Optical Activity and Chemical Constitution

The Optical Rotatory Dispersion of Glycidyl Phenyl Ether
and Related Compounds

Submitted to
The University of London
for the Degree
of
Doctor of Philosophy

by
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Introduction

In 1690 Huygens published his "Treatise on Light", in which he drew attention to the double refraction of Iceland spar, and also spoke of a property of light called "disposition" or "direction". This property was further investigated by Valus(l) who used a heliostat with a solar source to direct a beam of light in the meridian so that it fell on the first mirror of his apparatus, which had its normal in the meridian and pointed slightly forward.

![Diagram of mirrors and light path]

Then the second mirror faced east or west, no light was transmitted, whilst the maximum amount of light was transmitted when the mirror was turned toward the poles. Valus described this polarization as "the modification which gives to the light its properties relatively to those poles". The plane of the meridian in Valus' experiment came to be called the "plane of polarization"; Fresnel(2) showed by interference experiments that the vibrations of light were transverse to the direction of propagation and that the vibration of a plane polarised beam was perpendicular to its plane of polarization.
In 1811 Arago\(^{(3)}\) observed the colour effects produced when plates of nica, syringen, and quartz were examined in a polarising system. List\(^{(4)}\) investigated this phenomenon more thoroughly and differentiated between the rotation of the plane of polarisation of the polarised light by the medium, which he called rotatory polarisation, and the inequality of this rotation for different wavelengths, which he termed rotatory dispersion. List also showed that, within the accuracy of his experiments, the expression:

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

well represented the form of the rotatory dispersion of the substances he investigated. This expression is the mathematical form of what is known as List's Law of Inverse Squares. Twenty years later he observed the first exception to the rule when he was examining the rotatory dispersion of aqueous solutions of tartaric acid. This was the first case of "anomalous dispersion" to be observed, this being the name given to dispersions in which the rotation of the plane of polarisation does not increase as the wavelength of the light decreases. At about this time List also observed the "inversion" of cane sugar, whilst some years previously he had observed that equal thicknesses of laevor and dextro quartz, when examined in a polarising system, showed no rotatory power if placed in series.

List defined the "Specific Rotatory Power" \([\alpha]\) of a substance, as:

\[
[\alpha] = \frac{\alpha}{c \rho} \text{ or } \frac{\alpha}{c \epsilon \rho} \text{ for solutions}
\]
where \( \alpha \) = observed rotation of the plane of polarization in degrees.
\( \ell \) = length of the column of optically active medium traversed (in decimeters).
\( \rho \) = density of liquid.
\( \varepsilon \) = fraction by weight of optically active solute.

The "Molecular Rotatory Power" of a compound is now defined as:

\[
\left[ \beta \right] = \frac{\mu \alpha}{100}
\]

where \( \mu \) = the molecular weight of the optically active substance.

Thus, by the time of his death in 1863,riot had truly laid the foundations for the development of the later work on optical activity. Unfortunately soon after his death the study of rotary dispersion was largely abandoned in favour of experiments with monochromatic light, which had been made so easily available by the invention of the furnace burner. Thus the increased accuracy in the measurement of rotary dispersion, made possible by the polarimeter of Pizeau and Foucault(5), in which the wavelengths of the extinctions were those of the Fraunhofer lines of the solar spectrum, was not fully utilised.

Riot divided optically active substances into two classes; those in which the rotary dispersion obeyed his Law of Inverse Square, and those in which it did not. In 1863 the empirical relation of riot was modified by von Lang(6) to:

\[
\alpha = A + \frac{F}{\lambda^2}
\]

in order to embrace the more accurate measurements obtained with the Pizeau polarimeter, and on theoretical grounds Boltzmann(7) introduced a further modification :-
\[ \alpha = \frac{1}{\lambda} + \frac{C}{\lambda^2} \text{ etc.} \quad (5) \]

to comply with the theoretical requirement of zero rotatory power at infinite wavelength.

The most important step forward in the study of optical rotatory dispersion after the time of Piot, was made by Drude\(^{(6)}\) in 1900, with the introduction of the relation:

\[ \alpha = \frac{C}{\lambda^2} - \lambda^2 \quad (6) \]

Though this relation was based on theoretical reasoning which has since been shown, by v. Kuhl\(^{(9)}\), to be unsound, the work of T. H. Lowry\(^{(10)}\) showed that it was in good agreement with the results obtained in the study of the rotatory dispersion of organic compounds in the visible and ultraviolet regions of the spectrum. Moreover, a detailed study of the rotatory dispersion of quartz from 38,100 A to 2553 A by Lowry (et al.)\(^{(11)}\), and by Muciaux and Jeanet\(^{(12)}\), established the validity of the Drude equation in this case. Lowry was sufficiently satisfied with the accuracy of the work involved in his study, to suggest that the rotatory power of quartz for a given wavelength might provide an accurate wavelength standard. Lowry was able to show that the majority of substances required only one, or two, terms of the Drude equation to represent their rotatory dispersion, though in the case of quartz the great accuracy of the measurements made a further term necessary.

Keryon and Hickard\(^{(13)}\), who began their researches into the optical properties of the secondary alcohols, about the same
time, were the first to make optically active molecules of simple constitution readily available. Simplicity of constitution is desirable in the study of rotatory dispersion, since only molecules with a simple constitution are suitable for an attempt to relate the physicist's and the chemist's conception of the phenomena involved.

Much of the recent work in the field of optical activity has been concerned, more with its application as an experimental method, in the study of other problems, than with a further understanding of the phenomenon itself.

Having briefly described the results obtained from an examination of certain substances in a polarizing system, it is desirable to consider what may be the theoretical basis for such results.

The study of the mechanism by which optical activity is produced in certain substances, resolves itself broadly into two channels, which can, and have been, studied quite separately.

1. There appear to be certain structural conditions which may give rise to optical activity. The study of these structural conditions has been mainly the work of organic chemists.

2. The way in which these conditions influence polarized light, so as to produce optical activity, provides the second line of advance towards a complete understanding of the problem. The progress made in this field, which is in the sphere of mathematical physics, has been much slower.
owing to its great complexity; but it may be expected that the elucidation of the mechanism of interaction of light with the molecule of the optically active compound, will bring with it a further understanding of the structural conditions required for optical activity.

It is proposed to give separate short accounts of the development in these two fields.
I The Structural Conditions Necessary for Optical Activity

The work of Huy and Berzelius(14) showed that the optical activity of quartz could be related to a certain lack of symmetry in quartz crystals. Pasteur(15) found that tartaric acids, which rotated the plane of polarization of polarized light to the left, yielded crystals which were mirror images of those which were obtained from acids which rotated it to the right. These crystals were non-superposable. Such properties are only possible when the crystals contain neither a plane nor a centre of symmetry. Crystals which lack both a plane and a centre of symmetry, are said to be "dissymmetric". This term is used in contradistinction to the term "asymmetric", which means lacking in all symmetry.

Pasteur, who was a pupil of Döll, was the first to prepare optically active compounds artificially, originating all the main methods of resolution at present in use. Figures which are two-dimensional have a plane of symmetry, so that it was clear from the first, that molecules showing optical activity must be three-dimensional. Pasteur, tetrahedral suggested that, an irregular arrangement of the groups around a carbon atom might be the requirement for optical activity in organic molecules. The general principles governing optical activity were summarized by Le Bel(16) in 1874, and in the same year by van't Hoff(17) independently. Van't Hoff suggested that the lack of symmetry could either be, in the
molecule, or in the case of solid substances in the crystal itself.

The work of Pope, and his collaborators (14), was mainly concerned with the proof of the ideas of van't Hoff and Le Bel, and in showing that they applied to asymmetric atoms, other than carbon. The method of resolution provided a ready way of distinguishing between a planar, and a non-planar arrangement of four or more atoms.

Pope also showed that, the "second case of optical activity", postulated by van't Hoff could be practically realised.

Van't Hoff described as his "second case of optical activity", derivatives of the allene type, which are disymmetric, i.e. contain neither a plane nor a centre of symmetry, but also contain no asymmetric centre. Layworth and Rechler (14) failed to resolve an allene derivative in 1910, but in 1928 Pope, Perkin and Ballach (15) resolved a substance of similar type, namely 1-methylcyclohexenylidene-4-acetic acid (I):

It can be seen from the diagram that, though there is no actual asymmetric atom, the molecule, as a whole, lacks both a plane, and a centre of symmetry.

In 1936 Mills and Saitland (16) finally obtained an optically active compound (II) of the allene type,

\[ \alpha-[\text{II}] \neq \alpha-[\text{II}] \]

by disymmetric dehydration of the alcohol (III) with d-camphor.
Another allene derivative, similar to that which Lawrson failed to resolve, was resolved by Kohler and Whittle in 1940(1). Finally it was shown that diacetylene could be induced in a molecule by the presence therein of groups which restrict rotation about single bonds. 66′ dinitro-diphenic acid (IV) was resolved by Christie and Kermer in 1923(2).

Kermer (et al.) favoured formula (V) for their compound, but Turner and Le Feyre(3) showed that formula (IV) was the correct one, their work was confirmed by dipole measurements of substances of the type X.C_6H_4-C_6H_4.X and X.C_6H_4-X (26). A similar formula was proposed for compounds of this type, by Fett and Heryon(23), and by W.H. Mills(24). Some years later Turner and Lesvia(23) were able to demonstrate optical activity in 32′ dicyclo-hexane acid (VI), thus showing that a hydrogen atom was sufficient to provide restricted rotation, if the ortho substituent in the nucleus were large enough.

Mills and his collaborators proceeded to the preparation of optically active forms of compounds, of other than the diphenyl type, which showed restricted rotation, notably 3-(isopropyl-dimethylvinyl)-cyclohexyltrimethyl-ammonium iodide (VII).
Recent data on the energy barriers in the ethane molecule suggest that the aliphatic C-O bond may be subject to steric hindrance (the energy barrier for ethane is c. 3000 cal/mole), therefore substances such as ethylene dichloride should be capable of resolution at low temperatures, were the means available. Such isomerism was first suggested by Itern(26) in 1869. Debye(29) has demonstrated the existence of cis-trans isomerism in the vspour of ethylene dichloride. Cases are known in which the energy barriers are lower than those which normally allow the resolution of isomers, so that only one form is isolable by the normal means of resolution (the substance then being said to undergo a "second-order asymmetric transformation"(30)); or alternatively the activity of the substance may be limited to a preponderance of one disstereoisomer over the other, when the substance and its resolving agent are combined in solution (in this case the substance is said to undergo a "first-order asymmetric transformation(33)"

A first-order asymmetric transformation refers only to the attainment of an equilibrium in solution, whilst the second-order transformation results when the rate of interconversion of the isomers exceeds that of crystallisation, one diastereoisomer having a lower energy in the crystalline state than the other(31). In either case the optical
stability of the substance is increased by the lowering of the temperature, resolution in the normal way may be possible. The optical-stability of a substance such as ethylene dichloride, would however be much less than that of those substances in which first and second-order transformations have been demonstrated.
II The Interaction of Polarised Light with Optically Active Substances

The work of Fliit stimulated the interest of Fresnel, who produced a kinetic interpretation of the phenomena of optical activity.

Fresnel(32) showed that the behaviour of optically active substances in plane polarised light, could be explained on the assumption that, the light was analysed by them into two circularly polarised beams, of the same amplitude and phase, but of opposite sense and different velocity. Further if the two beams were differentially absorbed, then circular dichroism would occur, and the emergent light would be elliptically polarised.

If the velocity of the two beams is different, then their refractive indices must also be different, though W. Kuhn(9) has shown that this difference, even for a substance with a high rotatory power, is of the order of one part in a million.

Fresnel suggested that crystals which showed optical activity, might have a spiral structure, so that circularly polarised light of like hand, would pass through more readily than that of opposite hand, thus accounting for the difference in the velocity of the two beams. Fresnel's ideas of the structure of quartz were verified by the X-ray diffraction studies of W.H. Fogg(33) some hundred years later.
Fresnel had been able to explain satisfactorily the rotatory power of crystals, but it was not so easy to explain the rotation of the plane of polarisation by substances in solution. It was assumed that the activity of the molecule was connected with the fact that, looking along any one bond of an asymmetric carbon atom, the three other bonded groups will appear in a different sequence in the left and right handed isomers.

It was natural therefore, that an attempt should be made to deduce the rotatory power of a substance, by arranging the various radicals, bonded to the asymmetric carbon atom, in the order of their masses or volumes. Grim Frown and Guye suggested that the rotatory power would be proportional to the product of the "differences between the masses" of the four groups surrounding the asymmetric atom. This idea was short lived since Walden in 1895 showed that substances, in which two of the groups were identical as to mass, but differed in structure, and in which the other two groups were different, can exhibit optical activity.

