\lambda_2$ have to be considered, defining $\lambda_1 > \lambda_2$. (1, 2, 22).

((1) Both terms of the same sign, $\mu_1 > \mu_2$. The dispersion will always be normal than $\lambda > \lambda_1$. The $\lambda$ against $\lambda^2$ graph will be practically a straight line at long wavelengths, but will curve when $\lambda$ approaches $\lambda_1$. The dispersion in the visible will probably appear simple, and calculation of $\lambda_0$ for a single term Drude equation will give $\lambda_1 > \lambda_0 > \lambda_2$.

((2) Both terms of the same sign $\mu_1 < \mu_2$. This case is similar to (1), but the $\lambda^2$ graph will deviate more from a straight line, and will be concave towards the $\lambda^2$ axis, especially as $\lambda$ approaches $\lambda_1$. Both these cases will give normal dispersion, but it will be complex in the ultraviolet nevertheless. Lowry and Moseley (25) have pointed out that a considerable difference in the magnitude of the two dispersion constants would be required to detect complexity due to too contributions of the same sign.

((3) Two terms of opposite sign, $\mu_1 > \mu_2$. The $\lambda^2$ graph will deviate considerably from a straight line, and will be convex towards the $\lambda$ axis. Provided $\mu_1$ and $\mu_2$ are not too close in magnitude, the dispersion will appear simple in the visible, and calculation of $\lambda_0 > \lambda_1 > \lambda_2$. (Lowry and Moseley (2) state that $\lambda_0 - \lambda_1$ may vary as much as 1500A). The complexity of this case is often apparent from the smallness of the dispersion.
(iv) Two terms of opposite sign, \( E_1 \sim E_2 \). The complexity of
the dispersion is readily apparent, and the \( \frac{1}{\lambda^2} \) graph rises in
prominence at a straight line. The dispersion curve \( (\alpha = 1) \) with
increasing wavelength, reaches a maximum, decreases to zero and rapidly
increases in the opposite sense, exhibiting obvious anomaly in a region
of transparency. A striking example of this type of dispersion was
found recently by a study of tetrahydrofurfuryl alcohol in this
labatory by Irvin (26).

It is now evident that the graphical test of plotting \( \frac{1}{\lambda^2} \) against
\( \lambda^2 \), particularly when data is only available for the visible region,
does not distinguish between simple and complex, but between normal
and anomalous dispersions. Only in case (iv) is departure of the
\( \frac{1}{\lambda^2} \) graph from a straight line immediately noticeable. In all
other cases, departure from linearity becomes noticeable only in
regions close to an absorption band, which may lie in the inaccessible
region of the curve. The normal mechanism of resolving the elements in
ultraviolet. The predominance of substances exhibiting simple
dispersion (at least in the visible spectrum) can now be understood.

In many cases, however, particularly when ultraviolet measurements
are available, the \( \frac{1}{\lambda^2} \) graph can give information about the signs of
the contributions corresponding to the two Friede terms, and their
relative values. Laves and Rothen (2) have developed this treatment,
and in the light of supersaddled data have extended it to any series of configurally related compounds.

The dispersion rate of a spiroally cyclic compound can
be defined by Irvin (26) as the rate of \( \tau \); the relative power of the
spiroally cyclic mechanism, usually \( 202 \) and \( 223 \). Since it is
not related to any fundamental property of a molecule, its value is very
(11) The Characteristic Diagram

Armstrong and Walker (28) introduced another graphical method for the analysis of rotary dispersion data, on the assumption that the dispersion is due to two forms of a substance. Four cases were considered, involving variation in sign and/or dispersive power of the two forms.

The specific rotations of a series of related compounds for a selected wavelength are plotted graphically as abscissae, and the corresponding rotations at other wavelengths as ordinates. The resulting diagram, under favorable conditions, consists of a series of straight lines, and is described as the characteristic diagram. Then the dispersion is simple, the lines will all intersect on the ordinate of zero rotation, but when complex, the lines will not intersect at a point. If the dispersion is anomalous, furthermore, the area of intersection will be inside the diagram.

Patterson (28) increased the sensitivity of the diagram, by plotting on ordinates the algebraic differences between rotations at a given wavelength and at the standard wavelength.

If the dispersive powers of the components are independent of external conditions, it should be possible to construct a diagram for a substance possessing ten partial rotations, by replacing solutions in different solvents, or in the same solvent at varying concentrations.

(111) The Diminished Ratio

The dispersion ratio of an optically active compound was defined by Jones (27) as the ratio of its rotary powers at two arbitrarily chosen wavelengths, usually 4358 and 5461. Since it is not related to any fundamental property of a molecule, its value is very

15.
restricted, but it remains fairly constant in a homologous series of
hexane. The value for a crystal of (+)-tartaric acid in a mixture of
compounds. Hunter (23) has shown that for compounds exhibiting simple
dispersion, the minimum value of the dispersion ratio ($\alpha$ $\Delta$ $\delta$).

In solution, therefore, with a dispersion ratio less than
1.57, any compound is certainly exhibiting complex dispersion. Furthermore, the
characteristic features of the optical rotation of the simple dispersion ratio of a single compound should be unaffected by changes
precision. The total rotation power of the compound, and shift in
of solvent, temperature and concentration.

Optical activity dispersion will correspond with the particular characteristic
(iv) Solvent Effects
The magnitude of the optical activity exhibited by an optically
active substance is altered by the addition, or removal, of a solvent.
active substance in solution is a problematic phenomenon that is still
unsolved. The problem is that, in (23) that studied this a second approach was
by no means solved, in spite of the abundant experimental data available.
also then could neither the molecular power of rotation nor the velocity

In the complete Born expression for optical rotation, the
of the solvent, is expressed by the single constant. The introduction of a third
refractive index of the medium ($n$) appears. Wolf and Vollrath (23)
the solution did not yield a single effective, unambiguous, in the light,
have concluded that the expression
by utilizing the frequency dependence of the polar group the molecule.

$\chi$ is measurable constant whose value varies with

$\chi$, should remain constant from one solvent to another for non-polar solvents.

Bednarek and Cohen (23) suggest that the significant quantity in
studying solvent effects is the activity ($\alpha$) defined as

$\alpha$ is the second moment of $\om$ with respect to the frequency

since this quantity is supposed to be directly related to the orientation of the
molecules in a molecule. Rule and Chambers (30) found that although the
activity of the hydrocarbon plane remained approximately constant in
different solvents, variation in refractive index was not the only

factor operative. Kenyon and Hatt (31) have found no relationship
between the rotatory powers of (+) \( \gamma \)-methyl n-heptane in a variety of solvents, and the refractive indices.

Association between polar groups in a solvent and an optically active solute might occur, and partially neutralize the electric field in which a chromophoric electron was moving. This would reduce the group's contribution to the total rotatory power of the molecule, and shift the optically active absorption band associated with the particular electronic jump involved. Schachtschneider et al. (31) have shown that a definite relationship does exist between the rotatory power of a solute and the polarity of the solvent, as measured by its dipole moment. The hydrocarbon radicals of a polar solvent will exert a steric effect, proportional to its bulk, by relaxing the frequency with which the polar group can associate.

It is conceivable that a solvent might distort the molecular framework of a solute molecule, and affect the orientation of the active electrons. This might easily influence the rotatory power of the molecule, but would not be detectable in its absorption characteristics.

The principal effects of a solvent seem to operate on the absorption bands accordant to the visible spectrum, and these make the most important contribution to the rotatory power of a molecule. The high sensitivity of the rotatory power to solvents of the rotatory power of many substances is thus, at least partially, explained.

To changes in its static and electronic characteristics.
The effect of temperature on the magnitude of the rotatory power of an optically active substance is frequently as critical as the effects of solvents and concentration. Since chemical as well as physical influences may be involved in the reversible effects on a complex system prepared from a microcrystalline and hydrated material, changes in the type of dispersion exhibited may occur with change of temperature, apart from variations in rotatory power. An increase in temperature will increase the mobility of molecules in a liquid or gas, and may easily alter the effects of solvation, or the orientation of polar molecules. Furthermore, thermal expansion acts as a form of dilution, and this may alter their initial influence. Additionally, the temperature of the solvent itself will affect the rate of rotation in some cases.

In open chain compounds, a rise in temperature will result in an increase in free rotation about the bonds, which will result in reduced rotatory power (34). Conversely, molecular asymmetry attributable to ring structures, where relative movement between atoms is severely restricted, will not show the same sensitivity to temperature changes.

Since optical rotatory power depends on electronic perturbations, changes of temperature, by altering the energy levels of the molecule, may produce considerable changes in rotatory power (i.e. vibrational levels corresponding to a given electronic "jump" may be modified). The molten quantum - mechanical treatment of optical rotatory power shows, in fact, that the rotatory power of a molecule is very sensitive to changes in its atomic and electronic orientations, a point at 340, but with restrictions peculiar to low - a shorter period one studied.
III. PREPARATIVE WORK AND DISCUSSION

The preparation of 2 mercaptoacetophenone was covered by Dyer and Sharp (32) in 1938.

III. PREPARATIVE WORK AND DISCUSSION

Two methods of preparation have been tried, reaction of
2 iodide with acetyl chloride, and reaction of 2 mercaptoacetophenone
with a Grignard reagent prepared from 2 iodide and
acetyl chloride. In the preparation of the Grignard reagent
for the reaction of 2 acetylchloride,

(1) Preparation of 2,2 diacylthiothiophene.

(a) The method of Kirmse (33); 2 diacylthiothiophene being obtained.

\[ 2 \text{C}_6\text{H}_5\text{I} + 2 \text{I}_2 + \text{H}_2\text{O} \rightarrow 2 \text{C}_6\text{H}_5\text{I}_2 + \text{H}_2\text{I} + \text{H}_2\text{O} \]

The product reacted satisfactorily with magnesium in ether. On
addition of acetyl chloride to this Grignard reagent, the customary solid
complex resulted. Only a 2% yield of 2 diacylthiothiophene was
obtained on decomposition of this complex with ice and ammonium chloride,
and the thiothiophene was used with by-products of similar boiling-range, but
appreciably higher refractive index.

This method was therefore not pursued; it is interesting to
note that Backman and Lowell in a recent paper (33) report a yield of only
27% of 2 diacylthiothiophene by the Grignard reaction.

(b) Preparation of 2 acetylchloride.

Dyer and Sharp (37) obtained yields of 65-69% of
2 acetylchloride by the Friedel-Crafts method, from thiophene and
acetyl chloride. In the present work the method gave a yield of 52%,
but with troublesome quantities of tar. A clearer product was obtained.
by the use of stannic chloride, in place of aluminum chloride, as the
condensing agent, as reported by Johnson and Mey (53), when yields as
high as 30% were readily obtained.

Recently, a series of papers by Hartough and Knack (39) on the
condensation of thiophene and furan, has introduced a rapid and convenient
method for the preparation of 2 acetylthiophene, by the condensation of
thiophene and acetic anhydride in the presence of small amounts of
iodine, or other catalysts. The original method, using thiophene and
acetic anhydride, with a small quantity of iodine as catalyst, has been
41. Reported by E. L. Knack (32), 1940. The yield in this method
explored, a yield of 75% of 2 acetylthiophene being obtained.

Reduction of 2 acetylthiophene to 2 thiaryl methylcarbinol was
first reported by Emsley and Corn (40), who employed the Reissert-Semmler
method. A later paper by Hassani and Rylock (41) reported an
improvement in yield. In the present work even higher yields have been
obtained, and comparison of results is summarized in Table 1.

The attempt to obtain larger amounts of ketone (2 and 6 hours)
was disappointing, but the product from the reduction conducted for
6 hours had a low and extraction index corresponding to those for
41. (44) (in benzene) were given by Emsley and Corn. These authors
report the formation of dioxane in large amounts by heating
2 acetylthiophene in aluminum hypophosphite solution for 6 hours or more.
It was also notable that other acids, e.g., sulfuric, do not introduce
function of a modified type in the 2 acetylthiophene, as was for the
two yield of ketone isolated from the larger reaction.
### Table 1

Reduction of 2 acetylthiophene with aluminium isopropoxide

<table>
<thead>
<tr>
<th>No.</th>
<th>Author</th>
<th>Wt. of ketone</th>
<th>Time</th>
<th>Field of Carbinol</th>
<th>Other Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rahn and Barn</td>
<td>23 g</td>
<td>3 hrs</td>
<td>47%</td>
<td>2 thiolethyl isopropyl ether</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>dl (2\alpha'2' thiolethyl) other</td>
</tr>
<tr>
<td>2</td>
<td>Rahn and Bullock</td>
<td>70 g</td>
<td>6 hrs</td>
<td>63%</td>
<td>10% low b.p. material</td>
</tr>
<tr>
<td>3</td>
<td>Present Work</td>
<td>23 g</td>
<td>1.5 hrs</td>
<td>63%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>23 g</td>
<td>25 mins</td>
<td>70%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>50 g</td>
<td>6 hrs</td>
<td>0</td>
<td>dl (\alpha'2' thiolethyl) other</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>50 g</td>
<td>2.5 hrs</td>
<td>15%</td>
<td></td>
</tr>
</tbody>
</table>

The attempts to reduce larger amounts of ketone (5 and 6 above) were disappointing, but the product from the reduction conducted for 6 hours had a b.p. and refractive index corresponding to those for dl (\alpha'2' thiolethyl) ether given by Rahn and Barn. These authors report the formation of ethers in "large amounts" by heating 2 acetyltorphene in aluminium isopropoxide solution for 4 hours or more.

It then seems probable that other formation, subsequent to intermediate formation of a carbinol complex during the s-reduction, accounts for the low yield of carbinol isolated from the larger batches.
Palm and Dem (43) reported the characterization of their product (2-thiophenethyl carbinol) by the preparation of its phenyl ether. Attempts to prepare this derivative, however, have failed. Berry, Dornill and Hous (44) have failed to obtain the phenyl ether, or any other solid derivative of 2-thiophenethyl carbinol.

(iii) Resolution of 1,2-thiophenethyl carbinol

(1) 2-Thiophenethyl carbinol can be converted to its hydrogen phthalate ester in 75% yield by reaction with phthalic anhydride in pyridine solution. The structurally related 2-phenoxyethyl (45) and 2-phenylmethyl (44) carbinols give hydrogen phthalate esters in yields of 65% and 85%, respectively.

2-Thiophenethyl carbinyl hydrogen phthalate combined readily with halogen in hot acetone or ethyl acetate, and a salt crystallized on cooling. Four recrystallizations of this salt from ethyl acetate yielded a salt which gave optically pure (−) hydrogen phthalate on decomposition. The rotatory power of this 1,2-thiophenethyl carbinyl hydrogen phthalate was unchanged after recrystallization from carbon disulfide, and thus had the maximum rotatory power obtainable by this method: 

$$(1 + 2)$$ hydrogen phthalate ester, obtained from partially resolved optically active 2-thiophenethyl carbinol, can be separated into pure 1- and 2-esters by recrystallization from carbon disulfide.