The later theories of de Vellamen and Loye embodied the idea of differences in volumes. de Vellamen calculated the optical rotatory power from the polarisabilities of the different radicals (i.e. terms with the dimensions of volume), assuming that the radicals were isotropic spheres which did not react with one another. His calculations were therefore limited to molecules of the type CH3IBrI, for which he
obtained \( \xi = 13.3^2 \), which figure appears to be of the correct order of magnitude, though it has not been experimentally verified.

In 1934 Boys(36) advanced a theory rather similar to that which de Malleman first put forward, except that he assumed direct interaction between the four groups \( \text{R}_1\text{R}_2\text{R}_3\text{R}_4 \) in the molecule \( \text{C R}_1\text{R}_2\text{R}_3\text{R}_4 \). Boys was able to calculate the rotatory powers of some simple molecules from his theory, which were of the right order of magnitude, but he also was forced to assume that the four radicals were isotropic spheres, in order to simplify the calculation. This assumption may be justifiable in the case of the halogens and isoceric radicals, though the highly polarisable nature of the halogen atoms is against it, but it is clearly not valid in other cases.

**ELECTRONIC THEORIES OF OPTICAL ROTATORY POWER**

The theories outlined above have been classified as molecular theories of optical rotatory power, to differentiate them from the electronic theories developed by Bruda(6), Born(27,28), Kuhn(39) and others. These theories do not treat with the properties of an individual molecule, but with the substance as a medium. Bruda obtained his equation for optical rotatory dispersion by modifying those(14) of Maxwell, Bellmier, Kettler and Holmoholtz for refractive dispersion, introducing the concept of a spiral vibrator to account for the rotation of the plane of polarisation. Kuhn(9) has pointed out that,
Irvine's model was optically inactive; his equation does not however correspond to his model, and all equations which have subsequently been advanced, on an improved theoretical basis, can be reduced to that of Irvine.

In the development of equations for optical rotatory power on the electronic basis, as on the molecular basis, there are in each case two stages: firstly, the model is conceived, and the rotatory power calculated in terms of this model; secondly, the model has to be related to some experimentally determinable parameters, and it is at this stage that the difficulties usually arise.

With one exception, the later theories of optical rotatory power all depend on the idea of coupled oscillators, introduced independently about 1915 by Born(37), Cossel(40) and Gray(41).

The basic assumptions of these theories are:—

1. Each part of the molecule is considered as a discrete unit.
2. Each of these units is attached more or less rigidly to all the others.
3. Each part becomes polarized under the influence of an electric field (usually the electric vector of the light wave).
4. The polarized units exert a field which interacts with the other units.

Thus the state of any part of the molecule is the resultant of (a) the external field, and (b) the field due to other parts of the molecule. These interdependent units are said to be
"coupled", in analogy with the coupling between mechanical oscillators. The theory of Iones, and a revised theory of de Vries also included the idea of coupling in their basic assumptions, but this was vitiated by the simplifications introduced to ease the calculation. Born (27) treats each unit of the molecule as a charged particle which can move a small distance from its equilibrium position under the influence of an electric field, this movement being opposed by a force which is a linear function of the displacement of all the particles. In this way the idea of coupling is introduced mathematically. Born showed that at least four coupled isotropic non-planar vibrators were required to produce optical activity. In Born's theory uncoupled electrons do not influence the optical rotation. This early theory was based on molecular constants which are not experimentally determinable, but it was later modified (28) so that it was applicable to a model similar to that of Iones, and an equation was deduced for the rotation \( \chi \) of this simplified model (figure 1), entirely in terms of parameters, the values of which are known or may be readily estimated:

\[
\chi = 3.49 \times 10^{-11} c^{-1} t^{-1} \frac{\lambda^2}{n^2} \left( \frac{\lambda'}{n'} \right)^3 \left( \frac{\lambda''}{n''} \right) \left( \frac{\lambda'''}{n'''} \right) x \text{c}^2 \text{e} \frac{d}{(c^2 + e^2) + (d^2 + e^2) + (f^2 + g^2)}
\]

where
\( \chi \) = rotation in degrees per decimetre
\( \rho \) = density of medium
\( n \) = its refractive index
\( M \) = the molecular weight
\( l \) = the distance between the two halves of a pair of oscillators in Å
\( d \) = distance between the two lines joining the resonance pairs (in Å)

Figure 1
\( \lambda, \lambda_n \) are the characteristic wavelengths of vibrators \( A \) & \( I \)

\( \chi, \chi_n \) are the strengths of the vibrators \( A \) & \( I \).

Forn's model, like those of the molecular theories, gives the correct order of magnitude, but, as Lorry (14) has pointed out, several of the parameters are merely guesses, so that no exact result is to be expected, especially as the result depends on the eighth power of the distance "1".

The theory advanced by Werner Kuhn (39,9) in 1929 was the first to apply the idea of coupled oscillators to a simple molecule suitable for practical application. Kuhn's model consisted of two anisotropic linear oscillators, at right angles and separated by a distance. The combination of the two vectors may reproduce the spiral form of Prude, and, as Forn has pointed out, Kuhn's model is very similar to that of Prude in that it depends on one constant only, in the one case the separation of the resonators, in the other the pitch of the helix, neither corresponding to the ordinary active molecule. Kuhn's theory has however had considerable influence on all subsequent theories, since it was the first to show how the necessary simplifications could be made to the coupled oscillator theory so as to make it suitable for practical application. Kuhn's equation was also an improvement on that of Prude when applied in the region of absorption.
Equations Derived from Quantum Mechanical Considerations

The basic quantum mechanical calculations were made by Rosenwald(42) in 1926 and a little later by Poin and Jordan. Poin has shown that, while the basic problem of optical activity is a quantum mechanical one, the rotation effect is, in fact, due to the same set of virtual oscillators as those which determine the dispersion, and that this enables the problem to be treated on the basis of classical mechanics, with the rotation effect due to a set of harmonic oscillators coupled by electric and magnetic forces. It was in the light of this work that the later theory of Poin (above) was developed. The fundamental equation of the quantum mechanical theory may be written:

\[ [n] = \frac{C n}{h c} \cdot \left( \frac{\nu^2 + 2}{3} \right) \sum \rho \alpha \beta \frac{\epsilon_{\text{ini}}^2}{\nu_{\text{ini}} - \nu_{\text{fin}}} \] (6)

or

\[ [n] = \frac{2 \times 10^5 N}{X^2} \cdot \frac{n^2}{3} \beta \] (7)

where
- \( N \) = Avogadro's number
- \( n \) = refractive index of medium
- \( c \) = velocity of light
- \( h \) = Planck's constant
- \( \alpha \) = the probability that the molecule exists in a given electronic state corresponding to no rotation.
- \( \beta \) = the electronic state responsible for the rotation
- \( \nu_{\text{ini}} \) = the frequency corresponding to the change from the state "\( \alpha \)" to the excited state "\( \beta \)"

\( \frac{\epsilon_{\text{ini}}^2}{\nu_{\text{ini}} - \nu_{\text{fin}}} \) (a complex function) is the rotatory strength of the transition "\( \alpha \rightarrow \beta \)".

This equation (6) is of the form:

\[ [n] = \frac{n^2}{3} \sum \frac{\rho \alpha \beta}{\nu_{\text{ini}} - \nu_{\text{fin}}} \] (8)

and if the factor \( (n^2+2)/3 \) is assumed to be constant, as is usually the case, we get:

\[ [n] = \frac{2 \times 10^5 N}{X^2} \cdot \frac{n^2}{3} \beta \]
in the visible region, then the Prude equation results. The difficulty in applying this equation is due to the difficulty of assessing the complex function \( R \). Condon\(^{(44)} \) has obtained an expression for the optical activity of the Kuhn model, which is somewhat simpler than that used by Kuhn himself.

Kirkwood\(^{(45)} \) has applied the above equation (8) to a model based on the polarisabilities of the different groups. The theory of Kirkwood has the same defect as the other polarisability theories, namely that the wavelengths used in this method of calculation are those of the main absorption bands of the groups, which, in fact, are not so active as the weak absorption bands which these theories do not consider.

Recently, Condon\(^{(46)} \) has developed a theory of optical activity based on the behaviour of one electron in an anisotropic field, the equipotential surface corresponding to this field being a triaxial ellipsoid, which has been given a twist about one of its axes. This figure has the element of "chirality" common to the other electronic theories. Calculations based on this model can also yield results of the right order of magnitude. It is interesting to note that, on the basis of this model, Condon\(^{(46)} \) confirmed the finding of Born, that the residual rotation of the molecule may be accounted for on the principles of classical mechanics alone.
OPTICAL ROTATORY DISPERSION

So far as the fundamental theory is concerned, rotatory dispersion is inseparable from the theory of the origin of optical activity. It is however convenient to consider the form of the dispersion as a separate subject.

The early workers in the field of optical activity used the sun as their source of light, and were therefore forced to study the rotatory dispersion, through the visible spectrum, of the substances they investigated. But, as has been pointed out, the introduction of the Pyrex burner, as a convenient source of monochromatic light, caused a concentration on accurate measurements at one wavelength only, so that very little work was done on optical rotatory dispersion, between the time of Pictet, and about 1911 when Lowry, and Dickard and Kenvon, related their results to the Prade equation. Further, as Lowry was the first to point out, optical rotatory dispersion work which relies solely on measurements in the visible region is generally of little fundamental value. It is unfortunate therefore, that the apparatus for rotatory dispersion work in the ultra-violet region is so rarely available, and that the work is rendered so difficult, either by the tediousness of the methods, or their lack of precision. (A short review of the methods available is given on page 102).
In the study of the effects of temperature, solvents and substituents on the rotatory power of a substance, it is clearly of the utmost importance that the rotation and dispersion constants of the Drude equation should be determined in each case. So far as is known, no thorough investigation of temperature, solvents and substituents has been made for any compound. A glance at the mathematical working for the evaluation of the Drude equation, given in the Appendix, will suggest a possible reason for this. For the evaluation of an equation of more than one term a calculating machine is necessary, whilst for more than two terms the mathematical problems are considerable. No doubt with the increased availability of automatic calculating machines, interest in the form of rotatory dispersion curves may revive.

Pict was able to demonstrate his Law of Inverse Squares by plotting the reciprocal of the rotation of a given substance, against the square of the corresponding wavelength. This gave a straight line in all the cases he examined, except solutions of tartaric acid. This procedure also shows roughly whether a one term Drude equation will represent the dispersion under consideration, though a mathematical analysis may be necessary. The one-term Drude equation is written:

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

where $K =$ rotation constant, $\lambda_0 =$ wavelength corresponding to $\lambda_0 =$ dispersion constant, $\lambda_0$ corresponds to the wavelength of the optically active absorption band.
Lowry has shown that, in a large number of cases, only one term of the Drude equation is necessary to express the rotatory dispersion.

Fliot distinguished between two types of rotatory dispersion, those which obeyed his Inverse Square Law and those which did not. Ampteen in 1856 distinguished between those substances, in which the rotation increases with the refrangibility of the rays, and those in which it does not. These two classes of dispersion are now known as "normal" and "anomalous". More recently Lowry has defined normal dispersion as one in which:

\[ \alpha, \frac{d\alpha}{d\lambda}, \text{ and } \frac{d^2\alpha}{d\lambda^2} \text{ remain constant in sign throughout the whole range of observation.} \]

i.e. there must be

1. No reversal of the sign of the rotation \((\alpha = 0)\)
2. No maximum \((\frac{d\alpha}{d\lambda} = 0)\)
3. No point of inflexion \((\frac{d^2\alpha}{d\lambda^2} = 0)\)

The inflexion, maximum and reversal of sign always follow each other in the same order, so that the presence of one is regarded as evidence of the existence of the other two. Since the above are the characteristics of all rotatory dispersions which may be represented by two terms of the equation, though in the region of observation none of the features may be present, Lowry concluded that it would be more suitable to classify dispersions as:

1. Simple Dispersion, which may be represented by one term of the Drude equation.
2. Complex Dispersion, requiring more than one term of the
Drude equation for its representation.

A dispersion which is simple is of necessity normal, but the converse does not necessarily hold.

It was originally assumed that normal dispersion was the fundamental law. Piot was able to show, for example, that the rotation of quartz could be compensated for all visible wavelengths by a solution of cane sugar of suitable concentration, but he also found that 1-oil of turpentine and d-oil of lemon do not compensate each other perfectly for all wavelengths, either when mixed together, or when placed end on end in separate tubes.

Tschugsaff(48) found that the rotatory dispersion of 1-menthyl d-camphorsulphonate had the properties which would be expected of a mixture of 1-menthyl alcohol and d-camphorsulphonic acid. This observation was of great importance since it showed that anomalous rotatory dispersion may be produced by the superposition of the partial rotations produced by two asymmetric complexes contained within the molecule of the active body, provided that these partial rotations were of opposite sign and different dispersion.