(12) Since we have been unable to get pure (−) 2-thiophenethyl carbinyl hydrogen phthalate was hydrolyzed with aqueous sodium hydroxide solution, the resultant (−)

2 thiophenethyl carbinol was found to have undergone partial racemization on the action of sodium, and the optical rotation of this alcohol (17%). Even under the most favorable experimental conditions, nearly 50% being liberated either in an ether solvent or in a solution
hydrolysis of the hydrogen phthalic ester in alcoholic potassium hydroxide solution, a little racemisation took place: recrystallisation of the carbinol to its hydrogen phthalate gave an ester with a rotary power only 37% of that of the ester from which the carbinol had been obtained. Recrystallisation recrystallised bromine by two solutions. 23

Rotary powers of (-) 2-thiophenylcarbaryl hydrogen phthalate in solution are given in Table 12 and rotary powers of
(-) 2-thiophenyl carbinol (obtained by hydrolysis of this ester with alcoholic potassium hydroxide) are given in Table 13. Corresponding data for solutions of (-) 2-thiophenyl carbinol in various solvents in mmole. 23 However, the carbinol boiling at 101° is separable of

Decomposition of the more soluble portion of the bromine salt
of 2-thiophenylcarbaryl hydrogen phthalate gave a 1,3,4-ester, which did not give a crystallisable alkaloid salt. Recrystallisation of this ester from carbon disulphide failed to separate the 1- and 3-esters completely, the rotary power of the 1-ester rising to only 67% of that of the 1,3-2-thiophenylcarbaryl hydrogen phthalate obtained from the less soluble bromine salt.

(iv) Alkyl-oxygen fission in 2-thiophenylcarbaryl hydrogen phthalate

Certain reactions of carbon disulphides involving two alternative modes of bond fission, to which the terms alkyl-oxygen (I) and alkyl-oxygen (II) fission have been applied by Day and Engld (43)

I $R'COOR'' \rightarrow R'COO^- + R''^+$
II $R'COOR'' \rightarrow R'COO^+ + R''^-$

These two modes of fission result in the alkyl group R of the ester $R'COOR''$ being liberated either in an alkyl anion or as a carbamion.

23
Allyl-oxygen fission is the common mode of reaction, notably
in base-catalyzed ester hydrolysis (see Watson (16)). Recent papers
from this laboratory (47) have shown, however, that the alternative
process of allyl-oxygen fission occurs more frequently than had hitherto
been realized, the phenomenon being demonstrated by two criteria. If,
in the hydrolysis of an ester RCOOR', the group R is directly attached
to oxygen by an asymmetric carbon atom, and the ester is optically active,
fission of the 3-0 bond would result in the formation of a carbocation,
which assumes a planar configuration, so that the resultant alcohol ROH
is racemic. Furthermore, if the carbocation R' is capable of
mesomeric rearrangement, a mixture of isomeric alcohols results.

Belfe, Boyan et al (47) reported racemizable facility of allyl-oxygen
fission in derivatives of p-nitrophenylglycol. Two new reactions, the
formation of a racemic sulphide from active carbonyl sodium phthalate
and sodium p-toluene sulphonate in aqueous solution, and the separation
of carbonyl neutral phthalic ester from an aqueous solution of active
p-nitrophenylglycol, sodium phthalate were also recorded.

\[
\begin{align*}
\text{COOR'} & \rightarrow \text{COO}^- + R'_+ & \text{the initial fission} \\
R'_+ + \text{Na} \rightarrow \text{SO}_2^- & \rightarrow \text{Na} \rightarrow \text{SO}_2^- R_2, \text{ racemic sulphides} \\
R'_+ & \rightarrow \text{COOR'} & \text{neutral phthalic ester} \\
R_2 & = \text{active and } R'_2 = \text{racemic allyl group.}
\end{align*}
\]

In dilute solution, separation of neutral phthalic esters is
accompanied by deposition of the racemic alcohol R'_2 OH.
\[ \text{Relevant reaction: } R_C^+ + \text{H}_2\text{O} \rightarrow R_C^+ \text{H}_2\text{O} \]

so that the percentage of neutral ester formation will depend on the
concentration of hydrogen phthalic ester anions.

(47) A summary of the general conclusions to be drawn from these
investigations (47) contains the following relevant points.

(a) The observed effects of solvents in promoting cationic
esterification are formic acid > acetic acid > ethyl or
n-butyl alcohol + water > ethylene glycols.

(b) If the tendency of an ester to give ethyl-oxygen fission
This critical is strong, even on hydrolysia under high hydrolytic
concentration, it can only be suppressed by reducing the ionizing power
of the solvent.

(c) Certain electron-releasing power in the thioether ring can
be deduced from the hydrolysis data on 2-Thienylmethylcarbinyl hydrogen
phthalate, which in 1.0% aqueous sodium hydroxide gave an alcohol which
was 17% racemized. To reduce the ionizing power of the hydrolyzing
solution, the aqueous solution was replaced by a solution of potassium
hydroxide in 9% alcohol; even under these conditions, the most likely
conditions to induce ethyl-oxygen fission available, the resulting
2-Thienylmethyl carbinol led a rotatory power 97% of the racemate.

These data are comparable with those for the hydrolysis of
p-Athoxybenzyl hydrogen phthalate (47), in 9% alcoholic alkali,
which gave the carbinol with 60% of the maximum rotatory power. It
seems then that the facility of carbinyl ion formation in
2-Thienylmethyl carbinol is less than in p-Athoxybenzyl.
L-epithylcarbinol shows a slight tendency to give allyl-oxygen fission, and phenylmethyl carbinal exhibits little electron releasing power (47a). Allyl-oxygen fission is known in furylthethyl carbinal (44, 47a), but hydrolysis of the hydrogen phthalic ester in that case with 10% aqueous sodium hydroxide resulted in retention of optical purity in the alcohol. It seems that the series of alcohols exhibiting allyl-oxygen fission (47a) can be extended in that

\[
\text{p-epithylthethylcarbinal} \rightarrow 3 \text{ thiophenylmethylcarbinal} \rightarrow \text{furyl-methyl carbinal} \rightarrow \text{epithylmethyl carbinal} \rightarrow \text{phenylmethyl carbinal}.
\]

This evidence is supported by the ready formation of a monic sulphone by reaction of active 3 thiophenylmethyl carbinal sodium phthalate with sodium p-toluene sulphinate in dilute aqueous sodium hydroxide, and the deposition of neutral phthalic ester from an alkaline solution of the hydrogen phthalic ester alone.

By comparison of the ease of allyl-oxygen fission in 2 thiophenylmethyl and phenylmethyl carbinal, it is evident that the electron releasing tendency in the former must be largely provided by the thioane ring. Furthermore, since the sulphur atom possesses two "lone pairs" of electrons, it is not unreasonable to suppose that they are the source of the electron availability at the allyl-oxygen bond.

A comparison of this with \( \text{CH} = \text{CH} \) a value \( \frac{\text{CH} = \text{CH}}{\text{C} = \text{CH} - \text{Cl}_2} \rightarrow \frac{\text{CH} = \text{CH} - \text{Cl}_3}{\text{C} = \text{CH} - \text{Cl}_3} \) a compound which until recently appeared in the literature as in

\[ \text{Cl}^\circ \]
(v) Rotatory dispersion of (−) 3-thienylcarbinol

The optical rotatory dispersion of (−) 3-thienylcarbinol has been examined in the visible spectrum over the range of wavelengths 4330-6162 Å (Fig. 1) and shows little change over the range of temperature from 20° to 25°; the specific rotatory power only is in decreasing from $[\alpha]_{D}^{20} = 23.9$ to $[\alpha]_{D}^{542} = 23.3$ (Table 13, p. 65).

A comparison with the corresponding (structurally similar) phenylcarbinol and furylcarbinol carbinals is given in Table 2.

<table>
<thead>
<tr>
<th>Carbinal</th>
<th>$[\alpha]_{D}^{20}$</th>
<th>$[\alpha]_{D}^{542}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(−) 3-thienylcarbinol</td>
<td>−23.9</td>
<td>1.74</td>
</tr>
<tr>
<td>(−) 3-furylcarbinol (α)</td>
<td>−23.3</td>
<td>1.79</td>
</tr>
<tr>
<td>(−) phenylcarbinol (α)</td>
<td>−23.5</td>
<td>1.73</td>
</tr>
</tbody>
</table>

The reciprocal of the rotatory power of homogeneous (−) 3-thienylcarbinol at different wavelengths are plotted graphically against $\lambda^2$ in Fig. II. The resultant points lie nearly on a straight line, deviation of individual points appearing to be random. The dispersion in the visible spectrum is therefore simple.

Extrapolation of this graph to give a value of $\lambda_0$, corresponding with the reciprocal of the characteristic absorption wavelength of a single turn Drude equation, which would accurately represent the dispersion data in the visible spectrum, gives a value of 2702 Å.
The ultraviolet absorption of 2 thiophenyl carbinal in mixed solvents as solvent (measured by Dr. J.L. Barrow) shows a strong absorption band with a "peak" (i.e., max) at 233\(\mu\) (Fig. XII). This corresponds to the 233\(\mu\) band of the thiophene ring (Bawle (48)), and the intensity of the absorption at this wavelength is approximately twice as great in 2 thiophenyl carbinal as in thiophene, but without any significant displacement of max. The absorption spectrum of 2 thiophenyl carbinal also shows a weak absorption at 275\(\mu\), represented by an inclination on the graph (Fig. III). Allowing for the discrepancy \(\lambda_o - \lambda_{\text{max}} = 10\)\(\mu\) (see p.13) frequently observed between \(\lambda_{\text{max}}\) determined experimentally, and \(\lambda_o\) calculated from a Drude equation which accurately represents observed rotatory dispersion data, the discrepancy between \(\lambda_o = 217\)\(\mu\) and \(\lambda_{\text{max}} = 233\)\(\mu\) becomes even greater than the apparent 17\(\mu\) difference.

The 275\(\mu\) weak band is so far removed from \(\lambda_o\) that it obviously does not correspond.

If, in spite of the simple dispersion in the visible region, the dispersion over the whole wavelength scale is, in fact, complex, the above discrepancy is readily explained. A two-term Drude expression of the type

\[
\chi = \frac{1}{\lambda^2 - \lambda_1^2} + \frac{1}{\lambda^2 - \lambda_2^2}
\]

would result in rotatory power that would appear simple in the visible region, but would give \(\lambda_o\) values between \(\lambda_1\) and \(\lambda_2\) (i.e., \(\lambda_1 > \lambda_o > \lambda_2\))

even (Table 2) for the rotatory dispersion, and may be due to solvent effects, but the values of \(10\) for water should indicate another factor.

Please refer to Table 2 for the rotatory activity of the dispersion. The vis-irradiating
and could only be revealed by measurements of rotatory power in the ultraviolet region in the neighborhood of \( \lambda_1 \), when the contribution of the \( \Pi \lambda_2 \) term would be predominant (see p.13).

Investigation of the rotatory powers of \((-\) 2 thienylmethyl carbinal at room temperature in benzene, carbon disulfide, ethyl alcohol and di-ethyl ether (Table 14, Fig. VII) shows variations in dispersive power which are inconsistent with simple dispersion, and variations in \( \kappa_{444} \) from \(-21^\circ\) in ethyl alcohol to \(-45^\circ\) in carbon disulfide.

**Table 15**

Variations in the rotatory power of \((-\) 2 thienylmethyl carbinal in various solvents at room temperature.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole Moment</th>
<th>( \kappa_{444} )</th>
<th>( \kappa_{444}/\kappa_{544} )</th>
<th>( \lambda_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl alcohol</td>
<td>1.74</td>
<td>(-21.4^\circ)</td>
<td>1.65</td>
<td>10901</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>(-27.5^\circ)</td>
<td>1.69</td>
<td>10384</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>1.23</td>
<td>(-27.5^\circ)</td>
<td>1.69</td>
<td>10384</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0</td>
<td>(-42^\circ)</td>
<td>1.63</td>
<td>3932</td>
</tr>
</tbody>
</table>

* obtained from graph of \( \lambda_0 \) against \( \lambda^2 \) (Fig. V).

Graphical analysis of the dispersion data for all four solvents resulted in a straight-line relationship between \( \lambda_0 \) and \( \lambda^2 \) (Fig. V), with no visible regularity in small discrepancies. The difference in the dispersion ratios recorded for ethyl alcohol and benzene or diethyl ether (Table 15) are not necessarily significant, and may be due to solvent effects, but the value of 1.63 for carbon disulfide solution reveals the pseudo-simplicity of the dispersion. The side variation
in the value of $\lambda_0$, obtained for single-term Drude expressions by extrapolation of the $k = \lambda^2$ graphs, are obviously due to the effects of solvent molecules on the native excited molecules. They may be interpreted as indicating that the controlling active absorption bands giving rise to the dispersion constants of a two-term Drude equation, and of which the $\lambda_0$ of a single-term expression represents a weighted mean, would be found on either side of the range 1600-2500 Å (see Table 3). The red bands at wavelengths greater than 3100 Å are revealed by experiment, namely the strong band at 2570 Å, and the weak one represented by the inflection in the absorption curve at 2750 Å. Either, neither, or both may be "optically active". The 2750 Å band would seem to be the more probable contributor to rotatory power in view of (i) the closeness of $\lambda_0$ for carbon disulfide to the 2570 Å band and (ii) the relative "strength" of the 2570 Å band, which would indicate a small anisotropy factor, if active, and hence a small contribution to the total rotatory power of the molecule. This also is indicated by the type of dihydrogenation reaction. According to Branda (42) thiophene exhibits no unusual absorption region in the near ultraviolet. The hydroxyl group of alcohols is known to have two absorption bands in the Schumann region, represented by $\lambda_{max}$ at 1090 Å and at 1530 Å. Leven and Poelman (6) have concluded that in secondary alcohols the 1090 Å band is inactive, and also show that the dispersions of methyl isopropyl carbonyl and phenyl isopropyl carbonyl are represented by two-term Drude expressions containing the dispersion constant $\lambda_2 = 2500$ Å, which gives a $\lambda_0$ value of 2750 Å, but since the 3100 Å band appears to be inactive,
The electronic transitions which will provide the greatest rotatory contribution in my given molecule will be those which require the least energy to effect, and it is well known that valency electrons are more tightly held than non-binding electrons. Thus the hydrogen molecule requires about 2 volts more for its ionisation than the real hydrogen atom. The odd electron of a thiophene ring and similar derivatives (which see, Lowy and Baldwin (40) considered that the optical rotatory contribution of the carbonyl group in aldihydes and ketones is attributable to the non-binding (lone-pair) electrons of the oxygen atom, and that in minos the rotatory power is associated with the lone pairs of electrons of the nitrogen atom. The whole group is symmetrical, and can only become anisotropic by vicinal action on the lone-pair electrons. The sulphur atom of the thiophene ring has lone-pair electrons, which might easily become anisotropic in the electric force field due to the vicinal action of the rest of the molecule. That they are relatively loosely held by the sulphur atom is indicated by the ease of allyl-oxygen fission shown by derivatives of 2-thiophenethyl carbinal (see p.16) and it seems therefore that induced anisotropy in these lone-pair electrons is not unlikely. This would account for the anisotropy of the carbinal. Lawson and Botham, studying the vicinal effect of the phenyl group in a series of related carbinals, conclude that the partial rotation of the phenyl group, rather than that of the hydroxyl group, determines the rotation of the carbinal in the visible region. Furthermore the rotatory dispersion of phenylacetyl carbinal gives a value of 2070°, but since the 2600 displacement appears to be inactive, of, say, the lone-pair electron electron in a thiophenethyl carbinal,
this must mean that the pseudo-single dispersion in the visible is controlled by a two-term equation, the terms being of opposite sign, and $k_1 > k_2$. The $\lambda^0$ value obtained for a single term in the visible is then greater than either of the real absorption wavelengths (see p. -10). Since the observed rotatory power of phenyl-methyl cardinal is almost double that of 2 thienylmethyl or 2-furylmethyl cardinals (which are of the same order of magnitude - Table II p. 27) the contribution of the phenyl group to the total rotatory power, due to anisotropy, must be appreciably greater than that of either the thienyl or furyl rings. Indeed the polarizability of the phenyl group ($\lambda_{max} 2,000$) is greater than that of the thienyl group ($\lambda_{max} 2,300$) or furyl group ($\lambda_{max} 2,400$) and would give rise to a greater induced anisotropy under the influence of vicinal forces.

The variations in rotatory power shown by 2 thienylmethyl cardinals in solution in various solvents bear some relation to the dipole moment of the solvent, as proposed by Nite et al. (3), and it may be that the polar solvents such as ethyl alcohol, tend to associate with the anisotropic dipole lone pairs, and lower the rotoary contribution of the group (see p. 17). This would account for the magnitudes of the rotatory powers in ethyl alcohol and diethyl ether, but does not account for the relatively small rotatory power shown in benzene (Table 5). This general consideration is in accord with the known fact that the majority of changes in rotation produced by a solvent are brought about by the effect of the solvent on the absorption bands nearest to the visible region of the spectrum. Thus a reduction in the contribution of, say, the lone pair dipole electrons in 2 thienylmethyl cardinal,
caused by a polar solvent, would weight the value of $\lambda_0$ obtained from readings in the visible in favour of the high frequency dispersion constant $\lambda_2$ of the single-term Drude expression. This is found to be the case, the value of $\lambda_0$ for the homogenous carbinal being shifted by 570° into the Schumann region on dissolution in ethyl alcohol.

It may be, then, that the rotary dispersion of 2 thiophenemethyl carbinal is complex, and should be represented by a Drude type expression containing at least two terms, of the same sign, and having dispersion constants corresponding to absorption regions at about 2,500° and 1,500°. The former of these might be either the 2340° or 2750° band found experimentally in the absorption characteristics of the carbinal, and attributable to the -SO₂- chromophore in the thiophene ring. The 2750° band seems the more probable rotary contributor, and the shorter wave band (1500°) probably corresponds to the second absorption region of the -CH group, this being known to contribute to the rotary power of other secondary alcohols.

(74) Rotary dispersion of (-) 2 thiophenemethyl carbinal hydrogen phthalate

The rotary power of (-) 2 thiophenemethyl carbinal hydrogen phthalate in solution in benzene and carbon disulfide are recorded in Table II (Fig. VII), and are greater in carbon disulfide solution. Both solutions show a dispersion ratio $\lambda_0/\lambda_1$ of 1.8. A graphical plot of $\lambda/\lambda^2$ against $\lambda^2$ (Fig. VII) again gives straight line relationship. Extrapolation of the lines gives $\lambda_0$ values of 2380° for the solution in benzene, and 2750° for the solution in carbon disulfide. This variation in the values of $\lambda_0$ obtained for single-term Drude expressions, both solvents being non-polar (although both
have a high polarizability) may mean that the dispersion over the whole wavelength range is complex. Kenyon and Platt (3) have pointed out

"The effect of the solvent on the rotational dispersion may also be

Evidence for the existence of the chromophore, and its use in elucidating the

Estimation of the õ CC group of 2 thiophenyl carbonyl

with phenyl acetic acid affects the absorption spectrum by introducing a

flattening of the curve of the bands in the region of the "phenyl" band at 2100 õ. Layton and Brittan (2) in their analysis of

the dispersion curves of phenyl carbonylic acids of the type

\[ \text{C} = \text{O} \]

conclude that the 2,600 õ band is inactive, but point out that in

phenylacetic acid the benzene ring is in a single plane.

It furnishes the major contribution to the rotatory power, so that

If the rotatory dispersion of 2 thiophenyl carbonyl hydrogen

phthalate is controlled by a two-term Drude expression of the type

[\text{C} = \text{O}]

suggested for the parent carbonyl (p.33) it seems likely that the rotatory

contribution of the thiophenyl carbonyl will be retained. If the phenyl

group introduced in the ester acquires an induced anisotropy, so that the

dispersion over the whole wavelength range is complex, the resultant dispersion will be controlled

almost exclusively by a dispersion constant representing the mean of the

"thiophenyl" (2100 õ) and "phenyl" (2030 õ) bands. Contributions due to the
fixed geometry of the molecule, and represented by absorption bands in
the 3,000 band attributable to the —CO group of the carbinal having been
removed by esterification. If the thiophenyl and phenyl chromophores
provide contributions of the same sign, dominance by the 2,000-3,000
absorption region will be even more pronounced, resulting in single
dispersion. Furthermore, under these conditions, the rotary power of
the ester would be of the same sign as that of the carbinal, but greater
in magnitude (see Table 4).

Table 4

<table>
<thead>
<tr>
<th>Substance</th>
<th>Benzene</th>
<th>Carbon Disulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>[α]D 546L (–) 2 thiophenyl methyl carbinal</td>
<td>–27°</td>
<td>–43°</td>
</tr>
<tr>
<td>[α]D 546L (–) hydrogen phthalate</td>
<td>–70°</td>
<td>–90° (8.5 M)</td>
</tr>
</tbody>
</table>

(1) Precaution and Production

Ludinbore, in his classical synthesis of Gemin, in 1928, prepared \( \alpha \)-\( \alpha \)-piconylmethyl carbinal in poor yield by heating \( \alpha \)-picoline,
pyridine, and water under pressure. Many attempts to improve this
combination have been made but Hess et al (90) in 1927, reported that
a yield of more than 3.5% could not be surpassed by this method.

Similarly, (51), reviewing the reactions of α-picoline, points out that in
the presence of e.g. n-butyl chloride, condensation of the α-methyl group
with aldehydes results in an ethylene derivative, chloral, however, gives
the intermediate hydroxy body corresponding to α-picolylmethyl carbinal.
A highly satisfactory preparative method for α-picolylmethyl carbinal was
reported in 1943 by Welter, Hunt and Forbinder (52) employing the Cuignard
type reaction between the lithium derivative of α-picoline and acetaldehyde
\[
\begin{align*}
\text{CH}_3\text{CH} + \text{CH}_3\text{CHO} &\rightarrow \text{CH}_3\text{CH} (\equiv \text{CH}) \text{CH}_3 \\
\text{CH}_3\text{CH}(\equiv \text{CH}) \text{CH}_3 &\rightarrow \text{CH}_3\text{CH}(\equiv \text{CH})\text{CH}_3
\end{align*}
\]

This reaction has been employed in the preparation of α-α-picolylmethyl
carbinal, and has given overall yields of purified product of 43%.
Attempts to resolve this α-α-alcohol directly by condensation of the
pyridyl nitrogen with a variety of optically active acids were
unsuccessful, no crystallizable derivatives being obtained.

α-α-Picolylmethyl carbinal easily forms readily with phthalic
anhydride in acetone solution, without the addition of pyridine. The
hydrogen phthalic ester separates as a white crystalline mass; it is not
soluble in common organic solvents, or in cold water, but dissolves
readily in hot water and aqueous acids or alkalis. Its salt-like
characteristics suggest that it exists as a zwitterion
while its insolubility in cold water is probably due to resistance
of the ester to wetting by the water. (A solution in hot water does
not crystallize on cooling).

A suspension of $\alpha$-picolyloxyethyl carbaryl hydrogen phthlate
in hot acetone reacted readily with one equivalent of brucine, a clear
solution being obtained, from which crystalline brucine ($\alpha$) $\alpha$-picolyloxy-
ethyl carbaryl hydrogen phthlate separated on cooling. This salt,
after one recrystallisation from ethyl acetate, had attained its maximum
mass and possessed of the acetate with a small amount of solvated water or
rotatory power and melting point.

Decomposition of the brucine salt with hydrochloric acid in
aqueous-acetone, followed by precipitation of the optically active
hydrogen phthalic ester on dilution of the acetone liquor with ice, was
not applicable in this case, $\alpha$-picolyloxyethyl carbaryl hydrogen phthlate
being soluble in water, acid or alkali. Sprung and Wallis (53) in the
preparation of optically active sec. butyl alcohol, heated the optically
pure brucine salt of the carbaryl hydrogen phthlate with aqeous sodium
hydroxide, and removed the resulting optically active alcohol by
distillation in a current of steam. Application of this method to the
brucine salt of $\alpha$-picolyloxyethyl carbaryl hydrogen phthlate was found
to require an inordinately large volume of steam for complete removal
of the liberated active ($\alpha$) $\alpha$-picolyloxyethyl carbaryl, which is
appreciably soluble in water, and had to be "saled-out" of the large
volume of aqueous distillate obtained. By heating the brucine salt with
$aq$ saline sodium hydroxide and extracting the resulting slurry with
ether, ($\alpha$) $\alpha$-picolyloxyethyl carbaryl of sodium rotatory power was
obtained. There is no evidence of allyl-oxygen fission, with attendant racemisation, during the hydrolysis of \( \alpha \)-picoxyethyl carbimol ethers of derivatives. The chance that gives the principal racemisation result in

The more soluble portion of the original bromo salt was obtained as a gel on evaporating the solvent. This gel, on decomposition as above, gave \((1, 2, 3) \alpha \)-picoxyethyl carbimol, with a rotatory power corresponding to 70% of that of the fully-active \((+) \alpha \)-picoxyethyl carbimol. Recrystallisation of this alcohol to \((1, 2, 3) \) hydrogen phthalate ester and combination of this ester with a variety of alkaloids failed to yield a crystallisable derivative, and further attempts to obtain the levorotary were abandoned. 

(ii) Optical rotatory dispersion of \((+) \alpha \)-picoxyethyl carbimol.

The optical rotatory power of homogenous \((+) \alpha \)-picoxyethyl carbimol has been examined in the visible spectrum over the range of wavelengths 430-640A (Table 18, Fig. VIII). The specific rotatory power decreases from \( [\lambda]_{D} = +69^\circ \) at 20°C to \( [\lambda]_{D} = +44^\circ \) at 50°C, the variation with temperature proceeding regularly, and providing a satisfactory graph for each temperature (Fig. VIII) or (b) vs \( \lambda \) for each wavelength (Fig. IX).

A graphical plot of the reciprocals of the rotations (\( 1/\lambda \)) against the square of the wavelength (\( \lambda^2 \)) for data at 20°C (Fig. X) gives a straight line relationship, no systematic deviations being apparent, so that the rotatory dispersion in the visible spectrum may be described as normal and simple. Extrapolation of the \( 1/\lambda \) against \( \lambda^2 \) graph gives a
value (corresponding to the controlling absorption frequency of a single-term Drude equation) of 2,500. BRANDIS (48) in his review of the ultraviolet absorption data, gives two principal absorbing regions in the near ultraviolet for the pyridine ring, namely at 2,500 and 1950.

\( \alpha \)-picolylmethyl carbinal is not soluble in saturated hydrocarbons, but its absorption spectrum in ethyl alcohol (determined by Dr. G. E. Heaven, Fig. XI) shows an absorption region with a principal maximum at 2,000 and an (probably strong) band below 2100. Comparable absorption data for benzene, pyridine and \( \alpha \)-picolylnethyl carbinal are given in Table 5.

Table 5

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \lambda ) max</th>
<th>( \epsilon ) max</th>
<th>( \lambda ) max</th>
<th>( \epsilon ) max</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene (48)</td>
<td>1950</td>
<td>8,000</td>
<td>2,500</td>
<td>250</td>
<td>n-hexane</td>
</tr>
<tr>
<td>Pyridine (48)</td>
<td>1950</td>
<td>7,500</td>
<td>2,550</td>
<td>2,000</td>
<td>n-hexane</td>
</tr>
<tr>
<td>( \alpha )-picolylnethyl carbinal</td>
<td>1900</td>
<td>10,000</td>
<td>2,650</td>
<td>3,600</td>
<td>alcohol</td>
</tr>
</tbody>
</table>

The shift of the longwave band in \( \alpha \)-picolylnethyl carbinal and the increase in \( \lambda \) max may be ascribed to the effect of the substituent group (here - CH\(_2\)CH(=H)Me) which upsets the symmetry of the unsubstituted pyridine ring.

On the basis of \( \lambda \) max \(<\lambda \) \(_0\), the regular discrepancy noted by Lowry (see p. 11), it is evident that the dispersion of homogenous picolylnethyl carbinal is not controlled by the 2,000 band if the
dispersion is simple. The calculated value of \( \lambda_0 \), nearly 2,500\( ^\circ \), is, however, too far removed from the <600\( ^\circ \) band for the difference (i.e. 400\( ^\circ \)) to be accounted for by the rise in the general (as distinct from selective) absorption curve. As in the case of 2-thioethyl methyl carbinal (section III) it may be that the dispersion in the visible is pseudo-simple, a two-term equation being required to fit dispersion data for the whole wavelength range. Thus, if the dispersion were controlled by two bands having opposite contributions, and both being in the Schumann region, \( \lambda_0 \) calculated from the resulting pseudo-simple data in the visible would give a value of \( \lambda_0 > \lambda_1 > \lambda_2 \). In the extreme case \( \lambda_0 - \lambda_1 \) might be as much as 1300\( ^\circ \) (Levane and Rother (3)). If the dispersion, on the other hand, is controlled by a two-term dispersion equation having both contributions of the same sign, then the condition \( \lambda_1 > \lambda_0 > \lambda_2 \) would hold, and would imply that the ca 2900\( ^\circ \) band must be active, since it is the only band of longer wavelength than \( \lambda_0 \).