Tschugsaff(49) was also able to show that each chromophoric group can make its own contribution to the rotatory power of the molecule. When this chromophoric is not near the centre of asymmetry, if it shows optical activity, the contribution is said to be the result of the "induced asymmetry of the chromophore". Lowry(49) found that the \( \gamma \)C=O group in
camphor was optically active as a result of induced "asymmetry". (the term induced "asymmetry" was later introduced as corresponding letter to the facts).

This connection between the chromophoric group and optical activity had been demonstrated by Pickard and Hunter in 1923, who found that the dispersion constant of the equation (12) which represented the rotatory dispersion of d-\-nonyl nitrite,

$$[\alpha] = \frac{0.76}{\lambda - 0.135} + \frac{0.43}{\lambda}$$

(12)
yielded a wavelength for the optically active absorption band, within 50 A of that obtained from measurements of the refractive dispersion, and also within the experimentally determined absorption band. Unfortunately, in the majority of cases, it is not possible to confirm the existence of optically active absorption bands, since they mostly occur in the Schumann region (below 3000 A). Experimental difficulties for the determination of absorption in this region are formidable (owing to absorption by the atmosphere) and until the recent work of T.C.Price, A.D.Walsh and R.C.Mulliken practically no data were available for this region.
From the point of view of the organic chemist, the Drude equation may be considered as an empirical relation which is valuable in the correlation of the optical rotatory dispersion data. When so considered the following points arise:

1. The denominator of the Drude equation contains constants which are wavelengths.

2. When these wavelengths occur in an accessible region of the spectrum, it has been found that they correspond to the wavelengths of absorption bands in the molecule. The rotatory strength or "activity" of an optically active absorption band may be measured by its "dissymmetry factor", \( \varepsilon \), defined as \( \varepsilon = \frac{c_1 - c_r}{c} \), where \( c_1 \) and \( c_r \) are the molar extinction coefficients for left and right hand circularly polarised light and ordinary light respectively. (Kuhn\(^\text{14}\) describes the above as the "anisotropy factor").

3. In the series of secondary alcohols, a remarkably constant "active" absorption band occurs at c. 1600 A; this is no doubt due to a combination of C-C, C-H and C-OH absorption, the bands of which all lie in the Schumann region.

4. The frequency of an absorption band is a measure of the energy of the corresponding electronic transition. It is probable that all electronic transitions are influenced...
to some extent by the dissymmetry of the molecule, and that
the failure of some of these transitions to be represented by
an active band in the Drude equation is due to:-

(a) Cancelling out by similar transitions of opposite sign
and/or
(b) A low dissymmetry factor (only applies to bands in the
and
Schumann region)
(c) Formation of one complex term by the combination
of more than one absorption band.

If examination of the rotatory dispersion in the region of
the frequency of the transition shows no active band then
this must be due to (a). The definite existence of an
active band can only be established by examination in the
region of absorption.

* In the older theories of Born and Kuhn a coupling force
between the chromophoric electrons is required for the
production of optical activity. Condon(44) has recently
shown that this is not necessary, since a single electron
may produce optical activity when placed in a field of
suitable dissymmetry.

(b) It seems probable that a molecule containing two formally
asymmetric centres, each with an absorption wavelength in an
accessible region of the spectrum, would show corresponding
active bands in the Drude equation. In most of the cases
so far examined the second term of the Drude equation is due
to "induced dissymmetry" in a chromophore which is not itself
formally dissymmetric. (Kuhn(9), and Falke and Kenyon(52) use
the term "induced anisotropy").
(6) Only rarely is it necessary to explain the complex rotary dispersion of a substance in terms of an equilibrium mixture of two forms (A and B):

\[
\begin{array}{c}
\text{Liquid A} \leftrightarrow \text{Liquid B} \\
\text{Solid A}
\end{array}
\]

such an equilibrium was first suggested by Arrhenius. To explain the anomalous dispersion of tartaric acid, in this particular case his hypothesis is supported by the work of Winter on entropy changes in tartaric acid derivatives.

The experimental observations, outlined above, are in conformity with the conclusions drawn from the theoretical equations (7) and (8) discussed in the previous section. It is interesting therefore to see what further conclusions may be drawn from the electronic theories of optical rotary power.

If the equations for the rotary power, and the models upon which they are based, are examined it would clearly be expected that all electronic transitions within the molecule would influence the optical activity to some extent. Also, it is to be expected that those electrons which are most loosely bound will be most affected by the general geometry of the molecule. This applies to all loosely bound electrons, whether they take part in bond formation or not. Thus it would be expected that the electrons, which make up an ethylenic bond, will have a greater influence on the rotary power of the molecule than those electrons which form a carbon–carbon single bond.
this is in accord with experimental observation, and with the views of K. Kuhl(2), who suggests that, since observed rotations are generally low, and especially so when bands in the Schumann region alone are concerned, the bands which occur in this region must contribute relatively little to the rotatory power of the molecule.

Further, large and readily polarisable atoms such as the halogens should make a relatively large contribution to the rotatory power of the molecule, and the results of Levene and Rothen(55) are in agreement with this (though those of K. Kuhl(51) who worked with the same compound, α-iodostere are not).

The rotatory dispersion of a given compound will then be represented by a large number of terms of the type:

\[ \frac{A_{\alpha i} / \lambda^2 - \lambda_{\alpha i}^2}{A_{\alpha i} / \lambda - \lambda_{\alpha i}} \]

As Kuhl has pointed out, the majority of these terms will be in the Schumann region, where there is a tendency for the various terms to cancel out, and in addition their discymmetry factor "α" will be low since they correspond to the most tightly bound electrons. The number of groups in a molecule which have absorption bands in the photographic ultra-violet (chromophoric groups) are comparatively few, and there will thus be less tendency for their partial rotations to cancel out. In addition their discymmetry factors are large due to the weak bonding. A classical example of this is tetra-ae-tolyl-amalourose(57) H(CH_3C_6H_4O)_4CHO, in which
the partial rotations of the four asymmetric (C=OAc) groups cancel out, so that the resulting dispersion is simple with its characteristic frequency that of the absorption band of the aldehyde group.

The Brute equation deduced from the experimental curve is further simplified because absorption bands which lie close together yield one composite band, unless the measurements are carried close to the region of absorption. Thus it is generally impossible to distinguish between the various bands which lie in the Schumann region by measurements in the visible and near ultra-violet regions. To obtain the constant absorption band at c. 1500 Å deduced by Konyen and Dickard(54) from the rotatory dispersion of the secondary alcohols, and later verified by Lorry(56) in the ultra-violet region, is a composite band resulting from absorption by the C=O group, together with C-C and C-H absorption.

Here, on the other hand, the active bands are widely separated, two or even three terms of the Brute equation may be required to represent the dispersion curve.

In those substances which show simple dispersion the rotatory power is generally less sensitive to changes of temperature or solvent, than in those which show complex rotatory dispersion.
### The Effect of Solvents on the Specific Rotatory Power and the Rotatory Dispersion of Substances in Solution

One of the most noticeable characteristics of the specific rotatory power of a substance, is its susceptibility to change of solvent. No satisfactory explanation of this behaviour has yet been advanced. It has however been shown, (see page 16 above), that the optical rotatory power of a substance for a given wavelength may be expressed:

\[
\frac{[\alpha]}{\lambda} = K_x \frac{(n^2 + 2)^2}{3} \beta
\]

where

- \( n_x \) is the refractive index of the medium for light of wavelength \( \lambda \) A.U.
- \( \beta \) is a term depending on the rotatory dispersion and is constant for any given wavelength.
- \( K_x \) is a constant for any given wavelength.

Holf and Volkman(60) therefore conclude that \( [\alpha]/(n^2 + 2) \) should be constant for non-polar solutes. Volkman and Cohen(61) have suggested that in the study of solvent effects, the variation of \( 3\alpha/(n^2+2) \) should be considered rather than that of \( [\alpha] \). This quantity is denoted by the symbol \( \alpha' \):

\[
\alpha' = \frac{3[\alpha]}{n^2+2}
\]

This suggestion is a natural consequence of equations (6 A 14) above, in which the variation of \( \alpha' \) is seen to be of more fundamental significance than the variation of \( [\alpha] \). The
quantity "\( \Omega \)" is called the "rotivity" of the substance (in analogy to the relation between refractive index and refractivity). Feckmann and Cohen further suggest that the rotivity of a substance is a linear function of the electrostatic field acting on the active molecule:

\[ \Omega = \Omega_0 + \Omega' F \]

(15)

where \( \Omega_0 \) = rotivity in zero field
\( \Omega' \) = change in rotivity per unit field, acting along the resultant dipole of the molecule.
\( F \) = the applied field.

The significance attached by these authors to the rotivity is clearly seen from equation (14), but it appears that the refractive index may also enter into the term \( \beta \), which represents the dispersion. Rule and Chambers\(^{(63)}\) have shown that in non-polar solvents the variation in \( 3[1]/(n^2+2)^2 \), for \( \alpha \)-pinene, is less than that of \( 3[1]/(n^2+2) \), whilst the variation is least in \( 3[1]/(n^2+2) \) if all solvents are considered.

More recent work, by Pryde and Rule\(^{(63)}\) suggests that the improvement in constancy, observed in \( \alpha \)-pinene, was fortuitous, however, since their observations were confined to one wavelength it is impossible to tell whether the alteration in the rotatory power, due to the refractive index, is not masked by an alteration in the dispersion term .

The work of Kenyon and Platt\(^{(64)}\) with (+)\( \gamma \)-methyl n-heptane also suggests that the dependence of optical rotatory power on refractive index is not so simple as might be expected.
on the basis of current hypotheses.

The specific rotatory power of \((-\) glycine phenyl ether\) varies in different solvents by some \(250^\circ\) for \(\lambda = 5461\) A, and by \(450^\circ\) for \(\lambda = 4356\) A (calculated on the basis of the lowest rotatory power).

The activities of \((-\) glycine phenyl ether\) vary in a similar manner, as in Table I:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Refractive Index of Solvent</th>
<th>(\alpha^{\circ})</th>
<th>(= \frac{\alpha \lambda}{(n^2-1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.5330</td>
<td>24.4</td>
<td>12.9</td>
</tr>
<tr>
<td>Homogeneous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.5014</td>
<td>21.9</td>
<td>16.5</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1.5003</td>
<td>23.5</td>
<td>16.4</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>1.6296</td>
<td>23.7</td>
<td>14.8</td>
</tr>
<tr>
<td>Maximum variation</td>
<td></td>
<td>1 : 1.11</td>
<td>1 : 1.14</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.3314</td>
<td>17.7</td>
<td>13.5</td>
</tr>
<tr>
<td>n-Propyl chloride</td>
<td>1.3880</td>
<td>12.0</td>
<td>9.1</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.3500</td>
<td>16.2</td>
<td>12.5</td>
</tr>
<tr>
<td>Dioxan</td>
<td>1.4032</td>
<td>6.3</td>
<td>6.1</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>1.3542</td>
<td>6.3</td>
<td>6.4</td>
</tr>
<tr>
<td>Maximum variation</td>
<td></td>
<td>1 : 2.13</td>
<td>1 : 2.11</td>
</tr>
</tbody>
</table>

These figures show that the refractive index has a relatively small effect on the rotatory power of the \((-\) glycine phenyl ether\). The experiments of Kule(62, 63) and of Kemen and Platt(64) were carried out with hydrocarbons. Compounds of this type should be less susceptible to solvent action than those containing more polar groups, but the molecules employed necessarily contain a branched chain, which implies
an activated position in the chain. If solvent action occurs through this position, then the relative magnitudes of the active bands due to C-C and C-H absorption may well be altered with a consequent alteration in the magnitude of the rotatory power, though the rotatory dispersion will probably remain the same in the visible and near ultra-violet regions.

It seems that it may be necessary to make a complete analysis of the rotatory dispersion, in the regions of transparency and absorption, of a substance in which the main contributions to the rotatory power are due to bands in the near ultra-violet, before a satisfactory estimate of the effect of refractive index can be made. In such a case the relative effect of the indeterminable active absorption bands in the Schumann region would be much reduced.

Substances which show true simple rotatory dispersion usually have all their optically active absorption bands situated in the Schumann region and thus not separable in the Drude equation. As has been pointed out earlier (see page 38), absorption bands in this region correspond to tightly bound electrons, so that it would be expected that the influence of solvents on the rotation constants of such optically active absorption bands would be small, and would tend to influence the various opposing terms similarly, which would explain the generally small influence of solvents on the rotatory dispersion of substances which show simple rotatory dispersion.
in the visible region; it seems probable that the effect of solvents on the rotatory dispersion of such substances would be more marked if the observations were extended into the ultra-violet region.

In contrast to this, substances which show complex dispersion have more than one anisotropic absorption band, and the electrons corresponding to the band of longer wavelength are more loosely bound, and so much more likely to be influenced by solvents than those corresponding to bands in the Schumann region. Thus the relative magnitude of the partial rotations of the different bands is very susceptible to solvent action, with the result that the rotatory dispersion is markedly influenced in a similar manner.
ANALYSIS OF ROTATORY DISPERSION CURVES

An analysis of the form of rotatory dispersion curves in terms of the Brude equation, shows that its shape depends in a definite way on the relative magnitude of the different constants of this equation.

Analysis and comparison of the curves obtained from equations:

\[ \frac{x}{\lambda - \lambda_a} + \frac{K_0}{\lambda - \lambda_b} = \left[ \frac{x}{\lambda - \lambda_b} \right] \]


cshows that there are four types of complex dispersion to be considered, so far as a two-term equation is concerned.

(a) Both terms of the same sign

(1) \( K_1(\lambda - \lambda_a) > K_2(\lambda - \lambda_a) \)

(b) Terms of opposite sign

(3) \( K_1(\lambda - \lambda_a) > K_0(\lambda - \lambda_b) \)

(4) \( K_1(\lambda - \lambda_a) < K_0(\lambda - \lambda_b) \)

(a) (1) The values obtained for a corresponding one-term equation lie between \( \lambda_a \) and \( \lambda_b \). The \( \lambda L/\lambda \) curve is straight for the long wavelengths, but shows a slight curvature towards the \( \lambda \) axis as the absorption bands are approached. This type of dispersion is classified as "complex but normal" or "pseudonormal".

(b) (2) Similar to (1) but the curvature of the plot of \( \lambda L/\lambda \) is increased and \( \lambda_b \) is further displaced though \( \lambda \lambda_a < \lambda \).

(b) (3) In this case, \( \lambda \lambda_a < \lambda \) and the curvature of the plot is usually more pronounced than in (1) and (2). This type of dispersion is normal up to the active band. The curve of \( \lambda L/\lambda \) is convex towards the \( \lambda \) axis. This type is often called quasi-anomalous dispersion.

(b) (4) The curvature of the \( \lambda L/\lambda \) plot is convex towards the \( \lambda \) axis and \( \lambda \lambda_a < \lambda \). The curve also shows a minimum and then increases to infinity, returns from infinity and \( \rightarrow 0 \) for small wavelengths. This corresponds to the inflexion, maximum and reversal of sign of the plot of \( \lambda L/\lambda \) which are the characteristics of anomalous dispersion.
A general idea of the nature of the constants involved can thus be obtained, in some cases, by an inspection of the rotary dispersion curve, but in general it is necessary to calculate a crude equation in order to reveal the nature of the dispersion, since the observed complexity is usually small.

Use of the Dispersion Ratio in Analysis of Rotatory Dispersion

The ratio of the specific rotatory power of a substance, for the mercury violet line at 4358 A., to that for the green line at 5461 A., has been used as a diagnostic test of the nature of the rotatory dispersion in the visible region and is called the "dispersion ratio". Pickard and Kenyon(68) have shown that the dispersion ratios of the secondary aliphatic alcohols have a fairly constant value at 1.65, which corresponds to a one-term equation with $\lambda = 1500$ A. The dispersion ratio must be used with care, since it may be that the two points lie on a curve such that the slope between them would indicate simple dispersion, whilst a full investigation might reveal both complex and anomalous dispersion. If, however, the dispersion ratio is below 1.61, the dispersion is likely to be complex, since this would require an absorption band below 1100 A., an unusual figure for active absorption bands. If the dispersion ratio is below 1.57, the dispersion is certainly complex and anomalous, since this figure corresponds to an absorption band at zero wavelength.
The dispersion ratio may therefore be used as a diagnostic test, provided due caution is exercised:

(1) if the dispersion is definitely complex and anomalous
   1.61-2 possibly complex and anomalous
(2) = 1.65 and remains constant in different solvents, then the dispersion is "simple".
(3) c. 1.70 indicates an absorption band in the photographic ultra-violet region, if the value of the dispersion ratio is constant in different solvents. If the dispersion ratio varies with different solvents the dispersion is probably complex but normal or quasi-anomalous.

Anomalous dispersion usually results in a large variation in the dispersion ratio under different conditions. The chief advantage of the dispersion ratio as a test is that it can be applied immediately at the polarimeter.

**Characteristic Diagrams.**

Armstrong and Walker(65) used a slightly different graphical method of analysing rotatory dispersions. They plotted the rotations of a series of related compounds, for one wavelength as abscissae, and those for other wavelengths as ordinates. Substances which have related dispersions show straight lines, whilst those dispersions which are not related show marked divergences. The "Characteristic Diagrams" so obtained are of four main types:

(1) Those in which the straight lines of the diagram intersect on the line of zero rotation, outside the diagram. This type results from substances having the same dispersive power and the same sign.
(2) The straight lines intersect, but not at zero rotation, and not necessarily all at one point. This type of diagram corresponds to complex but not anomalous dispersion.

(3) The lines intersect at zero rotation but inside the diagram. This type corresponds to substances of similar dispersive power but of opposite sign.

(4) The lines intersect inside the diagram but not on the line of zero rotation. The colour sequence may be reversed. This type corresponds to complex and anomalous dispersion. This type of diagram may also be used to compare the rotatory dispersions of different solutions of the same substance.

Patterson(66) modified the Armstrong and Walker diagram so as to make it more sensitive, by plotting the differences of the rotations from those of a standard wavelength, thus increasing the scale of the diagram. When the dispersion is anomalous the lines for the different wavelengths do not converge to a point on the horizontal axis.

These methods of analysis are no substitute for the practical observation of the complete rotatory dispersion. It has been shown(14) that the infra-red region yields little information as to the nature of the rotatory dispersion, and practical difficulties prevent the measurement of both the absorption and the rotatory power in the Schumann region (i.e. below 3000 Å)

The outline given above refers only to the rotatory dispersion transparency in the region of absorption (measurements in the region of absorption have been discussed by Lowry(14)). Thus at the present time, to provide a proper basis for the discussion of rotatory dispersion it is necessary to measure the rotatory power from c.6700 down to the nearest absorption
band in the ultr-violet region. Means of making the measurements in the visible region are simple and widely available. Apparatus for measurements in the ultraviolet region, on the other hand, is rare and is tedious to use.

In the present investigation, however, through the kindness of Professor E.C.T.orrish F.R.S., it has been possible to make a limited use of the late Professor Lowry's apparatus, the results of this work, together with a short description of the methods employed are described in later sections of this thesis.
Preparation of (-) Glycidyl Phenyl Ether $\text{CH}_3\text{CH} = \text{CH}_2\cdot\text{OPh}$

$\beta$-Chlor $\beta'$-phenoxy-isopropyl alcohol is readily prepared by the reaction between equimolecular proportions of phenol and epichlorohydrin, with sodium hydroxide solution as a catalyst (Poyd & Marle J. 1910, 176).

\[
\begin{align*}
\text{CH}_2\text{Cl} & \quad \text{CH}_2\cdot\text{O.Phet} \\
\text{OH} & \quad \text{HO.Phet} \\
\text{NaOH} & \quad \text{CH}_2\text{Cl}
\end{align*}
\]

Epichlorohydrin $\beta$-chlor$\beta'$-phenoxy-isopropyl alcohol

Then a mixture of equimolecular proportions of $\beta$-chlor$\beta'$-phenoxy-isopropyl alcohol and phthalic anhydride, is allowed to stand for a fortnight in the presence of a slight excess of pyridine, $\beta$-chlor$\beta'$-phenoxy-isopropyl hydrogen phthalate is formed in good yield.

The addition of dry brucine to an equimolecular proportion of $\beta$-chlor$\beta'$-phenoxy hydrogen phthalate dissolved in hot ethyl acetate solution, yields a brucine salt, which slowly crystallises. After seven recrystallisations this salt yields the brucine salt of the (-) hydrogen phthalic ester, optically pure, since further recrystallisation of the brucine salt produces no further increase in the rotatory power of the hydrogen phthalic ester.

The (-) hydrogen phthalic ester is defined as that which a lefvo rotation of plane polarised light, when it is dissolved in diethyl ether.
The β-chlorβ'-phenoxy-isopropyl hydrogen phthalate, when heated in a current of steam in the presence of 12.5M potassium hydroxide solution, yields the (-) glycide phenyl ether.

It is concluded that this ether is optically pure since:

(a) Different specimens of the (-) hydrogen phthalic ester yield the (-) glycide phenyl ether of identical rotatory power on hydrolysis.

(b) The conversion of the supposedly optically pure (-) glycide phenyl ether into the (-)β-chlorβ'-phenoxy-isopropyl alcohol, and reconversion of this into its hydrogen phthalic ester, yields the (-) hydrogen phthalic ester possessing its original rotatory power, within the limits of experimental error.
The Optical Rotatory Dispersion of Glycide Phenyl Ether

A In the Homogeneous State

The rotatory dispersion of (-) glycide phenyl ether in the visible spectrum, plotted as $l\alpha/\lambda$ is nearly a straight line, and the dispersion ratio is 1.63. The dispersion may therefore correspond to a one term Bude equation:

$$\alpha = \frac{K}{\lambda^2 - \lambda_0^2}$$ (16)

Consideration of such an equation, and of the form of the curve of $\alpha/\lambda$ suggests that the dispersion may not be so simple as at first appears, since:

1. The value of $\lambda_0$ obtained (16), varies between 930 A and 1540 A according to the points selected for the evaluation of the equation.
2. The values of $\lambda_0$ in this range are rather low.
3. Examination of the rotatory dispersion of the substance in solution shows it to be complex.
4. The specific rotatory power of the (-) glycide phenyl ether is larger than that usually associated with bands in the Schumann region, and particularly it would be expected that if optically active bands occur at 1100 A, their dissymmetry factor would be low.

In both the visible and the ultra-violet region (670 A - 3160 A) it is possible, by a suitable selection of points, to obtain a straight line for the plot $l\alpha/\lambda$ for the whole range except the
three points of shortest wavelength. This suggests simple
dispersion, and further the first three values obtained for
\( \lambda_0 \) (Table II), are in fair agreement.

Table II

<table>
<thead>
<tr>
<th>Wavelengths used in the Calculation of equation (16)</th>
<th>Wavelength of Calculated Critically active band ( \lambda_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6706 &amp; 5552 A.</td>
<td>1107 A.</td>
</tr>
<tr>
<td>5461 &amp; 3292 A.</td>
<td>1160 A.</td>
</tr>
<tr>
<td>4359 &amp; 3292 A.</td>
<td>1118 A.</td>
</tr>
<tr>
<td>6706 &amp; 5461 A.</td>
<td>1040 A.</td>
</tr>
<tr>
<td>5461 &amp; 4358 A.</td>
<td>963 A.</td>
</tr>
<tr>
<td>4358 &amp; 3693 A.</td>
<td>938 A.</td>
</tr>
<tr>
<td>3693 &amp; 3292 A.</td>
<td>1359 A.</td>
</tr>
</tbody>
</table>

If, however, equations are calculated for points closer together
on the wavelength scale, the values of \( \Delta \) decrease to a minimum,
and then rise again, corresponding to a point of inflexion
on the curve of \( \Delta \). 

The dispersion curve corresponds therefore to complex
dispersion and a two-term equation:

\[
[X] = -\frac{X_1}{X-\lambda_1} - \frac{X_2}{X-\lambda_2}
\]  

A two-term equation of this type was required to express the
rotatory dispersion of tetrahydrofurfuryl alcohol \( \text{(C7)} \).