The dispersion of (+)-carbostyril carbinal in the first group of examination of the rotatory dispersion of (+)-carbostyril carbinal in solution in a variety of solvents at room temperature has revealed some very interesting dispersion phenomena. The solutions were examined in the visible region only, from 4500\( ^\circ \) to 6700\( ^\circ \), and the dispersion curves (\( \alpha \) against \( \lambda \)) fall into two main classes, those exhibiting simple dispersion (Fig. XIII) and those exhibiting obviously complex dispersion (Fig. XIII). In order to minimize solute-solute interaction, and yet have accurately readable observed rotations, a column of dilute (3%) solutions of (+)-carbostyril carbinal in the
various solvents were employed. Rotatory powers for these solutions are given in Table 13.

The rotatory dispersions in chloroform, carbon tetrachloride, ethyl acetate, diethyl ether, acetone, benzene and dimethyl formamide were obviously complex, maxima and minima being apparent. Rotatory powers in ethyl alcohol, water, acetic acid and acetonitrile, on the other hand, gave smooth hyperbolic curves (for $\alpha$ against $\lambda$) and straight line relationship between $\lambda$ and $\lambda^2$ (Fig. XIII). Nitromethane and a 3% solution of (+)-picoxyloxymethyl carbinal in benzene, appeared to lie in an intermediate position in the series, the dispersion curves appearing almost simple. The complex nature of the dispersion shown by the carbinal under these conditions is indicated by the dispersion ratios (i.e. $\alpha^{-1}435$/$\alpha^{-1}547$) of the solutions, 1.55 and 1.43 respectively, both below the theoretical minimum of 1.57 for simple dispersion (22). Any here in the ice-water bath approached typical to a $\lambda^2$.

The dispersions of (+)-picoxyloxymethyl carbinal in the first group of solvents above, clearly indicate that under these conditions the dispersions are anomalous and would require a Drude equation which contains the term of opposite sign (see section II (i) in adiabatic solutions (33)) to give the correct dispersion with the correct period. In chlorine, the dispersion is given by $\alpha = \frac{K_2}{\lambda^2 - \lambda_1^2}$, where $K_1 < K_2$ and $\lambda_1 > \lambda_2$. The product in these solvents is ethyl alcohol and plotted against $\lambda^2$ against $\lambda^2$, resulted in a similar line relationship, with very little scatter of individual points, and containing being made (Fig. XIII).
The $\lambda_2$ term will dominate in regions remote from $\lambda_1$ (i.e., at long wavelengths) and impose its sign on the total rotatory power. In the visible region, the sign of rotation of (+)-picolyolmethyl carbinol in all the solvents in which it displays complex and anomalous rotatory dispersion (including that in chloroform at wavelengths greater than 250 microns), the $\lambda_1$ term has a small absorption band providing the dextrorotatory contribution to the total rotatory power is that corresponding to the high frequency term of the two-term Drude expression. Furthermore, on dissolution in certain solvents, particularly L-nitrobenzaldehyde in chloroform; the rotatory dispersion displayed by (+)-picolyolmethyl carbinol becomes apparently simple, but is still dextrorotatory, and the actual magnitude of the rotatory power is greatly increased. Thus it would seem that under these conditions, the unsubstantially large rotatory contribution of the low frequency term $\lambda_2$ is made for those solvents in which it in which it is complex) is insensitive, or at any rate largely reduced.

It should be possible to relate the ultraviolet absorption data recorded by Dr. G.H. Beaver for (+)-picolyolmethyl carbinol in alcoholic solution (Fig. XI) with the rotatory dispersion data in the same solvent, any changes in the characteristic frequencies of chromophoric electrons due to solvent effects being obviously eliminated. Rotatory powers of the carbinol in 3% solution in ethyl alcohol when plotted graphically as $\kappa$ against $\lambda^2$, resulted in a straight line relationship, with very little deviation of individual points, such deviations being made (Fig. XIV).
Extrapolation of this graph gave a value for \( \lambda_0 \) of 2.300, which again cannot be definitely assigned to any "real" absorption band without further evidence. It might correspond to a band at ca. 2200\(^\text{a} \), although this is unlikely, since this band appears to have a large absorption coefficient, and would thus, according to Kuhn (section I) have a small anisotropy factor, and a consequent small direct contribution to rotatory power. It may be, of course, that the rotatory dispersion is in reality controlled by a two-term equation, although appearing simple in the visible. In this case the \( \lambda_0 \) might be related to the two characteristic frequencies \( \lambda_1 \) and \( \lambda_2 \) of the two-term expression by either of the ratios \( \lambda_0 > \lambda_1 > \lambda_2 \) or \( \lambda_1 > \lambda_0 > \lambda_2 \) depending on the relative signs of the two partial contributions; the latter relationship, corresponding to two-terms of the same sign, would again imply that the 2.300\(^\text{a} \) band must be active. A comparison between the \( \lambda_0 \) values obtained by extrapolation of the straight-line \( \lambda^2 = \lambda_0^2 \) graphs for those solvents which give apparently simple dispersion in the visible region is given in Table 6.

### Table 6

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \lambda_{4350} / \lambda_{5461} )</th>
<th>( \lambda_0 (\AA) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.61</td>
<td>2.300</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>1.71</td>
<td>2.300</td>
</tr>
<tr>
<td>Water</td>
<td>1.61</td>
<td>2.300</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1.70</td>
<td>2.100</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>1.0</td>
<td>0</td>
</tr>
</tbody>
</table>
From the \( \lambda_0 \) value obtained for \( (+) \alpha \text{picolyisethyl carbinal} \) in carbon disulphide solution, it can be deduced that this solvent in reality does not belong to the "complex" class, since the zero value for \( \lambda_0 \) can only result from the relationship \( \lambda_0 < \lambda_2 < \lambda_1 \), which corresponds to the two-term equation of type (iv) (see p. 14) already shown to be required for those solvents exhibiting obvious anomaly in the visible.

Graphs of \( \frac{1}{\lambda} \) against \( \lambda^2 \) for these "complex" solvents are given in Fig. XIV.

The variation in \( \lambda_0 \) for hydrochloric acid and water as solvents can be accounted for by displacement of the "active-bands" by solvent effects, but the objection still holds that the ca \( 2100 \) bend found in the absorption characteristics appears to be a given bend, and it is thus unlikely to have a large direct rotatory contribution.

(111) Solvent Effects

No relationship between rotatory power and the dipole moment of the solvent is shown by comparison of the experimental data recorded for \( \alpha \) solutions of \( (+) \alpha \text{picolyisethyl carbinal} \), and it seems that Hildebrand's general conclusion that \( \alpha = f \left( \frac{\mu}{\lambda_2} \right) \), where \( \mu \) is dipole moment of the solvent, is not applicable to this case. Furthermore, the unwavelengtth corresponding to \( [\alpha]_{\text{max}} \) for those solvents exhibiting anomalous "bend" dispersion can be seen to fall within the range 4,000-5,000 \( \AA \) (Fig. XIII) so that it would seem likely that the values of \( \lambda_2 \) and \( \lambda_1 \) are relatively little affected by solvents, changes in \( [\alpha]_{\text{max}} \) being due to variations in \( \lambda_2 \) and \( \lambda_1 \). No systematic relationship exists either between \( [\alpha]_{\text{max}} \) and the refractive index of the solvent.
The α-picolylmethyl carbinal molecules can assume a form in which the hydrogen of the α-Cl group is in close proximity to the α-
chloro carbon atom of the ring formed by hydrogen bonding. This
state of the pyridine ring,
will then be akin to a molecule having the asymmetric center at the α-
position for the two additional α-chloro substituted thiole derivatives.

The symmetry of the two α-chloro substitutions and the
chlorine has been demonstrated by Donald (41) as the existence of
chlorine and it may be that hydrogen bonding between the oxygen of the α-Cl group
and the lone-pair electrons of the ring α-Cl atom is set up. It has
been demonstrated that there is little or no tendency to alkyl-oxygen
fission in the α-picolylmethyl carbinal molecules, and thus the hydrogen
might be expected to tend towards ionization (i.e. as a proton) in the
normal manner for alcohols, which would, of course, facilitate bonding
with the electro-negative centre of the ring nitrogen, resulting in a
second six-membered ring being formed. Experience has shown that ring
formation in the sugar series invariably results in a large increase in
the magnitude of the rotatory power, but in all these cases ring closure
is the result of chemical change, and thus may not be really analogous.

Now if, as a result of hydrogen bonding between the α and N
atoms of the α-picolylmethyl carbinal molecules, certain orientations are
stable, it is possible to conceive pairs of mirror images, giving four
optical isomers; i.e. each isomer due to the asymmetric carbon atom is
capable of two enantiomophic forms, due to orientation of the Clα- and
Clβ-groups about the plane of the pyridine ring. It is most likely,
furthermore, that the four forms will not be equally probable, so that...
the result will be, in effect, two optical isomers (due to the asymmetric configuration of the two asymmetric centres) but each will have a second plane of symmetry due to the hydrogen bonding. Each of the two isomers will leave the molecule in active form to contribute power will then be due to a molecule having two asymmetric centres; this will show to what extent production, equal with that due to the usual method, account for the two contributions of the required Brdru equation.

In the optical isomeric disperison of (e) is not proportional. The complexity of the dispersion of tartaric acid and its esters has been attributed by Austen (54) to the existence of different ketonic forms of the hydrated ester with the possible minimum chance of maximum stability, and possessing different rotatory values. Since in a solution of tartaric acid, it is possible that dispersive powers, a necessary postulate in this case, since both half molecules are structurally identical. Lowry and Cutter (55) proved that the different forms, necessary to account for the isomeric forms of hydrogen bonding, might be attributable to the two possibilities bonding with both the asymmetric products due to a second hydroxyl group represented by

\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H}_2 & \quad \text{H}_2 \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}

with the possible existence of forms of tartaric acid with chelates present.

The complexity of the disperison in the visible region in the complex disperison in the visible region, as well as in the case of hydrogen bonds (e). (f) is explained to some extent by the strong chelate formation, even if the hydrogen bonding is not significant. The complex disperison would not affect the possibility of these structures, since there are further ways for combinations. There is no evidence that the bridged derivatives show simple dispersion, such as titrations, and addition these will be accounted for combinations of benzylidene tartaric esters.

The new system, benzylidene saccharide group, present (e) and (f). The complex disperison in the visible region by Jones (56), would disrupt the hydrogen bonded rings, giving a molecule in which the two benzylidene group for increasing the e far conclusion to (f).

\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H}_2 & \quad \text{H}_2 \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
If the complex and anomalous dispersion of (+)-picolylyethyl carbinal is due to ring formation by hydrogen bonding of the hydroxyl group with the pyridyl nitrogen atom, solution in an associating solvent, such as water or ethyl alcohol, will preclude ring formation. The formation of the pyridyl nitrogen, or the hydroxyl group, in preference to intramolecular hydrogen bonding, would mean that the postulated contribution due to a second plane of symmetry would not exist. Acetic acid, by salt formation with the pyridyl nitrogen lone-pair electrons will similarly preclude intramolecular hydrogen bonding. In all these cases the dispersion in the visible is, in fact, simple. In the case of homogeneous (+)-picolylyethyl carbinal, this theory would require inter-molecular, rather than intramolecular, association, to account for the simple dispersion exhibited under these conditions. Since, in the homogeneous state, each active alcohol molecule will be surrounded by molecules of the same species, intermolecular association appears not unlikely. The complex and anomalous dispersion displayed by (+)-picolylyethyl carbinal in 2% solution in benzene, where the active solute molecules are relatively far apart, tends towards the simple dispersion of the homogeneous carbinal on increasing the solute concentration to 2%.
(Figs. XIII and XV). Intramolecular hydrogen bonding, with its attendant anomalous dispersion apparently giving way to inter-
molecular association, giving simple (in the visible) dispersion, as
the concentration of solute is increased. A solution in dioxan still
exhibited complex dispersion on being heated to 60°C (Fig. XIX) which
implies that the hydroxyl-nitrogen bond is relatively strong, but is
disrupted in the powerful local field of the highly polar associating
solvents described above. Pauling and Brodsky (87) found that even
in the vapour state, formic acid is disrupted by hydrogen bonding.

\[
\text{OH} 
\xrightarrow{\text{Heating}} \text{H} - \text{O} 
\] 

Isotropification of the hydroxyl group of (\(+\)) p-chlorophenyl carbinol, while complicating the molecule, and introducing new
absorption bands into the spectrum of the compound, may, on the above
grounds, be reasonably expected to result in simple dispersion (at
least in the visible) since it will obviate the postulated hydrogen
bonding, and thus preclude the possibility of the resultant partial
correlation of the optical rotation.

(4v) Optically active carbinols and carbanilates

Examination of the rotational dispersion of the hydrogen
phthalic ester in those solvents in which (\(+\)) p-chlorophenyl carbinol
shows anomalous dispersion was not possible, because of the
insolubility of the compound (see p. 36). (\(+\)) p-Chlorophenyl carbinol
acetate was obtained from the (\(+\)) carbinol on treatment with acetic
anhydride, and its rotational dispersion was examined in 25% solution in
carbon tetrachloride and benzene, in both of which it displayed apparently simple dispersion. Extrapolation of the $\kappa - \lambda^2$ graphs gave $\lambda_0$ values which are shown in Table 7. (Figs. XVII and XVIII). Rotatory powers are given in Tables 29, 31.

### Table 7

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\kappa^{25^\circ}$</th>
<th>$\lambda_0^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.74</td>
<td>2130</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>1.75</td>
<td>2130</td>
</tr>
<tr>
<td>None</td>
<td>1.70</td>
<td>2130</td>
</tr>
</tbody>
</table>

An (+) α picolydimethyl carbinal acetate, readily soluble in the benzene, ethyl alcohol and carbon tetrachloride, was examined in solution in benzene, ethyl alcohol and carbon tetrachloride (Fig. XVII). A graph of $\kappa$ against $\lambda^2$ for these solutions gave straight line relationship (Fig. XVIII). Examination of the dispersion ratios and $\lambda_0$ values for these solutions (Table 8) immediately shows...
that the dispersion cannot be simple... 

Table 8

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \lambda_{250} )</th>
<th>( \lambda_{420} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.50</td>
<td>0</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>1.60</td>
<td>1.63</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>1.50</td>
<td>1.20</td>
</tr>
</tbody>
</table>

In view of the complex structure of the urethane molecule, however, this is hardly surprising.

(+) \( \xi \) picolylylphenyl carbaryl hydrogen phthalate, obtained from the (+) carbaryl in the usual manner, was examined in solution in water, and \( \xi \) hydrochloric acid, and exhibited apparently simple dispersion in both solvents (Figs. XNI and XVIII).

Table 9

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \frac{\lambda_{420}}{\lambda_{250}} )</th>
<th>( \lambda_{o} (\AA) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.00</td>
<td>2000</td>
</tr>
<tr>
<td>( \xi ) Hydrochloric Acid</td>
<td>1.03</td>
<td>2730</td>
</tr>
</tbody>
</table>
On dissolution in 1.01 sodium hydroxide solution, the rotatory power of the sodium phthalic ester immediately started to decrease, but reached a steady value after ca. 7 hrs. (Fig. XIII). Calculation of the rotatory power of an equivalent solution of (+) \( \alpha \)-picolyethyl carbinol in water gave a value of the same order of magnitude, and allowing for the difference in concentration and the difference in solvent (i.e. sodium phthalate in caustic soda in one case, water in the other) it may safely be deduced that hydrolysis of the (+) hydrogen phthalic ester to (+) \( \alpha \)-picolyethyl carbinol, without loss in rotatory power, has occurred.

**Table 10**

<table>
<thead>
<tr>
<th>Description</th>
<th>Method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original concentration of ester</td>
<td>+ 53°</td>
<td>1.05%</td>
</tr>
<tr>
<td>Equivalent ( \alpha )-picolyethyl carbinol of ester</td>
<td>2%</td>
<td>0.94%</td>
</tr>
<tr>
<td>Calco's ( [\alpha] ) for carbinol at time &gt; 7 hrs</td>
<td>+ 67°</td>
<td></td>
</tr>
<tr>
<td>Cherry's ( [\alpha] ) for 7% mol. of carbinol in water</td>
<td>+ 74°</td>
<td></td>
</tr>
</tbody>
</table>

The small variation in specific rotatory power on changing the ester to the alcoholsolutions at similar degrees of the environment of the (+) \( \alpha \)-picolyethyl carbinyl hydrogen phthalate (see Table II) is remarkable in view of the ionic changes produced in the molecule with corresponding rotation of the ester molecules.

---

a. The addition of water with a change of sign on ionisation of the quinone diimides. In all these cases, however, the change was not observed in the diimide, or the quinone compound; the diimide, the
The rotary power of the alkaloid may be increased by placing it in a solvating solvent. This effect is due to the solvent affecting the motion of the alkaloid in solution.

### Table II

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$[\alpha]_D^{197}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>+ 81.5$^\circ$</td>
</tr>
<tr>
<td>5% Acid</td>
<td>+ 82.6$^\circ$</td>
</tr>
<tr>
<td>1.5% Allali</td>
<td>+ 83$^\circ$</td>
</tr>
</tbody>
</table>

This table is obtained by extrapolation of $[\alpha]$ against time curve to zero time (Fig. XX).

In conclusion, it should be noted that, as in the case of the alkaloids, Betti (33), Rule (33) and others have found that in certain compounds, a close relationship exists between the rotary power exhibited and the dipole moment of substituent groups in the molecule. It might be expected that the shifts in ionic charges in a molecule would correspondingly exert a profound effect on its rotary power. Nicotine, for example, exhibits a change of sign on ionisation of the pyrrolidine nitrogen. In all these cases, however, the atom concerned in the ionisation, or the group carrying the dipole, was

### Diagram

[Chemical structure diagram]
directly attached to the asymmetric carbon atom, and it may be, in the
(+ ⇔ picolinylformyl carbinyl hydrogen phthalate molecule, that any
effect on the asymmetric centre of charge in ionic charge distribution,
is damped out by distance. This suggestion, however, is inconsistent
with Lory's view that all the electrons in an asymmetric molecule are
considered, more or less, in the production of rotatory power.

(v) General Conclusions

The complex and anomalous rotatory dispersion exhibited by
(+ ⇔ picolinylcarbinyl in solution in non-associating solvents
may be due to the development of a second asymmetric centre due to
hydrogen bonding between the hydroxyl group and pyridyl nitrogen atom.
This apparently introduces a new partial rotation of opposite sign to
those due to the fundamental asymmetry associated with the asymmetric
carbon atom, and with a characteristic frequency of longer wavelength
than those of the original components.

On dissolution in strongly associating solvents, or in the
homogeneous state, and also on esterification, or salt formation of the
ring nitrogen atom, such intramolecular association is ruptured, with
the consequent removal of the low-frequency contribution to rotatory
power, so that the resultant dispersion appears simple in the visible
spectrum. It is impossible without ultraviolet dispersion data to
allocate the rotatory power to any definite absorption bands, but it
seems not unlikely that the ca. 2000 A band of the modified pyridine ring
is involved, at least under those conditions when the (+ ⇔ picolinyl-
formyl carbinyl is exhibiting complex dispersion requiring a two-term
Drugs expression to express it adequately.

A. Introduction

1. A solution of ether (50 g) and concentrated sulfuric acid (100 ml) and slowly, during and loose
2. to the reaction of another solution with water (30 g) in 10% glacial
3. acid (100 ml). 10% for a few days periods. A total of 1.5 liters of
4. ether mixture was finally washed with water (100 ml) and the
5. ether mixture was distilled with water (100 ml) and the ether fraction collected.

B. Procedure

1. A mixture of 50 g of previously prepared sample intakes (25 g) in 10% acetic acid (50 ml) and ethanalysis with normal solutions
2. at 60°C, during the time. A period of unsaturated ester effective
3. (3 g) (1). 10% sulfuric acid (50 ml) and decomposition of the
4. mixture of ester expels the isomer with 4% propylene mixture of
5. ethanalysis and (50 ml) in 10% acetic acid (50 ml) and ethanalysis,
6. in 10% acetic acid (50 ml) and ethanalysis (3 g) (1).

C. Results of Experiments

1. A mixture of 50 g of ethanalysis effective (5.0 g) and
2. ether (2.0 g) was heated under vacuum for 10 hours (3 h), with next cold
PETUL - EXPERIMENTAL

A mixture of acetylene and ethylene was heated with 20% sodium hydroxide until the solution became solid, and finally with 10% sodium hydroxide.

V. - 2 THIENYLMETHYL CARBENE

2 Thiénylmethyl ketone

b.p. 207-210°C

Yield 50% (calc'd on thiophene)

(a) A solution of thiophene (50 g) and redistilled acetyl chloride (50 g) in light petroleum (100 ml) was added, during one hour, to a suspension of powdered aluminum chloride (50 g) in light petroleum (100 ml); (27) the mixture was vigorously shaken at frequent intervals. After gentle warming for 30 mins, the mixture was allowed to stand overnight; the solid complex which had separated was decomposed with cold dilute hydrochloric acid and the resulting tar extracted with ether. Evaporation of the dried etheral extract yielded 2 thiénylmethyl ketone, b.p. 207-210°C. Yield 22.1 g = 46% (calc'd on thiophene).

(b) A solution of thiophene (43 g) and redistilled acetyl chloride (50 g) in dry benzene (500 ml) was maintained with vigorous stirring, at 0-10°C, during the drywise addition of redistilled stannic chloride (150 g) (29). Reaction proceeded smoothly, and decomposition of the resulting solid complex was effected by the drywise addition of hydrochloric acid (25 ml in 25 ml water). Distillation of the clear benzene layer which separated after the decomposition yielded 2 thiénylmethyl ketone as a mobile pink liquid which darkened on standing, b.p. 207-210°C. Yield 47.2 g = 75% (calc'd on thiophene).

(c) A mixture of thiophene (94 g), acetic anhydride (98.5 g) and indene (1 g) was heated under reflux for one hour (30), and then cold
the mixture was vigorously extracted with water (100 ml). The crude 2-thienylmethy1 ketones layer which separated was washed with 10% sodium carbonate solution until free from acid, and finally with 10% sodium thiosulphate solution. Distillation yielded 2-thienylmethy1 ketones as a pale yellow liquid b.p. 161-165°C/21 mm n^20 p = 1.5200. Yield 07.3 g = 77% (calc'd on thiophene).

Due to a printing error, Bartough and Neale's (33) stated optimum ratio of reagents, a molar excess of thiophene and 3 x 10-3 mols of iodine per mol of acetylide, did not correspond to the quantities cited in their experimental section, which gave weights of reagents corresponding to the initial molar quantities of thiophene and acetic anhydride and only 4 x 10-3 mols of iodine. An experiment based on these weights gave, in fact, a slightly better yield of 2-acetylthiophene than one based on the stated optimum ratio of reagents, and in view of the initial high cost of thiophene and the troublesome recovery of a mol excess was used. Further batches were made on the basis of the proper quantities of thiophene and acetic anhydride, as described above.

**Semicarbazone of 2-thienylmethy1 ketones**

A solution of the ketones (1 g) in alcohol (15 ml) was added to a solution of sodium acetate (1 g) and semicarbazide hydrochloride (1 g) in water (5 ml), and the mixture heated on the steam bath for 15 mins. The semicarbazone crystallized out and was recrystallized from methyl alcohol. Colorless needles m.p. 125-130°C (Steinberg and Jaas (50)) repeated two or three times. The name 2-acetylthiophene acetone (50) give m.p. 120-120°C).

**Ethylene oxide distillation in stilbenes** thiophene from ketones by the end of the reduction period. The reaction of larger batches
of ketone (37 g) and the solution was stirred for a reaction time
2-Thienylacetyl carbinal

(a) 2-Thienylacetyl carbinal was prepared by Norrish-"ene" the
Fornin" reduction of 2 thienylacetyl ketone (40, 41).

Clean dry aluminium turnings (6 g) were added to anhydrous
isopropyl alcohol (25 ml); the reaction was initiated with two or
three crystals of mercuric chloride and the mixture was heated under
rubber until reaction ceased (4-5 hrs). The resulting clear solution
of aluminium isopropoxide was decanted while hot from a slight
residual sludge. 2-Thienylacetyl ketone (22 g) was added to the
aluminium isopropoxide solution and the reaction mixture was slowly
distilled through a short column for about one hour, until 5 drops of
the distillate gave no precipitate within 50 secs. on treatment with
3 ml. of 0.1% aqueous 2:4 dinitrophenylhydrazine hydrochloride
solution. The column was then removed, and the excess isopropyl
alcohol rapidly distilled off. The residue, when cold, was decomposed
with sulphuric acid (25 ml) and ice (200 g) and extracted with ether.
Evaporation of the dried ethereal solution and distillation of the
residue yielded 2 thienylacetyl carbinal as a colourless pleasant
smelling mobile liquid, b.p. 131-132°C/30 mm Hg, D 1.5633.

Yields: Expected reductions of small batches of ketone (20 g) have
given yields of 2 thienylacetyl carbinal varying from 53% for a
reduction time of 1.5 hrs. to 70% for a reduction time of 55 mins.
the isopropyl alcohol distillate in all cases being free from acetone
by the end of the reduction period. The reductions of larger batches

37.99
of ketone (50 g) was unsatisfactory; one, carried for a reduction time of 1.5 hrs., yielding 15% of 3-thiophenylmethyl carbinal, the other, reduced for 6 hrs., yielding no carbinal. The major product from the latter (b.p. 145-147°C/14 mm Hg, 1.5483) was C6 (α<sub>H</sub>, 21° thiophenylth) ether, ethanol soln. (pH 8) a yellowish, a mixture, with

(b) 2-thiophenylmethyl carbinal was also prepared by the addition of acetalddehyde to a Grignard reagent prepared from 2 iodothiophene.

2-Iodothiophene (33 g). A solution of thiophene (53 g) in dry benzene (50 ml) was cooled in ice, and yellow mercuric oxide (75 g) and iodine (100 g) were added alternately in small amounts, with vigorous stirring, keeping the mixture cool. The red mercuric iodide was filtered off and washed with ether; the combined ether-benzene filtrates were washed with 10% sodium thiosulphate solution and acidified. Evaporation of the filtrate on a steam bath yielded 2 iodothiophene, which distilled as a pleasant purple liquid (b.p. 90°C/1.1 mm Hg) and solidified on cooling to a shining pale yellow liquid b.p. 75-76°C/12 mm. Yield 14.4 g = 70%

(c) a new Grignard reaction. The Grignard reagent was prepared by the dry-dry method. The Grignard reagent was prepared with the dry-dry method. The addition of an ethereal solution of 2 iodothiophene (50 g) to flake

and ground dry potassium carbonate (100 g) in benzene (600 ml) and magnesium (6.6 g) covered with ether (100 ml total); reaction was complete. The reaction vessel was cooled thoroughly, and the reaction was initiated with a crystal of iodine, and addition of the 2 iodothiophene

was continued with ether, producing the Grignard (67.2 g) exp. 65-67°C.

was regulated so that the ether was boiling gently under reflux. The reaction was kept sufficiently with the dry-dry method. The Grignard reagent was then cooled to 0°C, and an ethereal solution of freshly distilled acetalddehyde was added dropwise with

vigorously stirring, so as to maintain the temperature of the reaction

and reduce the reaction solution and extracting the solution with

ether, with the ether taken, the impure solution was taken into
mixture at 2-5°C, until decomposition of any temperature rise indicated that reaction was complete. After warming to room temperature, the greenish-black solid complex was decomposed with ice and aqueous ammonium chloride, and the product extracted with ether. Evaporation of the dried ethereal solution yielded 2-thienylmethyl carbinal, which distilled at 87-90°C/20 mm, \( n^0 = 1.5466 \). Yield 11.7 g = 30%.

2-Thienylmethyl carbinal (2 ml) was added to saturated alcoholic mercuric chloride solution (9 ml) and 33% aqueous sodium acetate (9 ml) (40). The solid 5 chloro-2-thiocyano compound \( \left( \text{C}_4 \text{H}_7 \text{OS}_2 \text{CH}_3 \right) \) produced was recrystallised from 95% ethyl alcohol m.p. 150-160°C. (Klin and Lass (40) give m.p. 157°C). Phthalate (1.6 g, m.p. 136°C) in 40% solution was used in this reaction.

2-Thienylmethyl carbinal hydrochloride

A mixture of 2.2-thienylmethyl carbinal (53.6 g), phthalic anhydride (63 g) and dry pyridine (50 ml) was heated at 60-70°C for 6 h, with occasional shaking. After cooling, ethereal ether was added to the mixture, and the mixture was filtered and washed with cold water, and the filtrate was concentrated to a thick syrup, which was heated to 150°C for 5 h. After standing overnight at room temperature, the reaction mixture was diluted with 1.5 volumes acetone and poured onto hydrochloric acid (200 ml) and crushed ice (ca one
cube per millilitre), and the precipitated product collected by suction filtration. The filtrate was evaporated, and the residue was washed with cold water, powdered and dried (57.5 g) m.p. 95-97°C.