Fleis, Phepa, Irwin and Kenyon found that, even in this case,
where the plot of \( \Delta \) showed very obvious anomalous dispersion,
the calculation of the two-term Bragg equation presented
considerable difficulty; it was necessary to use a ten-figure
calculating machine to achieve a result. Therefore there
seemed little hope of evaluating such an equation for
glycine phenyl ether, in which the dispersion is only
slightly erroneous; in fact, though the values used in the calculation were chosen from a smoothed curve through the experimental points, a factor of $\sqrt{-1}$ appeared in the result, so that the preceding was justified. The evaluation of the equation from the dispersion curve alone, having proved impossible, it was attempted from two experimental observations, and two known, or likely absorption bands. A series of equations was evaluated in this manner for different pairs of probable optically active absorption bands, and those which showed signs of fitting were considered in greater detail. An examination of Graph 12 will show that it is likely that one of the absorption bands at 2.5980 A. is optically active, and that another band, in the 24200 region, possibly at about 3920 A. is also active. The values, obtained from the equation which gives the best fit, vary from those experimentally determined by rather less than the experimental error. The theoretical curve does not fall off near the absorption band quite as it should. Attempts were made to see whether an improvement would result from the use of a three-term equation, though, as Lowry has pointed out, the experimental accuracy does not usually warrant the use of more than two terms. Three-term equations have, however, been used, notably by Levene and Rothn (25) for 2-bromodestane, which showed optically active bands at 1644 A., 3681 A., and 1330 A.. In the case of the (-)-glycidyl phenyl ether it might be that two of the maxima of the experimentally determined absorption curve are optically active. But the justification of the use of a
three-term equation lies in the fact that it uses a further experimental point (see appendix)

The calculations of the three-term equations were therefore made, using the two observed absorption bands of glycidyl phenyl ether at 2770 A. and 2650 A. about 50 A. being added in each case to allow for the fact that bands, determined by measurements of rotatory dispersion, are usually nearer to the visible region by that amount than the experimentally determined bands. The third band used was that found by Alfr, Fiske, Irwin and Kenyon(6) in tetrahydro-furfuryl alcohol i.e. at 1300 A. The equations resulting from these calculations show some improvement in the magnitude and distribution of the differences from the experimental values, over a two-term equation.

The evaluation of a three-term equation from the experimental dispersion curve alone, would involve the determination of the roots of cubic equations, for which an exact solution is not possible, so that no such operation was attempted. It is difficult, for the same reason, to determine the points of inflexion etc. of a three-term equation.

The calculated Drude equations indicate that there is probably at least one optically active absorption at c. 2600 A., and another in the Schumann region, possibly at about 1300 A. or.

Though, at first sight, it may seem unlikely that induced
Disymmetry should arise in the benzene ring, when the effect of the \(-\text{CN}^-\) group on the absorption spectrum of the benzene ring is considered, it would appear possible that disymmetry could also be transmitted.

The absorption spectrum of the compound, in octane solution, was determined for the ultra-violet region by Dr. F. H. Ewens; it shows:-

1. A shift of the normal benzoid band at 3000 A to 2770 A.
2. The intensity of the above band is increased from $\varepsilon_{\text{max}} = 150$ in benzene, to $\varepsilon_{\text{max}} = 1800$ in phthalic phenyl ester; i.e. the intensity has been increased approximately sixfold.
3. The phthalic band at 1260 A in benzene has been moved to 1100 A.; the intensity remaining approximately constant.

The shift of these two bands toward the longer wavelengths is almost identical, which is in contradiction to the observation of Fieser(69) that conjugation of the ring chain produces a much larger shift in the 3000 A. band. A more satisfactory way of considering the alteration spectrum may be to compare it with a chelal or a chelatic ether, epoxide in particular is appropriate, as the effect produced may be regarded as due to the substitution of the hydrogen of the ester group by the \(-\text{CH}(-\text{O})_{\text{3}}\) group. The following figures are quoted from a table of results given by Fieser(70):
Table III

<table>
<thead>
<tr>
<th>Substance</th>
<th>λ max</th>
<th>ε max</th>
<th>λ max</th>
<th>ε max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph.H</td>
<td>194</td>
<td>6000</td>
<td>298</td>
<td>350</td>
</tr>
<tr>
<td>Ph. Me</td>
<td>-</td>
<td>-</td>
<td>336</td>
<td>300</td>
</tr>
<tr>
<td>Ph. Br</td>
<td>-</td>
<td>-</td>
<td>370</td>
<td>300</td>
</tr>
<tr>
<td>Ph.O Me</td>
<td>-</td>
<td>-</td>
<td>390</td>
<td>300</td>
</tr>
<tr>
<td>Ph. O</td>
<td>-</td>
<td>-</td>
<td>397</td>
<td>1850</td>
</tr>
</tbody>
</table>

Unfortunately, there appears to be no data for the 3000 A. band in the case of piperid and oxazole, so that a proper comparison of the shift of the two bands is not possible.

It can be seen from the above, that the substitution of the hydrogen in the methyl group of anisole by the acetyl ring greatly modifies the absorption of the benzene nucleus, the intensity of the 3500 A. absorption band being increased sixfold, though the wavelength λ max remains approximately constant. Thus it seems possible that the diazymetry of the acetyl ring will have a vicinal action on the symmetry of the absorption bands in the benzene nucleus. Further, Gansh (69) has pointed out that the 3500 C. band in benzene represents absorption "forbidden" by symmetry, and would not take place if vibrations did not occur to destroy that symmetry; it may therefore be that the further destruction of this symmetry, (represented by the increase in intensity of this band) by the action of it of a diazymetric chromophore, may render the band optically active.

Further discussion of these results is deferred to page 64, where it is considered in relation to other effects.
The Optical Rotatory Dispersion of (-)Glycine Phenyl Ether

In Solution in Various Solvents

The rotary dispersion of the (-)glycine phenyl ether has been examined from 6700 Å to 7500 Å in fourteen solvents. In account of the short time available in Cambridge, the observations in the ultra-violet region had to be restricted to one solvent, diethyl ether. The present discussion is therefore mainly confined to results obtained in the visible region.

Solvents may be divided into three classes as far as their effect on the rotary power and dispersion of (-)glycine phenyl ether is concerned.

<table>
<thead>
<tr>
<th>Magnitude of</th>
<th>Solvability of</th>
<th>Rotary Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[α]d</td>
<td>[α]d</td>
<td>[α]d</td>
</tr>
<tr>
<td>(1) Non-polar solvents</td>
<td>Greatest</td>
<td>Least</td>
</tr>
<tr>
<td>(2) Non-homogeneous substance</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>(3) Other solvents except ethers</td>
<td>Intermediate</td>
<td></td>
</tr>
<tr>
<td>(4) Others</td>
<td>Least</td>
<td>Greatest</td>
</tr>
</tbody>
</table>

(The figures are given in Tables VII & VIII pages 32 & 33)

A plot of [α]d against the dispersion ratio shows that the specific rotary power is roughly proportional to the dispersion ratio. It is difficult to ascribe any physical significance to this fact.

It has been shown (see page 32) that the effect of solvents on the rotary power of the (-)glycine phenyl ether must be
ascribed to variation in the term $\beta$ of equation (14).

It is therefore proposed to consider the various factors which may affect this term, each in turn, whilst realising that more than one may be operative in any given case.

The effect of solvents on the quantity $\beta$, i.e. on the dispersion terms, may be due to:

(1) Direct action of the electrostatic field, due to the solvent, on the active molecule.

(2) The diluting effect of the solvent.

(3) The solvent acting as a chromophore.

(4) Alteration in the position of the absorption bands of the active molecule.

(5) Compound formation between solute and solvent.

(6) Alteration of the freedom of rotation about single bonds in the active molecule.
H.C. Rule and his co-workers have accumulated a vast amount of data concerning the influence of dipole moment of the solvent on the rotatory power of the solute. Unfortunately much of this work was concerned with only one wavelength, their more recent observations, alone, being of value in the study of rotatory dispersion. Rule observed a regular decrease in the rotatory power of the solute with increasing polarity of the solvent, in the majority of cases examined.

It has been suggested (71) that the sometimes large influence of solvents on the rotatory power of rigid molecules, may be due to the action of the field, due to the solvent, on the chromophore of the active molecule. Further, the effect of such vicinal actions will be greatest when the resultant dipole of the molecule does not lie along the axes of the important chromophoric groups. Detye (72) has shown that dipolar association will cause a reduction in the internal field of the active molecule, and will generally tend to reduce the rotatory power of the molecule in this way.

The rotatory dispersion of the (-) glycide phenyl ether is not in accordance with the above scheme. Though its solutions in most solvents of low dipole moment, have a higher rotatory power than those in most solvents with a high dipole moment, there are two important exceptions.
1.4.-Dioxan and pyridine. The figures given here have been taken from Tables VII & VIII.

Table IV

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$[\alpha]_{\text{Scl}}^0$</th>
<th>Dispersion Ratio</th>
<th>Dipole Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitromethane</td>
<td>20.65</td>
<td>1.46</td>
<td>3.05</td>
</tr>
<tr>
<td>Acetone</td>
<td>19.72</td>
<td>1.41</td>
<td>3.7</td>
</tr>
<tr>
<td>Pyridine</td>
<td>27.77</td>
<td>1.61</td>
<td>3.11</td>
</tr>
<tr>
<td>n-propyl chloride</td>
<td>14.87</td>
<td>1.38</td>
<td>1.04</td>
</tr>
<tr>
<td>Methyl ether</td>
<td>15.17</td>
<td>1.35</td>
<td>1.34</td>
</tr>
<tr>
<td>1,4-Dioxan</td>
<td>9.93</td>
<td>1.36</td>
<td>0.45</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>35.07</td>
<td>1.70</td>
<td>0.06</td>
</tr>
<tr>
<td>Benzene</td>
<td>50.14</td>
<td>1.68</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The lack of relation between the rotatory power and the dipole moment of the solvent is, no doubt, due to the fact that the epoxide and benzene ring electrophiles are separately affected by the field of the solvent. There is also no apparent relation between the dispersion ratio and the dipole moment of the solvent.

A suggestion that the dipole moment may not be the only factor determining the electrostatic effects of solvents has been made by Davies (73), who shows that the effectiveness of the dipole of the solvent may be reduced by "steric protection". However, even if the dipole moments of the solvents, given above, were corrected for the "steric protection" it would still be impossible to explain the large effect of dioxan compared to that of nitromethane, in terms of the electric field due to the solvent.
(2) The Diluting Effect of the Solvent

If the molecules of a homonuclear substance were to exist in an associated state, such as a dimer, then the tendency of the solvent would be to change the rotatory dispersion from that of a dimer, into that of the simple monomer. The effect solvents would increase in the order of increasing polarity, in accord with the views ofina rule (71). We prefer the use of the term "diluent" in place of the more usual "solvent"; since the effect of a solution on any one molecule of solute is due to (a) other molecules of the same species, and (1) those of the solvent; the advantage of the term "diluent" is therefore obvious.

Intermolecular association through the phenolic ether group would give a dimer, (VIII), in which there is no centre of symmetry if the dimer consists of two molecules of the same configuration, similarly reflection of one molecule in a plane of symmetry produces the other configuration, so that a dimer, produced from one isomer alone, must also lack this element of symmetry.

\[
\text{(VIII)}
\]

The large influence of ethers, might be explained by supposing that the solvent substitutes itself for the partner in the dimer (71), thus causing an alteration in the internal field...
of the active molecule, with a consequent change in the
rotatory power.
This mechanism is one of the most likely, it is therefore
proposed to treat it in more detail in conjunction with
other likely effects at a later stage (see page 64).

(3) Solvent Acting as a Chromophore

If the solvent forms a compound with the solute it may act
as a chromophore. This type of mechanism cannot, however,
satisfactorily explain the rotatory dispersion of solutions
of glycine phenyl ether, since it depends on compound formation
between solute and solvent, which is not in accord with the
observed effect of temperature on ethereal solutions of this
substance.

(4) Displacement of Optically Active Absorption Bands by

Solvent Action

In the determination of ultra-violet absorption spectra it is
usual to employ non-polar solvents, such as n-hexane, so as to
minimize solute-solvent interaction, which may have an
appreciable effect on the absorption spectra, particularly
of a polar molecule. This effect, however, is mainly
confined to alteration in the "fine structure" of the
absorption bands.

Such effects would not have an appreciable influence on the
rotary dispersion unless it were controlled by two hands close together, and only one of them were displaced. The observed anomalies in the rotary dispersion of the (−) glycidyl phenyl ether must therefore be due to some other cause.

(5) Compound Formation between Solute and Solvent

It was at first thought that compound formation, between the solute and the solvent, might explain the pronounced effect of certain solvents on the rotary dispersion of the (−) glycidyl phenyl ether. If compound formation between the epoxide ring and the solvent, or between the oxygen of the phenolic ether group and the solvent, were the cause, then it might be expected that some similar effect would be observed in the rotary dispersion of an optically active phenolic ether, when dissolved in an inactive epoxide or ether.

(−)sec-Butoxy phenyl ether was therefore prepared, and its rotary dispersion examined in the homogeneous state, in solution in diethyl ether, and in solution in di-2-propylene oxide. The observed variations in the dispersion ratio were very small, compared with those observed in the (−)glycidyl phenyl ether, being 1.74 in the homogeneous state, and 1.78 in ether and di-2-propylene oxide. This suggests that the phenolic ether group is not the primary cause of the anomalous dispersion of the (−) glycidyl phenyl ether in solution in ethereal solvents.
Further evidence may be obtained from the study of the effect of temperature on solutions of the (-)glycide phenyl ether. If two molecules were to associate together to form a moderately stable compound it would be expected that on raising the temperature, this compound would tend to dissociate with a final return to the simple state. If, therefore, the complex addition compound between solute and solvent were to exhibit complex rotatory dispersion, and the simple substance simple rotatory dispersion, then it would be expected that, on raising the temperature, the rotatory dispersion of the solution would pass from the complex towards simplicity.

However, a solution of the (-)glycide phenyl ether in n-butyl ether, at room temperature, shows complex dispersion, and on warming to 100°C the dispersion becomes more, rather than less, complex since the curve of passes from a simple curve at room temperature, to one which shows a maximum at 41°C, and finally to one showing a reversal of sign at 61°C. It may therefore be concluded, despite the limited region of the spectrum examined, that on raising the temperature the dispersion moves further away from that shown by the homogeneous substance.

It would therefore appear that direct compound formation between solute and solvent, does not provide an explanation of the change in the rotatory dispersion of the (-)glycide phenyl ether when dissolved in ethereal solvents. Further
it is a reasonable assumption that compound formation is
clearly not directly responsible for the alteration of
the rotated plane of the homogeneous (-) glycine proyl
ether when dissolved in other solvents.

(6) Restriction of Rotation about Single Bonds

If steric hindrance is possible about a single bond in the
molecule, then a new symmetric centre may be introduced.
This restriction need not be complete to affect the optical
activity of a substance.

If there are two positions A & B in which a group is
predominantly found, with respect to rotation about a single
bond, then the rotivity of the substance will be given by:

\[ \Lambda = n_A \Lambda_A + n_B \Lambda_B \]  

where \( n_A \) & \( n_B \) are the fractions of the total number of
molecules which are in positions A & B respectively.

\( \Lambda_A \) & \( \Lambda_B \) are the rotivities due to these positions
in addition each of the terms \( \Lambda_A, \Lambda_B \) will consist of two parts:

\[ \Lambda_A = \Lambda_0 + \Lambda'' \]

where \( \Lambda_0 \) = the rotivity assuming free rotation,

\( \Lambda'' \) = the increment of rotivity due to position A.

Thus when all positions are equally probable, the terms
\( \Lambda'' \) & \( \Lambda''_B \) etc. cancel out, and no contribution to the rotatory
power of the molecule occurs. If there are preferred
positions about a single bond, then the rotivity will be
influenced by these positions, and by the extent to which
they are held.
Since restricted rotation has been shown to occur, even in ethene at room temperature, it is probable that the pure term is seldom observed except in molecules of the type \( \text{CH}_2\text{CH}_2\text{C} \) \text{H}_4\text{Cl} \), in which the various atoms attached to the central atom, are circularly symmetrical about the bond axis.

Considering the rotation of a non-circularly symmetrical group about a bond vertical to the paper (IX) it can be seen that none of the positions of the energy troughs is equivalent to any other, since these positions will depend on the relative magnitude, polarisabilities etc. of the groups. The magnitude of the restricted rotation so produced will depend on the probability of each state, and will generally be small, but it is no different in kind from the restricted rotation which causes optical activity in the diphosphoryl series.

The effect of this type of restricted rotation on the properties of an optically active substance will be:

(1) where one position is predominantly preferred for each optical isomer, a new element of chirality will be produced, with a corresponding contribution to the optical rotatory power of the substance.

(2) when two equivalent positions, on opposite sides of the bond, are equally held the result will be to produce diastereoisomers.
The effect of restricted rotation would be expected to decrease with increasing temperature, and similarly a decrease might be expected on solution in polar solvents, since these associate with polar parts of the molecule, tending to neutralise the partial charges of the dipole, and thus making free rotation easier, where the restriction is due to electrostatic forces. The results obtained for the (-)glycine phenyl ether are more in accord with this mechanism than with any other. If it be assumed that some kind of interaction takes place between the hydrogen atom in the ortho position in the benzene nucleus, and the \(-\text{CH} - \text{CH}_2\) group of the molecule, it may be shown that only one preferred position exists, so that another centre of dissymmetry is introduced, the phenyl group itself being affected.

As has been pointed out earlier it is not necessary that restriction of rotation should be complete for an effect to be produced on the rotatory dispersion, but merely that at any given instant more molecules are to be found in one position, with respect to rotation about a single bond, than in any other position, though the magnitude of the effect in this case would suggest that the predominance of one position is large.

Hydrogen bonding provides the most ready explanation of the postulated affinity between the hydrogen atom of the benzene nucleus and the \(-\text{CH} - \text{CH}_2\) group. The possibilities of such bonding have been reviewed by Hunter\(^{(73)}\) as follows:
Hydrogen bonding of the type CH-O and CH-N is so weak that it is manifested only under the influence of activating atoms, or groups tending to promote the ionisation of the hydrogen atom, as in chloroform, hydrogen cyanide and phenyl acetylene. Even under these conditions it appears not to have been detected by molecular weight methods, except perhaps in hydrogen cyanide. However, the application of more sensitive methods shows the existence of intermolecular bonding of a weak type, and the participation of CH groups in chelate hydrogen bond formation has frequently been postulated to account for certain anomalies in the di-substituted derivatives of benzene and other compounds. For example, the superior volatility of o-nitrotoluene has been attributed to chelate hydrogen bonding. The evidence from other sources referring to such a mechanism is not strong, but Hückel(74) has suggested that measurements of optical activity may be more sensitive to this type of bonding than the usual methods of detection.

o-Nitrotoluene presumably retains its chelate bond formation up to its boiling point, but it is possible that a weak type of hydrogen bond, such as is postulated for glycolide phenyl ether, could be disrupted as the temperature of the liquid is raised.

Arguments developed in this thesis concerning the restriction of rotation in glycolide phenyl ether by weak hydrogen bond formation, apply equally to a mechanism similar to that postulated to account for the rearrangement of phenyl allyl ether*.

C The Effect of Temperature on the Rotatory Dispersion of

(-)-Glycide Pheryl Ether

When the temperature of a liquid is raised the molecules acquire increased freedom of rotation about single bonds, which, Kaurnann Walter and Eyring(71) state, results in a diminution of the first order contributions to the rotatory power, and thus in a lowering of the specific rotatory power. In addition the rotatory power will be lowered still further as a result of the decreased density, which causes lowering of the refractive index (see equation 9). This provides another argument in favour of the use of the rotivity, as being a more fundamental quantity than the specific rotatory power.

Raising the temperature should have a much less effect on compounds with a rigid structure, such that the rotation of the groups which affect the rotatory power is prevented, than in the case of open chain molecules. Reduction in the rotatory power of such molecules consequent upon increased temperature, would be due to the reduction of the refractive index, and possibly also to an alteration of the molecular framework, such alterations would be small.

There is a further effect of temperature increase to be considered, namely the possibility that the energy levels

\[ \phi^2 \frac{\pi^4 N}{\lambda^2} \cdot \frac{\pi^2 \tau^2}{3} \beta \]  

(9)
of the molecule may be altered, thus causing a change in the ground and excited states which make up the factors \( \beta \), etc., which together form the term \( \beta \), (see page 10), in equation (9). This may occur even in isolated molecules, as for example in the dilute vapour\(^{(24)}\), and is not necessarily dependent on interaction with other molecules.

Kenny and Pickard\(^{(76)}\) showed that, in the carbinol series \( R.C\text{H}(\text{CH})\_2 \cdot \text{CH} \), the maximum decrease in rotatory power per 100°C rise in temperature was 30° for \( R = \text{ethyl} \), and 10° for the higher homologues. Carbinols of the general formula \( R.C\text{H}(\text{CH})\_2 \cdot \text{CH} \)\(^{(77)}\) showed a similar decrease. A measure is thus provided of the reduction in rotatory power, to be expected in simple open chain molecules. Kenny and Pickard\(^{(78)}\) also examined the effect of temperature on \( \text{1-menthol} \), and showed that the rotatory power was nearly constant over a range of 100°C. Whilst \( \text{Core and Jersey} \)\(^{(72)}\) showed that the difference between the rotatory power of \( \text{camphor} \), in solution in \( \text{cyclohexane} \) at 20°C, and in the vapour state at 180°C, was only some 20° in the region of absorption.

These results therefore support the conclusion that open chain compounds show only a small decrease in their specific rotatory powers with rise in temperature, and that under similar conditions, the effect of temperature on closed ring compounds is even smaller.
The homogeneous (-)-glycide phenyl ether shows a marked reduction in rotatory power and dispersion ratio with rise in temperature, as shown:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>[α] 646.1</th>
<th>[α] 1365° 646.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.6</td>
<td>28.8</td>
<td>1.06</td>
</tr>
<tr>
<td>42.8</td>
<td>23.5</td>
<td>1.68</td>
</tr>
<tr>
<td>61</td>
<td>19.8</td>
<td>1.63</td>
</tr>
<tr>
<td>80</td>
<td>16.7</td>
<td>1.55</td>
</tr>
<tr>
<td>98</td>
<td>14.3</td>
<td>1.55</td>
</tr>
<tr>
<td>141</td>
<td>7.5</td>
<td>1.24</td>
</tr>
<tr>
<td>174</td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

This marked reduction in the rotatory power with increasing temperature, together with the accompanying change in the dispersion ratio, lends weight to the view that the cause of the anomalous dispersion is not to be found in the vicinal actions of the solvent, but is due to a change in the molecular state. In the discussion of solvent action it was pointed out that restricted rotation of the side chain of glycide phenyl ether could provide a fairly satisfactory explanation of the observed rotatory dispersion; this explanation is also valid for the effect of temperature.

The results of Gerrard and Konyon (82) for d-phenyl terephthyl cortisol are somewhat analogous:

\[
\begin{align*}
[\alpha]_{5461}^{60} & = 51.88' \\
[\alpha]_{4355}^{60} & = 61.60 \\
[\alpha]_{5461}^{60} & = 6.51' \\
[\alpha]_{4355}^{60} & = 14.70 \\
\end{align*}
\]

Thus on raising the temperature by 65° the rotatory power for \( \lambda = 946.1 \) dropped to 20° of its former value. The d-phenyl
Benzyl carbinal also behaved in a highly anomalous manner when dissolved in solvents, there being no apparent connection between the polarity of the solvent and the rotatory power of the solute, or the dispersion ratio. Methyl benzyl carbinal, on the other hand, showed no dependence of rotatory power on temperature, other than might be attributed to alteration in refractive index: \([-\alpha]^0_{\text{D}} = 26.85^\circ\] \([-\alpha]^0_{\text{D}} = 26.38^\circ\], its n-alkyl ethers behaved similarly, except the methyl ether which showed a large temperature dependence in its rotatory power, the dispersion ratio being also slightly affected.

There seems to be little reason why phenyl benzyl carbinal should show a much greater tendency to molecular association than methyl benzyl carbinal, so that these results, also, might be interpreted on the basis of restricted rotation caused by the introduction of a phenyl group.

The rotatory dispersion of \((-\)glycide phenyl ether) in n-butyl ether solution, changes progressively with rise in temperature. At 41°C an inflexion (in the curve of \(\alpha/\lambda\)) occurs in the visible red region of the spectrum and a maximum in the blue region. At 50°C both these have disappeared and a reversal of sign occurs in the green. The temperature effect in this solution is in the same direction as in the homogeneous substance, but is much more pronounced. These observations are in accord with the view that internal association occurs in homogeneous glycide ether at room temperature, which is partly broken down on raising the temperature.
The Relation Between the Rotatory Dispersion, and the Structure of Glycidyl Phenyl Ether

In the foregoing sections it has been shown that the anomalous rotatory dispersion of the (-)glycidyl phenyl ether may be due to either of two mechanisms:—

(a) Intermolecular association between molecules of the homogeneous compound.

(b) Intramolecular ring formation.

It is therefore proposed to consider these two mechanisms in greater detail.

The effect of increasing the temperature of the homogeneous substance, is to cause its rotatory dispersion to simulate that shown by its solutions in polar solvents. Comparison with the results of other workers (76, 77) makes it certain that the large change in the rotatory dispersion, which is produced by increasing the temperature of the homogeneous substance, is due to a change in the state of the molecule, since the changes in the external field due to the rise in temperature, would not directly affect the chromophores of the molecule sufficiently to account for the magnitude of the effect.

Since the dispersion ratio of the homogeneous substance, at 141°C, is 1.48, the rotatory dispersion at this temperature must be complex; but since increasing the
temperature encourages free rotation and tends to disrupt association complexes, at a high temperature the compound is in a simpler molecular state than at room temperature, i.e., the simple molecule of glycidyl phenyl ether has a more complex rotatory dispersion than the complex molecule; in which the increased dissymmetry, consequent upon the restriction of the freedom of rotation, produces a partial rotation which largely nullifies one of the terms of the brute equation of the simple molecule.