The 2-thienylmethyl carbinal hydrochloride was recrystallised from ethanol (200 ml) on rapid titration with 0.1 N NaOH, 0.5937 g required 18.3 ml, corresponding to HCl wt. 321. \( \text{C}_4 \text{H}_7 \text{O}_4 \text{S} \) requires HCl wt. 270.

The crude material (57 g) was purified by dissolving it in cold sodium bicarbonate solution and extracting the solution with ether. The product obtained by initial concentration of the ether solution was then dried under vacuum, and the mixture was run into a 50% solution of sodium carbonate by slow addition.
hydrochloric acid and ice, and when solid, the acid ester was
separated, dried and recrystallised from carbon disulphide. Bulky
clusters of needles (49 g) m.p. 93-94°. (Found, on rapid titration with
0.1N NaOH, 0.3559 g required 12.7 ml, corresponding to Mol. wt. 270.
Calc'd for C_{14} H_{20} O_4 S Mol. wt. = 270).
The melting point of a sample of the hydrogen phthalic ester
was raised to a maximum value of 91-92.5° by one further recrystallisation
from carbon disulphide.

(−) 2 Thiophenylacetyl hydrogen phthalate

Anhydrous bromine (901 g) was added to a solution of
2-2 thiophenylacetyl hydrogen phthalate (145 g, m.p. 93-94°) in
hot, dry ethyl acetate (one-litre). Crystallisation commenced almost
immediately; after standing 12 hrs., the crystals were filtered off,
and recrystallised four times from ethyl acetate; yielding bromine

(−) 2 thiophenylacetyl hydrogen phthalate m.p. 155-157° (63 g)
with [α]_{D}^{25} = −50.5°, [α]_{D}^{500} = −33.0°, [α]_{D}^{500} = −142.5° in
chloroform solution (c=0.45, l=2). A further crop of this salt (11 g)
was obtained from the filtrates.

This salt (23 g) mixed with about twice its weight of acetone,
was decomposed with cold dilute hydrochloric acid, and the resulting

(−) 2 thiophenylacetyl hydrogen phthalate (9.3 g) was precipitated
by the addition of crushed ice. It separated from carbon disulphide in
bulky clusters of short needles m.p. 93-94°.

**Note:** The product obtained by seven recrystallisations of the original
bromine salt from acetone yielded a hydrogen phthalic ester with
only 90% of the maximum recorded rotatory power by this method.
Table 12

Rotatory powers of (-) 2-thiophenyl acetyl hydrogen phthalate in solution in benzene and carbon disulphide at 27-12°C (1 = 2).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Benzene</th>
<th>Carbon Disulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.07</td>
<td>2.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>λ (°)</th>
<th>[α]</th>
<th>[α]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4338</td>
<td>-47.1°</td>
<td>-172°</td>
</tr>
<tr>
<td>4338</td>
<td>5.35</td>
<td>135</td>
</tr>
<tr>
<td>5063</td>
<td>5.07</td>
<td>113</td>
</tr>
<tr>
<td>5481</td>
<td>2.61</td>
<td>90</td>
</tr>
<tr>
<td>5723</td>
<td>2.39</td>
<td>64</td>
</tr>
<tr>
<td>6163</td>
<td>2.10</td>
<td>70</td>
</tr>
<tr>
<td>6480</td>
<td>1.78</td>
<td>62.6</td>
</tr>
</tbody>
</table>

Graphical relationships between [α] and λ are given in Figs. VI and VII.

(c) 2-Thiophenyl acetyl hydrogen phthalate

Decomposition of the more soluble fractions of the brucine salt of 2-thiophenyl acetyl hydrogen phthalate (filtered from the first crop of crystals) with ice and hydrochloric acid, yielded (1 + Cl) 2-thiophenyl acetyl hydrogen phthalate. During removal of the ethyl acetate, however, even under vacuum, some decomposition of the salt occurred, with deposition of crystalline brucine hydrogen phthalate.
Attempts to form crystallisable salts of (+) 2 thiocyanethyl carbonyl hydrogen phthalate with atyline, quine, quindine, cinchonine and cinchonidine all proved unsuccessful.

Recrystallisation of a carbon disulfide solution of (d + dl)
2-thiocyanethyl carbonyl hydrogen phthalate with dl 2 thiocyanethyl carbonyl hydrogen phthalate resulted in the separation of principally dl-ester; repeated crystallisations by seeding with dl-hydrogen phthalate raised the optical rotatory power of the hydrogen phthalate ester remaining in solution to a maximum value by this method of

\[ [\alpha]_20^d = +55.0^\circ (c = 2.1) \text{ in carbon disulfide solution.} \]

This corresponds to only 37.5% of the rotatory power of (−) 2 thiocyanethyl carbonyl hydrogen phthalate obtained by recrystallisation of its brimming salt, described above.

Preparations of 2 thiocyanethyl carbonyl hydrogen phthalate

(a) Neutral phthalic ester

dl-2 Thiocyanethyl carbonyl hydrogen phthalate (5 g; 0.02 m.) was dissolved in 1.0 molar sodium hydroxide (45 ml; 0.095 m. NaOH) and the solution diluted (to 100 ml) when it immediately became cloudy. After twelve hours, a small quantity of oil had deposited and was extracted with ether. From the dried ether solution, 2-thiocyanethyl carbonyl b.p. 95/18 mm n\(^D\) 1.5415 (1.12 g) and a viscous residue (0.7 g) were isolated. This residue was hydrolysed with alcoholic potassium hydroxide solution (3.25%). of the residue required 11.0 ml 0.10 alcoholic KOH (during 2 hrs heating under reflux) corresponding to equiv. wt. 205; dl (2 thiocyanethyl methyl carbonyl) phthalate.
C₆₂H₄₂O₄S₂ requires equiv. wt. 183. The aqueous portion of the 0.36% thioacetate solution was evaporated to dryness. After a few minutes the solution was acidified, and immediately precipitated fine needles of phthalic acid (1.42 g) m.p. 180° with decomposition.

These crystals were filtered off, and the filtrate evaporated to dryness; the crystalline residue was extracted with alcohol, and the alcohol solution, on evaporation, gave a further crop of phthalic acid (1.15 g) m.p. 180° with decomposition.

Preparation of thioacetic acid from the thioacetate. This experiment constitutes an approximate estimation of the percentage. A mixture of thioacetamide 3.5 g and hydrochloric acid 60 ml. was heated under reflux condenser in a 250 ml. flask to about 40° C. The solution was then cooled to room temperature and the thioacetamide was added in small portions with stirring. The mixture was then allowed to stand for 24 hr. The reaction mixture was then filtered, the filtrate evaporated to dryness, and the solid material was crystallized from alcohol. The solid material was then dissolved in a mixture of benzene and alcohol, and the resulting solution was then treated with an excess of sodium bicarbonate. The mixture was then filtered, and the filtrate was evaporated to dryness. The solid material was then crystallized from alcohol, and the resulting solid was then weighed and found to contain 85% of the thioacetic acid.

A mixture of thioacetic acid (1.65 g) in water (15 ml.) was heated under reflux condenser in a 250 ml. flask to about 40° C. The solution was then cooled to room temperature and the thioacetamide was added in small portions with stirring. The mixture was then allowed to stand for 24 hr. The reaction mixture was then filtered, the filtrate evaporated to dryness, and the solid material was crystallized from alcohol. The solid material was then dissolved in a mixture of benzene and alcohol, and the resulting solution was then treated with an excess of sodium bicarbonate. The mixture was then filtered, and the filtrate was evaporated to dryness. The solid material was then crystallized from alcohol, and the resulting solid was then weighed and found to contain 85% of the thioacetic acid.

(b) Estimation of thioacetic acid

Prepare an aqueous solution of thioacetic acid at 0.05 M, to serve as the base and standard solutions.

(1) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(2) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(3) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(4) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(5) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(6) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(7) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(8) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(9) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(10) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(11) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(12) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(13) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(14) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(15) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(16) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(17) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(18) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(19) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(20) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(21) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(22) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(23) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(24) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(25) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(26) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(27) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(28) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(29) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(30) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(31) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(32) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(33) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(34) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(35) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(36) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(37) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.

(38) A 0.05 M solution of thioacetic acid (2.0 ml.) was pipetted into a 25 ml. volumetric flask, and the volume was made up to 25 ml. with distilled water.
the then opaque solution had deposited large crystals. After a further
34 hrs., the supernatant liquor was clear, and the crystals of 2-thienyl-
ethyl carbinyl p-tolyl sulfone were filtered off and dried (0.65 g); they recrystallized from alcohol. Long colorless needles m.p. 61-63°
(found 61.3; C_{13} H_{24} O_{2} S_{2} requires 61.1%), [α]_D = 0 (3% in
alcohol) 3.5 | 1.12 | 1.18 | 1.20 | 1.075
Comparison of this experiment with the formation of a sulfone from
p-ethylbenzhydryl hydrogen phthalate (475) shows the formation of
100% sulfone in 20 mins for the p-ethylbenzhydryl derivative against
a 35% yield of sulfone in >1 hr for 2-thienylcarbinyl hydrogen
phthalate. |

(−) 2-Thienylcarbinyl.

A solution of potassium hydroxide (4.55 g) in water (2 ml) was
added to a solution of (−) 2-thienylcarbinyl hydrogen phthalate
(0.3 g) in cold absolute ethyl alcohol (200 ml). After heating the
mixture rapidly on the steam-bath for 10 mins., a bulky precipitate of
potassium hydrogen phthalate had separated. Addition of water (50 ml)
to the ice cold suspension resulted in the formation of a clear solution,
which was diluted with ether (500 ml) and washed with brine until free
from alkali. The resulting ethereal solution was dried with sodium
sulfate and evaporated under vacuum at 25-30°, to remove the ether and
ethyl alcohol. Distillation of the residue from an oil bath yielded
(−) 2-thienylcarbinyl was a colorless liquid b.p. 63-65°/11 mm
(3.13 g).
### Table 13

Rotatory powers of (-) 2-thiazolinyl etheral.

<table>
<thead>
<tr>
<th>λ(Å)</th>
<th>0.1</th>
<th>0.25</th>
<th>0.50</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ(Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Graphical relationships between \([ε]_λ\) at 2.5 and λ are given in Figs. I and II.

Graphical relationships between \([ε]_λ\) and λ are given in Figs. I and II.

A mixture of (-) 2-thiazolinyl etheral (2.5 cm \([ε]_λ\) \(10^3\) = -3.10) obtained by the hydrolysis of the ethereal solution of the hydroxyl camphor ether (\([ε]_λ\) \(10^3\) = -25.20, 2.05% in aqueous solution), phloridzin ethereal (0.25 g) and phloridzin (0.5 ml) was found at 2.5 cm.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diethyl Ether</th>
<th>Carbon</th>
<th>Ethyl Alcohol</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°</td>
<td>-63.5°</td>
<td>-70°</td>
<td>-3.59°</td>
<td>-1.90°</td>
</tr>
<tr>
<td>20°</td>
<td>5.06</td>
<td>5.22</td>
<td>13.3</td>
<td>23.8</td>
</tr>
<tr>
<td>20°</td>
<td>4.43</td>
<td>4.31</td>
<td>25.5</td>
<td>29.2</td>
</tr>
<tr>
<td>50°</td>
<td>5.75</td>
<td>42.8</td>
<td>21.9</td>
<td>27.5</td>
</tr>
<tr>
<td>20°</td>
<td>3.59</td>
<td>32.0</td>
<td>15.7</td>
<td>21.1</td>
</tr>
<tr>
<td>50°</td>
<td>5.17</td>
<td>31.3</td>
<td>17.7</td>
<td>22.9</td>
</tr>
<tr>
<td>50°</td>
<td>4.60</td>
<td>32.0</td>
<td>15.7</td>
<td>21.1</td>
</tr>
<tr>
<td>0°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.95</td>
</tr>
<tr>
<td>0°</td>
<td>2.60</td>
<td>23.0</td>
<td>15.1</td>
<td>21.6</td>
</tr>
<tr>
<td>0°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Graphical relationships between $[\alpha]$ and $\lambda$ are given in Figs. IV and V.

Determination of (-) 2-thiophenethyl cardiol into its (-) hydrogen phthalic ester

A mixture of (-) 2-thiophenethyl cardiol (0.01 g, $[\alpha]_20^0 = -28.7^0$) obtained by the hydrolysis in alcoholic solution of its hydrogen phthalic ester ($[\alpha]_13^0 = -37.0^0$, 1.67% in benzene solution), phthalic anhydride (0.45 g) and pyridine (0.5 mL) was heated at 65-70°
for 3 hrs. After standing overnight, the viscous product was diluted with 2 vol. acetone and poured onto ice and hydrochloric acid. The resulting (-) 2 thienylmethyl carbonyl hydrogen phthalate was thoroughly washed with cold water and dried (0.5 g). A solution in benzene had 
\[
\left[\alpha\right]_{D}^{20^0} = -53.8^0 \quad (c = 1.625),
\]
demonstrating that the rotatory power of the (-) 2 thienylmethyl carbinal obtained by the hydrolysis of its (-) hydrogen phthalate in alcoholic potassium hydroxide solution, described above, was \(\frac{53.8}{57.3} \times 100 = 97\%\) of its original value.

Hydrolysis of (-) 2 thienylmethyl carbonyl hydrogen phthalate with aqueous sodium hydroxide

- Partially active (-) 2 thienylmethyl carbonyl hydrogen phthalate (4.5 g, \(\left[\alpha\right]_{D}^{20^0} = -33.5^0; 1.73\%\) in benzene solution) and 15% aqueous sodium hydroxide (1.56 g NaOH and 2.3 ml water) were mixed in the cold, and then distilled in a current of steam. The aqueous distillate was extracted with ether, and distillation of the dried ethereal solution yielded (-) 2 thienylmethyl carbinal b.p. 69-70.5^0/10 mm (1.07 g); this had \(\left[\alpha\right]_{D}^{20^0} = -7.53^0\). (81 g) was converted to the above benzene solution.

Comparison of this experiment with the hydrolysis of (-) 2 thienylmethyl carbonyl hydrogen phthalate in alcoholic potassium hydroxide solution, described above, shows that more extensive racemization of (-) 2 thienylmethyl carbinal occurs during the ammonification of its hydrogen phthalate in aqueous solution, than the resultant carbinal has only 6% of its original optical rotatory power.

(-) 2 Thienylmethyl carbinal obtained by hydrolysis of its hydrogen phthalic ester in alcoholic solution retains 97% of its original value.

Aromatic hydrochloride separated as yellowish, which on a solution of sodium carbonate (4.6 g) of the phthalic acid in 150 ml water, and the
Ultraviolet absorption of 2-thienylcarbinal

A solution of 2-thienylcarbinal in ice-octane was examined by Dr. G.H. Boekel in the ultraviolet region, and showed a strong absorption band at ca. 2,540 Å, \( E_{	ext{molar}} \) ca. 6,000 and an inflection at ca. 3700 Å, \( E_{	ext{molar}} \) ca. 11. A graphical relationship between \( E_{	ext{molar}} \) and \( \lambda \) for this solution is given in Fig. III. (\( E_{	ext{molar}} \) = the extinction coefficient of a molar solution).