It may be shown (see appendix) that, while the rotatory dispersion of the homogeneous glycidyl phenyl ether may be represented by a two-term brute equation, (a three-term equation gives only a slight improvement), a three-term equation is required to represent the rotatory dispersion of its ethereal solution (when this is calculated partly from the wavelengths of absorption bands).

Comparison of the constants, obtained by this method for the least three-term equations of (a) the homogeneous substance, and (b) its solution in diethyl ether (both based on the same absorption bands), shows that in the ethereal solution the contribution of the 2620, 2700 & 1300 λ bands is increased by factor 30, 25, and 2 respectively, above the values

\[ [\alpha] = \frac{-1,234,474}{\lambda - 0.372924} + \frac{8,047,224}{\lambda - 0.072550} - \frac{8,772,850}{\lambda - 0.185500} \]

\[ [\alpha]_b = \frac{-40.122,236}{\lambda - 0.372924} + \frac{50.991,837}{\lambda - 0.072550} - \frac{14,462,129}{\lambda - 0.185500} \]
partaining to the homogeneous material. Thus, in ethereal solution, the difference between the rotation constants of the two bands in the 2600 Å region (which are opposite in sign), becomes of the same order as the rotation constant of the band in the Schumann region, and opposite in sign to it.

The observed rotation is, thus, much reduced, and the anomaly becomes more marked than in the homogeneous material. In the homogeneous material this difference between "p" and "q" is of the order of one tenth of "p" the rotation constant of the band in the Schumann region.

Thus the most significant effect of the solution in ether is to increase considerably the first order contribution of the benzene nucleus.

A similar conclusion may be drawn from the position of the maximum and reversal of sign (in the curve of δ/λ) shown by a solution of the (-)-glycine phenyl ether in n-butyl ether.

These points are related to the constants of a two-term equation by the following expressions (14):

\[
\begin{align*}
\text{Maximum: } & \frac{\lambda_1 - \lambda_2}{\lambda_1 - \lambda_3} = \sqrt{\frac{K_1}{K_2}} \\
\text{Reversal of Sign: } & \frac{\lambda_R^* - \lambda_2}{\lambda_R^* - \lambda_1} = \frac{K_1}{K_2}
\end{align*}
\]

where \(\lambda_1\), wavelength of maximum; \(\lambda_R^*\), wavelength of reversal of sign; \(\lambda_1^*\), wavelength of last and last optically active bands. \(K_1\) and \(K_2\) are the corresponding rotation constants.

Either of these relations enables the ratio of \(K_1/K_2\) to be calculated, if the wavelengths of the absorption bands are assumed. The maximum (with \(\lambda_1 = 9820\) Å and \(\lambda_2 = 1390\)) yields \(K_1/K_2 = 0.67\) for the solution at 41°C, whilst the reversal of
sign yields $K_1/K_2 = 0.75$, for the solution at $100^\circ C$. Both these results are slightly higher than the value of 0.64 for the solution in diethyl ether (obtained by reducing the three-term equation to a two-term equation with $\lambda_\alpha$ as above).

In the above discussion it has been assumed that the position of the optically active absorption bands is unaffected by the solution in solvents, since the displacement of the bands is not likely to be large enough to alter the order of magnitude of the various terms of the Debye equation.

An experimental determination of the effect of ethereal solvents on the absorption spectrum of glycidyl phenyl ether is, however, awaited with interest.

As the rotatory dispersion of phenolic ethers seems to have been only cursorily examined, it was considered desirable to prepare a specimen of active sec. octyl phenyl ether for the observation of its rotatory dispersion in the ultra-violet region of the spectrum. Although, in the region examined, down to 3600 A, the plot of $\delta/\lambda$ for this substance is a straight line, it is probable that the dispersion is really complex, since the dispersion constants, obtained from different pairs of wavelengths by means of a one term equation, (Table VI) vary by some 12°, which is unlikely to be due to experimental error. The figures have a minimum value, which corresponds to an inflexion on the curve of $\kappa_\alpha$ and $\kappa_\beta/\lambda^2$. The occurrence of this inflexion would necessitate two terms of
Since the alkoxy group is known to have a strong influence on the absorption of the benzene nucleus (Table III), and further since the nucleus has been shown to be subject to vicinal actions in glycidic phenyl ether, it is possible that the absorption band at 2800 Å in sec-octyl phenyl ether may also be optically active. The values for $\lambda_0$ must therefore lie between the band at 2800 Å and a further band in the Schumann region.

Thus both glycidic phenyl ether and octyl phenyl ether show complex dispersion.

The change in the rotatory dispersion of the (-)glycidic phenyl ether as a result of its solution in different solvents can be ascribed to either intermolecular association or intramolecular ring formation. The question arises as to how these two mechanisms can bring about this change. Important in this connection is the principle of Optical Superposition of van't Hoff, and Guye and Gauthier, which suggests that the contribution of each asymmetric carbon atom to the total rotatory power of the molecule...
is independent of the configurations of the other atoms.

Guye and Gautier expressed this as follows:-

(1) In a molecule containing several asymmetric carbon atoms each of them behaves as if the rest of the molecule were inactive.

(2) The optical effects of the different carbon atoms in the same molecule can be added algebraically.

As a result the rotatory power of molecule containing several asymmetric carbon atoms will be equal to the algebraic sum of the rotatory powers of each asymmetric atom. This principle applies only where the different asymmetric atoms differ in configuration alone. But it may be applied with caution to the problem of association between molecules such as glycidyl phenyl ether, substituting the term "centre of dissymmetry" for "asymmetric atom".

Association is believed to take place between ether molecules if this were to occur so that two molecules of glycidyl phenyl ether were linked by weak forces from the ethereal oxygen atoms then the alteration in the vicinal actions owing to the association would be small. A slight increase in the rotatory power might be expected, as a result of the increased restriction of rotation, but the total effect would not be large enough to explain the observed alteration in the rotatory dispersion of glycidyl phenyl ether when dissolved in polar solvents.

If, however, association were to occur through the oxygen atoms in the epoxide ring, then some modification in the frequency
and activity of this chromophore would be expected; it would however have less influence on the partial rotation of the phenyl group, which has been shown to be mainly responsible for the change in the rotatory dispersion.

It may however be that association takes place at two points in the molecule, corresponding to its two oxygen atoms. This association may be achieved in two ways:

(1) The molecules may lie parallel to one another and in the same direction, as shown (X):

(X)

The above dimer has no plane of symmetry since both halves are of the same configuration. In this case, if the bonding were strong enough to resist disruption under the conditions of observation, a first order increase in the partial rotations of each centre of dissymmetry might be expected.

(2) The molecules might associate so that they lie parallel to one another, but in opposite directions (XI):

(XI)

For the reason outlined above (page 62) this dimer contains neither a plane nor a centre of symmetry. The effect of such a conformation would be similar to that observable with
"dipolar association", namely a general decrease in rotatory power, since the partial rotations of each half of the dipolar association will be in opposition and the residual rotation will then be that due to the association complex itself. This conclusion is in line with the principle of Optical Superposition of van't Hoff. Both of the above mechanisms are contrary to the observed changes in the rotatory dispersion of the (−)glycidyl phenyl ether, though the first case would suffice to explain the change in magnitude of the rotatory power, since the substance is dissolved in polar solvents. Furthermore, they do not account for the change in the rotation constant of the long wave band whilst the rotation constant of the band in the Schumann region remains nearly constant.

There is however a further consideration, namely that since the contribution of the long wave band is due to induced dissymmetry, then any influence which tends to "drain off" the bathochromic effect of the epoxide ring, would be expected to affect the partial rotation of the 2800 Å band. It is improbable that the kind of association which is postulated (74) to occur in ethers will involve forces strong enough to achieve this, since the association is not detectable by molecular weight methods of determination.

* When a group is substituted for a hydrogen atom, attached to a chromophoric system, the increase in χ₁ of its selective absorption peaks is called the "bathochromic effect" of the substituting group.
The alternative hypothesis of partial restricted rotation resulting from weak hydrogen bond formation is more in conformity with the observed optical data.

A consideration of the various radii of the atoms, together with the angles between the bonds (Figure 9), shows that the rotation of the side chain about the C-N bond is not restricted by strong forces since there is a maximum clearance of 1.8 Å, and a minimum clearance of 0.6 Å between the relevant atoms as represented by their covalent radii. If however van der Waals radii are used in the calculation, then there is a minimum overlap between the H of the 2CH₃ group and the H of the benzene nucleus of 0.3 Å and a maximum overlap of 0.9 Å. The restriction of rotation about this bond will therefore result in the positions of minimum energy. The effect of solvents on this restriction should be slight so that it does not, in itself, explain the observed dispersion.

The only remaining way in which the rotation of the side chain may be restricted is by interaction between the -OH - CH₃ group and the hydrogen attached to the benzene nucleus; this might occur through hydrogen bonding between the oxygen of the oxazoline ring and the hydrogen of the nucleus (see page 85). This would result in a seven-membered ring. It can be seen more readily from a model that (XII) and (XIII) are not identical, nor are they mirror images of one another, so that they correspond more to geometrical isomers. The
Figure 2

The values of the bond distances and angles used in this diagram are given on page 74.

SCALE: 5 cm = 1 Å.
### Values Used in Figure 2

Figures taken from Pauling (84).

Scale: 5 cm = 1 Å.

#### Covalent Bond Distances

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O</td>
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</tr>
<tr>
<td>C-H</td>
<td>1.07 Å</td>
<td>3.25 cm</td>
</tr>
</tbody>
</table>

#### Covalent Radii

<table>
<thead>
<tr>
<th>Atom</th>
<th>Radius</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
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<td>3.85 cm</td>
</tr>
<tr>
<td>O</td>
<td>0.65 Å</td>
<td>3.30 cm</td>
</tr>
<tr>
<td>H</td>
<td>0.30 Å</td>
<td>1.50 cm</td>
</tr>
</tbody>
</table>

#### Van der Waals Radii

- **Methylene group, maximum radius**: 2.0 Å (10 cm)
- **Methylene group, minimum radius**: 1.4 Å (7 cm)
- **Hydrogen atom**: 1.2 Å (6 cm)

#### Found

**For Covalent Forces**

- Maximum clearance: 6.0 cm 1.8 Å
- Minimum clearance: 4.0 cm 0.8 Å

**For van der Waals Forces**

- Maximum overlap: 4.5 cm 0.9 Å
- Minimum overlap: 1.5 cm 0.3 Å

---

![Diagram](attachment:image.png)
(*)-glycine phenyl ether will produce a similar pair, each of which will be the mirror image of one of the forms produced from the (-)-glycine phenyl ether. There will thus be four possible active forms of glycine phenyl ether if ring formation takes place. Further since XII and XIII are structural isomers, rather than optical isomers, they will differ in physical properties and, in particular, in internal energy. Then ring formation occurs therefore there will be a greater tendency for one isomer to be formed rather than the other. In this way a new contribution to the dissymmetry of the molecule will be produced.

Since the induced dissymmetry lies in the benzene ring and in the seven-membered ring, it would be expected that the contribution of the ring formation to the rotatory power would be due mainly to the absorption band of the phenyl radical. This expectation is, in fact, realised. The partial rotation of the phenyl radical produced by this ring formation, is opposite in sign, and almost equal in magnitude, to that already present, so that the rotatory power of the group is reduced; and since this is opposite in sign to the partial rotation of the Schumann region, the total rotatory power of the molecule is increased, as is commonly observed with ring formation(71). The reduction of the partial rotation of the phenyl radical results in pseudo-simple dispersion in the visible and near ultra-violet regions. The partial rotation due to the absorption band in the Schumann region is also reduced somewhat.
The effect of ring formation may be considered in another way; if the original dielectric of the phenyl radical were due to "induction" along the side chain, then a contribution of opposite sign might be expected as a result of "induction" from the other end of the side chain, which is weakly bonded to the hydrogen atom of the benzene nucleus.

In the above treatment the particular effects of different solvents have been neglected. It is noticeable that the solvents which produce the greatest alteration of the rotatory dispersion from that of the homogeneous substance, are all ethers. Even 1,4-dioxan, which at c = 20 shows a small effect behaves very similarly to ether at c = 10. In diethyl ether, on the other hand, the dispersion ratio at c = 10 is very nearly the same as at c = 1. These observations are in conformity with the view that the change in the observed rotatory dispersion is due to the break down of association complexes or of ring formation, since the greater ease with which diethyl ether acts, is no doubt due to its smaller moment. In the case of other solvents with a low dipole moment the dispersion resembles pyridine in, so that diastere appears to act more as an ether than as a non-polar solvent.