VI. \( \alpha \)-PYRIDYLCARBINAL (1 (\( \alpha \)-pyridyl) propene-2-ol)

\( \alpha \)-Pyridylcarbinal (50)

A solution of bromobenzene (79 g) in dry ether (100 ml) was added dropwise, in an atmosphere of nitrogen, to a suspension of lithium metal chips (6.9 g) in dry ether (400 ml). Reaction was initiated by gentle warming, and the mixture was continuously stirred until solution of the lithium was complete (ca. 3 hrs.). Freshly distilled \( \alpha \)-picoline (45 g) was then added, the mixture becoming dark-red in colour; it was stirred at room-temperature for one hour, and then chilled in a bath of ice and salt. A solution of freshly distilled acetaldehyde (ca. 20 g) in ether (50 ml) was then added dropwise to the chilled \( \alpha \)-picolidyl-lithium solution, with constant stirring, until the red colour of the reaction-mixture was completely discharged. After a further 15 mins, the solid yellow complex which had separated was decomposed by the addition of (i) cold water (100 ml), followed by (ii) concentrated hydrochloric acid (100 ml). The red aqueous layer which separated was removed, added to a solution of sodium carbonate (500 g, of the dehydrated in 100 ml water) and the
resulting slurry of lithium carbonate filtered. Crude \( \alpha \)-picolylinmethylic carbinal separated as an oil in the filtrate, and was extracted with chloroform; the solid lithium carbonate was thoroughly washed with chloroform. Evaporation of the combined dried chloroform solutions gave an oil, which on distillation yielded \( \alpha \)-picolylinmethylic carbinal was a colorless liquid which darkened on exposure to light b.p. 100-120/10 m.

Yield 30.7 g = 60% (calc'd on \( \alpha \)-picouline).

Attempted resolution of \( \alpha \)-picolylinmethylic carbinal with optically-active acids.

Attempts were made to form crystallizable salts between \( \alpha \)-picolylinmethylic carbinal and \( L \)-salic, \( L \)-tartaric, \( L \)-cumaric, \( L \)-cumaric, \( L \)-cumaric-10-sulphonic, \( L \)-cumaric-10-sulphonic and \( \gamma \)-dicycloxyl-tartaric acids, by adding the equivalent amount of each acid to solutions of \( \alpha \)-picolylinmethylic carbinal (1 g.) in water, acetone, ethyl acetate or methyl alcohol (5-10 ml.). In each case, however, the product was either an oil or gum, which could not be induced to crystallize. In an attempt to react \( \gamma \)-dicycloxyl-tartaric anhydride with the carbinal in acetone solution had the same result.

\( \alpha \)-picolylinmethylic carbinal hydrogen phthalate

A solution of \( \alpha \)-picolylinmethylic carbinal (51 g.) in acetone over (20 ml) was added to a hot solution of phthalic anhydride (55 g.) in \( \alpha \)-picolylinmethylic carbinal hydrogen phthalate (130 ml). The clear solution was heated under reflux for 30 min and left for 18 hrs. Crystalline \( \alpha \)-picolylinmethylic carbinal hydrogen phthalate separated and was filtered off and dried m.p. 133-142°. Yield 51 g = 60%.
The hydrogen phthalate was insoluble in carbon disulphide, cyclohexane, benzene, acetone, and ethyl acetate; sparingly soluble in chloroform and cold water, readily soluble in hot water, alcohol, acids, and alkalies.

A solution of \( \alpha \) picolyinethyl carbaryl hydrogen phthalate in 0.51 aqueous sodium hydroxide exhibited no sign of neutral water formation on standing for fifteen days.

\( \alpha \) Picolyinethyl carbaryl

Anhydrous bromine (197 g) was added to a slurry of \( \alpha \) picolyinethyl carbaryl hydrogen phthalate (123 g) in hot dry acetone (1000 ml) to give a clear solution. After standing overnight, the crystals which had deposited were filtered off m.p. 142-150°C, and after one recrystallization from ethyl acetate (500 ml) yielded bromine \( (+) \) picolyinethyl carbaryl hydrogen phthalate (100 g) m.p. 154-156°C with \( [\alpha]_{D}^{503} = -30.2^\circ \) in chloroform solution \( (c = 2.167, l = 2) \). Further recrystallization of this salt did not raise the magnitude of its rotatory power.

This salt (10 g.) was added to 51 aqueous sodium hydroxide (10 ml) (53), the mixture heated on the steam bath for 30 mins., cooled, and thoroughly extracted with ether. The ethereal solution was dried over potassium carbonate, and evaporation of the ether yielded \( (+) \) picolyinethyl carbaryl, b.p. 110/10 mm \( n_{D}^{20} = 1.5162 \) (53 g).
<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>20</th>
<th>25</th>
<th>43</th>
<th>59</th>
<th>Total 93 state</th>
<th>23 state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_+^+$</td>
<td>1.049</td>
<td>1.045</td>
<td>1.030</td>
<td>1.016</td>
<td>0.933</td>
<td></td>
</tr>
<tr>
<td>$\chi(\lambda)$</td>
<td>$\lambda$</td>
<td>$\lambda$</td>
<td>$\lambda$</td>
<td>$\lambda$</td>
<td>$\lambda$</td>
<td>$\lambda$</td>
</tr>
<tr>
<td>4353</td>
<td>+63.00°</td>
<td>+12.0°</td>
<td>+51.75°</td>
<td>+110°</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4900</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5505</td>
<td>43.20</td>
<td>92.3</td>
<td>40.45</td>
<td>77.4</td>
<td>+35.10°</td>
<td>+63.2°</td>
</tr>
<tr>
<td>5751</td>
<td>35.30</td>
<td>69.6</td>
<td>34.45</td>
<td>65.9</td>
<td>23.65</td>
<td>57.6</td>
</tr>
<tr>
<td>7705</td>
<td>31.30</td>
<td>59.6</td>
<td>23.85</td>
<td>57.2</td>
<td>23.85</td>
<td>57.2</td>
</tr>
<tr>
<td>5335</td>
<td>29.14</td>
<td>55.5</td>
<td>-</td>
<td>-</td>
<td>22.95</td>
<td>43.9</td>
</tr>
<tr>
<td>6133</td>
<td>24.53</td>
<td>46.3</td>
<td>22.95</td>
<td>43.9</td>
<td>22.65</td>
<td>43.9</td>
</tr>
</tbody>
</table>

Graphical relationships between $\lambda$ and $\chi(\lambda)$ are given in Figs. VIII, IX and X.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Methyl</th>
<th>Ethyl</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>Ethers</th>
<th>Acetic Acid</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>18</td>
<td>21.5</td>
<td>13</td>
<td>19.5</td>
<td>21</td>
<td>17.5</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>5° per</td>
<td>2.103</td>
<td>1.837</td>
<td>21.06</td>
<td>2.155</td>
<td>2.302</td>
<td>2.152</td>
<td>2.011</td>
<td></td>
</tr>
<tr>
<td>100 ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4353</td>
<td>+0.29°</td>
<td>+6.7°</td>
<td>+1.19°</td>
<td>+31.6°</td>
<td>+12.26°</td>
<td>+32.5°</td>
<td>+0.42°</td>
<td>+9.2°</td>
</tr>
<tr>
<td>4303</td>
<td>-</td>
<td>-</td>
<td>1.19</td>
<td>31.6</td>
<td>10.54</td>
<td>58.3</td>
<td>0.63</td>
<td>-</td>
</tr>
<tr>
<td>5836</td>
<td>0.51</td>
<td>12.1</td>
<td>1.17</td>
<td>31.1</td>
<td>9.46</td>
<td>45.1</td>
<td>0.73</td>
<td>17.1</td>
</tr>
<tr>
<td>5461</td>
<td>-</td>
<td>-</td>
<td>1.12</td>
<td>29.7</td>
<td>8.26</td>
<td>39.4</td>
<td>0.75</td>
<td>17.6</td>
</tr>
<tr>
<td>5736</td>
<td>-</td>
<td>-</td>
<td>1.03</td>
<td>27.3</td>
<td>7.42</td>
<td>35.4</td>
<td>0.72</td>
<td>16.9</td>
</tr>
<tr>
<td>5393</td>
<td>0.43</td>
<td>10.2</td>
<td>0.99</td>
<td>26.1</td>
<td>7.19</td>
<td>34.4</td>
<td>0.71</td>
<td>16.6</td>
</tr>
<tr>
<td>6194</td>
<td>-</td>
<td>-</td>
<td>0.83</td>
<td>23.6</td>
<td>6.63</td>
<td>31.7</td>
<td>0.66</td>
<td>15.5</td>
</tr>
<tr>
<td>6363</td>
<td>0.40</td>
<td>9.5</td>
<td>0.83</td>
<td>22.0</td>
<td>6.16</td>
<td>29.4</td>
<td>0.60</td>
<td>14.1</td>
</tr>
<tr>
<td>6703</td>
<td>-</td>
<td>-</td>
<td>0.83</td>
<td>22.0</td>
<td>5.49</td>
<td>26.2</td>
<td>0.53</td>
<td>13.6</td>
</tr>
</tbody>
</table>

Graphical relationships between $[\alpha]_\lambda$ and $\lambda$ are given in Figs. XIII and XIV.

Cont'd ........
Table 16 (Concl'd)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Carbon Disulphide</th>
<th>Water</th>
<th>Methanol</th>
<th>Ethyl Alcohol</th>
<th>Acetic Acid</th>
<th>Nitromethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>21.5</td>
<td>18</td>
<td>16.5</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>5 per 100 ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.122</td>
<td>2.236</td>
<td>2.167</td>
<td>2.074</td>
<td>2.139</td>
<td>2.169</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( \beta )</td>
<td>( \gamma )</td>
<td>( \delta )</td>
<td>( \epsilon )</td>
<td>( \zeta )</td>
<td>( \eta )</td>
</tr>
<tr>
<td>4.358</td>
<td>4.068</td>
<td>5.1</td>
<td>2.166</td>
<td>3.579</td>
<td>2.559</td>
<td>5.727</td>
</tr>
<tr>
<td>4.000</td>
<td>4.057</td>
<td>4.82</td>
<td>2.75</td>
<td>2.76</td>
<td>2.75</td>
<td>2.75</td>
</tr>
<tr>
<td>5.000</td>
<td>3.92</td>
<td>87.7</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
</tr>
<tr>
<td>5.500</td>
<td>3.92</td>
<td>87.7</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
</tr>
<tr>
<td>5.621</td>
<td>3.12</td>
<td>74.3</td>
<td>2.72</td>
<td>4.14</td>
<td>4.14</td>
<td>4.14</td>
</tr>
<tr>
<td>5.789</td>
<td>2.82</td>
<td>63.5</td>
<td>1.29</td>
<td>2.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.000</td>
<td>2.75</td>
<td>61.0</td>
<td>1.20</td>
<td>2.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.148</td>
<td>2.59</td>
<td>61.0</td>
<td>1.20</td>
<td>2.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.433</td>
<td>2.25</td>
<td>50.3</td>
<td>1.03</td>
<td>2.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.768</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>2.75</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Graphical relationships between \( \lambda \) and \( \alpha \) are given in Figs. XII and XIV.
(+) \(\alpha\) picolylmethoxyl carbaryl crystals \(\lambda \alpha\) \(\alpha\) picolylmethoxyl carbaryl crystals \(\lambda \alpha\) \(\alpha\) picolylmethoxyl carbaryl crystals \(\lambda \alpha\) \(\alpha\) picolylmethoxyl carbaryl crystals

<table>
<thead>
<tr>
<th>(\lambda (\alpha))</th>
<th>(\alpha_2^\circ)</th>
<th>(\alpha_6^\circ)</th>
<th>(\alpha_4^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4550</td>
<td>+1.00 (^\circ)</td>
<td>+0.00 (^\circ)</td>
<td></td>
</tr>
<tr>
<td>5568</td>
<td>0.62</td>
<td>0.72 (^\circ)</td>
<td>0.77 (^\circ)</td>
</tr>
<tr>
<td>5661</td>
<td>0.79</td>
<td>0.49 (^\circ)</td>
<td>0.79 (^\circ)</td>
</tr>
<tr>
<td>5720</td>
<td>0.80</td>
<td>0.47 (^\circ)</td>
<td>0.82 (^\circ)</td>
</tr>
<tr>
<td>5630</td>
<td>0.53</td>
<td>0.49 (^\circ)</td>
<td></td>
</tr>
</tbody>
</table>

A graphical relationship between \(\lambda \alpha\) and \(\lambda \alpha^2\) is given in Fig. XVI.

(+) \(\alpha\) picolylmethoxyl carbaryl

The filtrate from the original brine (+) \(\alpha\) picolylmethoxyl carbaryl obtained in the above isolation was filtered off (24 \%) and heated under reflux for 30 mins., and re-crystallized. The (+) \(\alpha\) picolylmethoxyl carbaryl hydrochloride from this mother liquor was dissolved off (5.5 \%) to form a crystalline mass between isooctane. The isooctane was then evaporated, and methanol, crystallization with ether, and thinning of the mother liquor, were used to isolate further crystals of (+) \(\alpha\) picolylmethoxyl carbaryl having a very sticky dark-brown residue, which set to a glass after standing for several weeks. This glass (10 \%) mixed with 24 \% aqueous sodium hydroxide (15 \%) was heated on the steam bath for 60 mins., cooled, and thoroughly extracted with ether. The etheral solution was dried over potassium carbonate, and concentration of the ether yielded crude

This product, as p. 135-136 \(^\circ\), on heating with aqueous sodium hydroxide, as described above (p. 70), yielded partially active (+) \(\alpha\) picolylmethoxyl carbaryl with \(\lambda \alpha \sim 18^\circ\) in carbon disulfide solution

\(c = 1.003, l = 2\).
(-) L-picolylmethy carbim, b.p. 111°/10 mm (1.25 g) and had

\[ [\alpha]_{D}^{25} = -49° \text{ in carbon disulfide solution (c = 3.25, l = 1)} \] - this
corresponds to 67% of the optical rotatory power of the (+) L-picolylmethy
carbim described above.

This (1 + 1) L-picolylmethy carbim (1 g) and phthalic
anhydride (1.05 g) in acetone solution (5 ml) were heated under reflux for
30 mins., and left to crystallize. The (1 + 1) L-picolylmethy carbim
hydrogen phthalate which separated was filtered off (0.9 g). Attempts to
form crystallizable salts between this hydrogen phthalate and cinchonine,
cinchonidine, quinidine and strychnine, by mixing equal parts of the hydrogen
phthalate ether and each alkaloid in hot acetone solution, and leaving to
stand, resulted in each case in gums which could not be induced to
crystallize.\[ [\alpha]_{D}^{25} = +2.5° \]

(+)-L-picolylmethy carbim hydrogen phthalate

A solution of (+) L-picolylmethy carbim (1.4 g) and phthalic
anhydride (1.5 g) in dry acetone (5 ml) was heated under reflux for 30 mins
and left overnight; the (+) L-picolylmethy carbim hydrogen phthalate
A melting modification between \( \alpha \) \( \text{ and } \alpha' \) was obtained (130°),
which crystallized was filtered off and dried (2.55 g).

<table>
<thead>
<tr>
<th>( [\alpha]_{D} )</th>
<th>+25°</th>
<th>+27°</th>
<th>+26°</th>
<th>+25°</th>
<th>+25°</th>
<th>+25°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\alpha]_{D}^{25} )</td>
<td>-49°</td>
<td>-49°</td>
<td>-49°</td>
<td>-49°</td>
<td>-49°</td>
<td>-49°</td>
</tr>
</tbody>
</table>
Table 18

Rotatory power of (±) α-picolylmethyl carbonyl hydrogen phthalate in solution at room temperature (1 = 1).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda^2$</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t^0$</td>
<td>2.009</td>
<td>0.015</td>
</tr>
<tr>
<td>$\text{pH}$</td>
<td>2.008</td>
<td>0.015</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda^0$</th>
<th>$\alpha$</th>
<th>$[\lambda^2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4350</td>
<td>+7.32°</td>
<td>+150°</td>
</tr>
<tr>
<td>4350</td>
<td>+5.40°</td>
<td>-</td>
</tr>
<tr>
<td>5000</td>
<td>4.53</td>
<td>112</td>
</tr>
<tr>
<td>5000</td>
<td>5.73</td>
<td>92.5</td>
</tr>
<tr>
<td>5720</td>
<td>3.24</td>
<td>70.5</td>
</tr>
<tr>
<td>6420</td>
<td>2.20</td>
<td>50.5</td>
</tr>
</tbody>
</table>

A graphical relationship between $[\lambda^2]$ and $\lambda^0$ is given in Fig. XX.

Table 19

Rotatory power of (±) α-picolylmethyl carbonyl hydrogen phthalate in 1.0M aqueous sodium hydroxide (1 = 1, c = 1.007) at 20°.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>24</th>
<th>45</th>
<th>63</th>
<th>90</th>
<th>210</th>
<th>2070</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda^2$</td>
<td>+1.52°</td>
<td>+1.37°</td>
<td>+1.02°</td>
<td>+1.02°</td>
<td>+0.70°</td>
<td>+0.63°</td>
</tr>
<tr>
<td>$[\lambda^2]$</td>
<td>+75°</td>
<td>+70°</td>
<td>+61°</td>
<td>+59°</td>
<td>+39°</td>
<td>+35°</td>
</tr>
</tbody>
</table>
A graphical relationship between $[\alpha]$ and time is given in Fig. XII, and by extrapolation from this $[\alpha]$ at zero time = +0.0°.

(+)$\alpha$ picolyxanthyl oximethyl (2.2 g) was mixed with an equal volume of acetic anhydride and maintained at 60°C for 1 h. The mixture was then diluted with ether, the resultant solution washed with cold 1% aqueous sodium hydroxide, till free from acid, and dried over sodium sulphate.

Evaporation of the ether gave an oil, b.p. 134-135°C/19 mm Hg, $d_2^3$ 1.048 (1.32 g).

<table>
<thead>
<tr>
<th>$\lambda$ (Å)</th>
<th>$\alpha$</th>
<th>$[\alpha]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>+0.4°</td>
<td>+21.9°</td>
</tr>
<tr>
<td>463</td>
<td>+1.0°</td>
<td>+21.6°</td>
</tr>
<tr>
<td>503</td>
<td>+2.0°</td>
<td>+21.3°</td>
</tr>
<tr>
<td>543</td>
<td>+2.9°</td>
<td>+21.0°</td>
</tr>
<tr>
<td>593</td>
<td>+3.8°</td>
<td>+20.7°</td>
</tr>
<tr>
<td>623</td>
<td>+4.7°</td>
<td>+20.4°</td>
</tr>
<tr>
<td>653</td>
<td>+5.5°</td>
<td>+20.1°</td>
</tr>
</tbody>
</table>

Table 22

Rotatory power of (+)$\alpha$ picolyxanthyl oximethyl acetate at 589 (1 = 0.10)

<table>
<thead>
<tr>
<th>$\lambda$ (Å)</th>
<th>$\alpha$</th>
<th>$[\alpha]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>+0.4°</td>
<td>+21.9°</td>
</tr>
<tr>
<td>463</td>
<td>+1.0°</td>
<td>+21.6°</td>
</tr>
<tr>
<td>503</td>
<td>+2.0°</td>
<td>+21.3°</td>
</tr>
<tr>
<td>543</td>
<td>+2.9°</td>
<td>+21.0°</td>
</tr>
<tr>
<td>593</td>
<td>+3.8°</td>
<td>+20.7°</td>
</tr>
<tr>
<td>623</td>
<td>+4.7°</td>
<td>+20.4°</td>
</tr>
<tr>
<td>653</td>
<td>+5.5°</td>
<td>+20.1°</td>
</tr>
</tbody>
</table>
Table II

Rotatory powers of (+) α-picolylcarbonyl acetoacetate in solution in 2-propanol (1 = 2)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Tetrachloride</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-per</td>
<td>1.033</td>
<td>2.132</td>
</tr>
<tr>
<td>[α]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4553</td>
<td>+0.95°</td>
<td>+25.5°</td>
</tr>
<tr>
<td>6083</td>
<td>0.60</td>
<td>15.1</td>
</tr>
<tr>
<td>6461</td>
<td>0.53</td>
<td>11.5</td>
</tr>
<tr>
<td>5799</td>
<td>-0.43</td>
<td>11.5</td>
</tr>
<tr>
<td>6433</td>
<td>0.57</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Graphical relationships between [α] and λ are given in Figs. XVII and XVIII.

(+)-α-Picolylcarbonyl acetoacetate

A solution of (+)-α-picolylcarbonyl acetoacetate (0.5 g) and p-anisyl acetate (0.75 g) in dry benzene (10 ml) was heated on the steam bath under reflux for 30 mins. On cooling, (+)-α-picolylcarbonyl acetoacetate p-anisyl methanol crystallised out as colourless very plates, and was recrystallised from benzene and petrol m.p. 130° (0.25 g).

A solution of β-l-phenylalanine methylester hydrochloride in absolute ethyl alcohol was obtained by Dr. C.H. West in the ultraviolet region, and displayed a single absorption band, with two broader fine structures in the same region. The complete list of results is given in Table II in a separate sheet and at en ultraviolet in indicated, but no solvent...
Table 22

Rotatory powers of (+) α-picolinylmethyl carbonyl p-ethyl acetate in various solvents at room temperature (I = 2).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Benzene</th>
<th>Ethyl Alcohol</th>
<th>Carbon Tetrachloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>t°C</td>
<td>+0°</td>
<td>+17.5</td>
<td>+19°</td>
</tr>
<tr>
<td>25° 100 ml</td>
<td>2.873</td>
<td>2.236</td>
<td>1.337</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>λ (Å)</th>
<th>[α]</th>
<th>[α]</th>
<th>[α]</th>
<th>[α]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4553</td>
<td>+0.05°</td>
<td>+12°</td>
<td>+2.67°</td>
<td>+2.2°</td>
</tr>
<tr>
<td>5208</td>
<td>0.05</td>
<td>15.9</td>
<td>1.03</td>
<td>43.3</td>
</tr>
<tr>
<td>5422</td>
<td>0.05</td>
<td>15.7</td>
<td>1.03</td>
<td>33.8</td>
</tr>
<tr>
<td>5780</td>
<td>-</td>
<td>-</td>
<td>1.45</td>
<td>32.7</td>
</tr>
<tr>
<td>6038</td>
<td>0.42</td>
<td>11.3</td>
<td>1.40</td>
<td>31.6</td>
</tr>
<tr>
<td>6453</td>
<td>0.41</td>
<td>12.0</td>
<td>1.14</td>
<td>25.7</td>
</tr>
</tbody>
</table>

Graphical relationships between [α]λ and λ are given in Figs. XVII and XVIII.

Ultraviolet absorption of α-picolinylmethyl carbonyl

A solution of α-picolinylmethyl carbonyl in absolute ethyl alcohol was examined by Dr. G.H. Daven in the ultraviolet region, and displayed a single absorption band, with some resolved fine structure, in the range 2950-3150 Å. The complete list of features is shown in Table 23. A probable strong band at ca 2900-3100 Å is indicated, but no selective

70.
absorption occurs at longer wavelengths than the 2000 band.

Table 23

<table>
<thead>
<tr>
<th>( \lambda (\text{nm}) )</th>
<th>Feature</th>
<th>( E_{\text{molar}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A graphical relationship between \( \lambda \) and \( \log E_{\text{molar}} \) is given in Fig. 11.

Fig. 11: Plot of \( \lambda \) vs. \( \log E_{\text{polar}} \).

References


(9) Pickard and Hunter - J. Inst. 257, 454 (1923).

(10) Lowry and Cotton - J. Inst. 257, 634 (1923).


(14) Pope and Jones - Chem. and Ind. (1932) 218.


(16) Cohn, Syngor et al. - J. Chin. Phys. 6, 733 (1927)


(20) Lowry and Baker - Nature 114, 300 (1924).
(27) Patterson - J 1939, 1178 (1919).  
(28) Holf and Hovellmarn - Z. physik. Chem. 125, 139 (1929).  
(33) Rado in J (1951) 676 et seq., 1578 (1951).
(36) Buchman and Lowry, J.A.C.S. 72, 2075 (1950).
(37) Ekerin and Reson, J (1932) 3200.  
(39) Hargro and Neve, J.A.C.S. 73, 306 (1951) et seq.
(40) Ham and Ross - Am. 557, 359 (1949).  
(41) Ham and Bullock - J.A.C.S. 62, 811 (1940).
(42) Lowry, Reson and Haver - J.A.C.S. 53, 1105 (1941).
(43) Neve and Hudson - J (1939) 2202.
(44) Dawson and Kevon - J (1932) 631.

(45) Dry and Hayward - Trans. Far. Soc. 27, 608 (1932).


(47) Helfe, Kevon et al. (a) J (1942) 533
(b) J (1942) 635
(c) J (1942) 707
(d) J (1943) 503
(e) J (1943) 897


(50) Hess et al. - Ber 60, 348 (1927).

(51) Sidgwick - "The Organic Chemistry of Nitrogen" (Oxford Univ. Press 1943).

(52) Walter, Hunt - J.A.C.S. 62, 2771 (1940)

(53) Spring and Wills - J.A.C.S. 56, 173 (1934).


(55) Lowry and Gutter - J 128, 1403 (1924).

(56) Dreyfuss Jones - J (1933) 703


(58) Betti - Gazetta 32, 1, 934 (1901) et seq.
Trans. Far. Soc. 22, 337 (1933)

(59) Steinheif and Jaffe - ARN 215, 539.
Figure 1: (-) 2-thienyl methyl carbinol at 20°C.
Figure II. (-) 2-Thienyl Methyl Cearsole at 20°C.
Figure III. Ultraviolet Absorption Spectrum
2-Phenyl Methyl Cardine
Solvent - Mixed Octanes

Log \(_{10}\) Molar Extinction Coefficient

Wavelength Å
Figure IX. 
(-) 2- Thiethyl methyl carbamol in various solvents at room temperature.
1. 5.06% in carbon disulphide
2. 5.01% in diethyl ether
3. 2.16% in benzene
4. 5.10% in ethyl alcohol
FIGURE V. (-)2-THIENYL METHYL CARBINOL IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

1. 5.10% ETHYL ALCOHOL
2. 2.16% BENZENE
3. 5.01% DIETHYL ETHER
4. 5.06% IN CARBON DISULPHIDE
FIGURE VI. (-) 2-THIENYL METHYL CARBINYL HYDROGEN PHTHALATE IN VARIOUS SOLVENTS AT 17-18 °C.

1. CARBON DISULPHIDE.
2. BENZENE.
FIGURE VII. (-) 2-THIENYL METHYL CARBINYL HYDROGEN PHTHALATE IN VARIOUS SOLVENTS AT 17-18°C.

1. BENZENE (1.87%)
2. CARBON DISULPHIDE (2.10%)
FIGURE C: (A) PICOXYL METHYL CARBONATE
AT VARIOUS TEMPERATURES
FIGURE XI. ULTRAVIOLET ABSORPTION SPECTRUM
α PICOLYL METHYL CARBONOL
SOLVENT - ETHYL ALCOHOL

LOG10 MOLAR EXTINCTION COEFFICIENT.

WAVELENGTH Å
FIGURE XIX (c) picolyl methyl carbonil
in various solvents at room temperature

1. 2% in benzene
2. 2% in carbon tetra-chloride
3. 2% in acetone
4. 2% in diethyl ether
5. 2% in ethyl acetate
6. 2% in chloroform

λ λ₀

5000 6000 7000
Figure XV. (4) \( \text{Picolyl Methyl Carbinol in various solvents at room temperature} \)

1. 2% in Chloroform
2. 2% in Diethyl Ether
3. 2% in Ethyl Acetate
4. 2% in Acetone
5. 2% in Carbon Tetrachloride
6. 2% in Benzene
7. 20% in Benzene
FIGURE XVII. ESTERS OF (+)-PICOLYL METHYL CARBINOL IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

1. ACETATE (NO SOLVENT)
2. 2% SOLN. OF ACETATE IN CARBON TETRACHLORIDE
3. 2% " " " BENZENE
4. 2% " " " p-XENYL URETHANE IN BENZENE
5. 2% " " " ETHER ALCOHOL
6. 1.5% " " " CARBON TETRACHLORIDE
FIGURE VIII. ESTERS OF (+) 2-PICOLYL METHYL CARBINOL
IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

6. p-XENYL URETHANE IN CARBON TETRACHLORIDE
5. " " IN ETHYL ALCOHOL
4. " " IN BENZENE
3. ACETATE IN BENZENE
2. " IN CARBON TETRACHLORIDE
1. ACETATE (NO SOLVENT)
(+) α-Picolyl Methyl Carbinyl Hydrogen Phthalate

2% Solution in 1N NaOH.

Figure XIX

(+) α-Picolyl Methyl Carbinyl Hydrogen Phthalate

1% Solution in Water.

2.2% in 5N HCl.

$\lambda$ vs. $[\alpha]$ in 10$^8$ vs. 7