The rotatory dispersion in polar solvents, except pyridine, was intermediate in character between that shown in solution in non-polar solvents, and that observed for solutions in ethereal solvents. The dispersion of the solution in pyridine
It is difficult to fit into the general picture.

The behaviour of the rotatory dispersion of the (−)-glycidyl phenyl ether when dissolved in atheral solvents may sometimes be considered as the sum of two factors:

(a) The polar character of the ether molecule.

(b) The presence of an atheral oxygen atom, which appears to have a specific action. Possibly this may be connected with the presence in the molecule of alycidic ether of atheral oxygen atom (C-hydro-hydro-sulfuryl alcohol also behaves anomalously in atheral solution).

Since it seems probable that the rotatory dispersion of alycidic phenyl ether may be largely influenced by the alycidine ring it is proposed to give a brief consideration to its structure.

**Structure of the Epoxy Ring**

Walsh[88] has recently suggested that the structure of the alylene oxide ring should be represented as OCH₂⁻CH₂⁻, which contains a strong dipole OCH₂⁻CH₂⁻. This suggestion has been supported by Linnet[77].

The abnormal effects of ethers upon the rotatory dispersion of alycidic phenyl ether may be due to the stability of the complexes formed by dipolar association between the alycidine ring and the solvent ether (XIV).
In this way the strong dipole (Welsh 16) compares it to lactone of the crotonic ring will be partially neutralized, and its affinity for the hydrogen atom of the benzene nucleus consequently reduced, resulting in the opening of the seven-membered ring, and a change in the rotatory dispersion.

**GENERAL CONCLUSIONS**

The conclusions reached as to the cause of the rotatory dispersion shown by the (-)-crotonic phenyl ether, may be briefly summarized:

1. The rotatory dispersion is complex, requiring at least two terms of the crude equation for its representation. It is probable that an optically active absorption band occurs at c. 2500 A and another in the Schumann region.

2. The effect of temperature on the dispersion of the homogeneous substance, and on its solution in ether, suggests that in the homogeneous state it exists either as an association complex, or as an internal ring compound.

3. The nature of the variation of the rotatory dispersion with change of solvent suggests that internal ring formation is the most probable cause of the anomaly.
The rotatory dispersion of the (−) hydrogen phthalic ester of \(\beta\) chlor\(\beta\) hydroxy-isobutyric alcohol appears to be complex since the dispersion ratios are high and variable in different solvents, and the magnitude of the specific rotatory power varies markedly from solvent to solvent. When an Arrhenius and solvent diagram is plotted for different solutions of the (−) hydrogen phthalic ester, the lines for the different wavelengths converge at the origin except that for \(\lambda = 656 \text{ Å}\); the line of the Patterson diagram behave similarly. The low values observed for solutions in pyridine and carbon tetrachloride also indicate complexity in the dispersion.
Experimental Section

Preparation of \(\text{Cl-\(\beta\)}\)Chlor\(\beta\)-Chenoxyl-Isoproxy-Alcohol\(\text{(EG)}\)

To a solution of phenol (376 gms.) in epichlorhydrin (376 gms.), 2 gms. of caustic soda in 20 ccm. of water were added, and the mixture allowed to stand for six weeks with occasional shaking.

The mixture was then dissolved in ether, and the ethereal solution was washed three times with dilute caustic soda solution to remove unchanged phenol, and then three times with water. (The separation of the two layers was difficult owing to the formation of foam, which was lessened by the addition of sodium chloride). The ethereal solution was dried over anhydrous potassium carbonate. The ether was then removed on the steam bath, and the residue distilled under reduced pressure. The following fractions were collected:-

Fraction (1) t.p. 25-125/18mm.
(2) t.p. 134-139/7mm. 349 gms.
(3) t.p. 139-144/7mm. 40 gms.
(4) Solid residue Small amount

Fractions (2) & (3) were combined and redistilled giving:-
364 gms. t.p. 134-136/0mm. i.e. 41% of the theoretical yield.

The solid residue was glycerol\(\alpha\) diphenyl ether, m.p. 89° (69)

Found, C = 78.4 H = 6.4 0 = 15.2, \(\text{C}_{15}\text{H}_{10}\text{O}_3\) requires:
C = 75.7 H = 6.6 0 = 18.7
Preparation of the dl-Hydrogen Phthalic Ester of

$\beta$-Chloro$\beta$-Phenoxy-Isopropyl Alcohol

Phthalic anhydride, 222 gms. (1.8 moles) was dissolved in hot dry pyridine, 188 gms. (1.7 moles), the mixture was allowed to cool somewhat; $\beta$-chloro$\beta$-phenoxy-isopropyl alcohol, 370 gms. (1.5 moles) was added, and the mixture allowed to stand for seven to fourteen days. It was then diluted with acetone and the resulting homogeneous solution poured into an excess of dilute hydrochloric acid and ice with stirring. The precipitated gummy mass was pounded until it became a crystalline powder, it was then filtered off and dissolved in ether. The ethereal solution was extracted with sodium bicarbonate solution, and the extracts cooled with ice and acidified with hydrochloric acid. The precipitated hydrogen phthalic ester was dissolved in ether, and the ethereal solution dried over anhydrous calcium chloride. This solution was then concentrated, and light petroleum-ether added, the hydrogen phthalic ester separated as an oil which crystallised on scratching. Yield 436 gms. i.e. 87% of the theoretical amount.

A test portion dissolved in chloroform, leaving only a slight turbidity, thus proving that the material contained only a trace of phthalic acid, since this is practically insoluble in dry chloroform.

When recrystallised from ether-light petrol mixture, the hydrogen phthalic ester is obtained as colourless plates
m.p. 97-98°C. The equivalent weight was determined by rapid titration with N/10 caustic soda solution, using phenolphthalein as indicator:— Found, E.W. = 334.7

\[ \text{C}_{17}\text{H}_{10}\text{O}_5\text{Cl} \text{ requires 334.5.} \]

Sometimes the hydrogen phthalic ester so obtained is deep yellow in colour, in which case it may be decolourised by recrystallisation from glacial acetic acid.

Then a small quantity of toluene is added to the pyridine hydrogen phthalic ester mixture, in place of the acetone, as described above, the hydrogen phthalic ester crystallises in the toluene layer during the extraction of the pyridine by means of hydrochloric acid. The material so obtained is in a pure condition.

Preparation of \((-\beta\text{Chloro})\beta\text{Phenoxo-isopropyl hydrogen phthalate}\)

\(\beta\text{Chloro}\beta\text{phenoxo-isopropyl hydrogen phthalate, 360 gms., was dissolved in ethyl acetate (distilled from calcium chloride), and 765 gms. of dry brucine added. The crystals of the brucine salt which had separated after two weeks, (m.p.128-117°C) were recrystallised, four times from ethyl acetate, followed by five times from acetone. The weight of the tenth crop was 44 gms.}

The ninth and tenth crops of crystals yielded, after decomposition, hydrogen phthalic esters of identical rotatory power \([\alpha]_D^{19} = -18.2\) (in ether), thus suggesting that optical resolution was complete.
The resolution proceeded smoothly so far as increase in optical purity was concerned, but was marred by the production of quantities of brucine hydrogen phthalate at each stage of the fractional crystallisation, this impurity was largely removed by taking advantage of its very sparing solubility and filtering off the solid, which was slow in dissolving, at each recrystallisation.

The (-)hydrogen phthalic ester of \(\beta\)-chloro-\(\beta\)-phenoxymethyl alcohol was obtained from the crop of the brucine salt by pouring cold dilute hydrochloric acid into a slurry of the brucine salt in acetone. The liquid hydrogen phthalic ester so obtained was extracted with ether, the ethereal extract washed with dilute hydrochloric acid, and the ester then extracted from the ethereal solution with an excess of cold saturated sodium bicarbonate solution. The acid ester was then reprecipitated by pouring the alkaline solution into cold hydrochloric acid and removed by extraction with ether. The ethereal solution was washed with water and then dried over anhydrous sodium sulphate. The main bulk of the ether was removed under slightly reduced pressure in a bath of warm water, and the last trace of ether by prolonged evacuation in a desiccator.

The hydrogen phthalic ester so obtained is a clear, pale brown, viscous liquid, having \(\delta_2^\circ = -12.2^\circ\) (in ether), which shows no tendency to crystallise.
(-)\(\beta\)-Chlor\(\beta\)'-phenoxo-isopropyl hydrogen phthalate of 80% of the maximum possible activity, may be obtained by recrystallising the original brucine salt (of the di-hydrogen phthalic ester) twice, liberation of the hydrogen phthalate ester, and then allowing a concentrated solution of the ester in ether to stand, when a crystalline crop of low activity \(\left( [\alpha]_D = -65^\circ \text{ (in ether)} \right)\) separates, leaving in solution an uncrystallisable oil having \(\left( [\alpha]_D = -10.47^\circ \text{ (in ether)} \right)\).
Hydrolysis of the Hydrogen Phthalic Ester of \( \beta \)-Chloro-\( \beta \)-Phenoxo-iso-propyl Alcohol

Some fourteen experiments were undertaken with a view to discovering the most suitable conditions for the hydrolysis of \( \beta \)-chloro-\( \beta \)-phenoxo-iso-propyl hydrogen phthalate. It was found impossible to obtain the pure \( \beta \)-chloro-\( \beta \)-phenoxo-iso-propyl alcohol \( \left( n^0_{D} = 1.5395 \right) \) from its hydrogen phthalic ester. An attempt was therefore made to find the most suitable method for the production of glycide phenyl ether \( \left( \text{glycine} \right) \) \( \left( n^0_{D} = 1.5310 \right) \).

The method employed in all cases, except No. 3 (page 63), was to place the hydrogen phthalic ester in a distilling flask, with a suitably bent side arm, to add the reagent and to pass a current of steam immediately. The aqueous distillate was extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate. The ether was then removed on a warm water bath under slightly reduced pressure, and the residue then distilled under reduced pressure.

The results of these experiments are summarized in the table given overleaf (page 65). It will be seen that the best yield of \( \text{xxx} \) glycide phenyl ether was obtained using 3 gms. of the hydrogen phthalic ester, and 5 cc. of 12.5% potassium hydroxide, the volume was kept approximately constant during the steam distillation in all cases.
<table>
<thead>
<tr>
<th>Test for</th>
<th>Distillate</th>
<th>Residue Excluding Phthalate Acid</th>
<th>Phthalate Acid</th>
<th>Gas or Distillate</th>
<th>No. of Gas or Hydrogen Phthalate Val</th>
<th>Solvent</th>
<th>No. of Ccs of Reagent</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogen in Distillate</td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
<td><img src="image.png" alt="Image" /></td>
</tr>
</tbody>
</table>
This procedure (as employed in 12, 15 and 16) gave:

glycidyl phenyl ether, for which was found:

C = 71.95  H = 6.67  O = 21.46  C₂H₄O₊ requires:
C = 72.00  H = 6.67  O = 21.34

Hydrolysis of (−)-β-Chlor-β'-phenoxyl-isocoumaryl hydrogen phthalate

(−)-β-Chlor-β'-phenoxyl-isocoumaryl hydrogen phthalate, [α]ᵣ = −12.4⁰ (in ether), 5 gms., was added to 12.5 N potassium hydroxide, 5 cc., contained in a 200 cc. distilling flask with a bent side arm, and a current of steam passed into the mixture immediately. The distillates from two such experiments were combined and extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate. The ether was then removed, under slightly reduced pressure in a bath of warm water, and the (−)glycidyl phenyl ether then distilled:

Yield 1.95 gms., b.p. 133⁰C/23 mm., [α]ᵣ = 1.5110
[α]ᵣ = −24.4⁰, d₄₀ = 1.106  , d₁₀₀ = 1.049

The rotatory power of (−)glycidyl phenyl ether under varying conditions will be found in Tables VII - XII, and the rotativities of various solutions in Table I page 80.

Conversion of (−)Glycidyl phenyl ether into

(−)-β-Chlor-β'-phenoxyl-isocoumaryl Alcohol

A preliminary experiment was first undertaken:

41-glycidyl phenyl ether, 0.5 gms., were shaken for half an hour with a solution of concentrated hydrochloric acid, 5 cc.,
in cold water, 6 cc. The mixture was extracted with ether and the ethereal extract washed three times with 30 cc. of 0.1
sodium hydroxide, and then with 20 cc. of water. The ethereal extract was dried over anhydrous sodium sulphate, the ether removed on the water bath and the alcohol distilled under reduced pressure:

Fraction (1) b.p. 140-145/20mm 3 gms.

\[ \eta^\theta = 1.5386 \]

Fraction (2) b.p. 145-150/20mm 2 gms.

\[ \eta^\theta = 1.5420 \]

Using (-)gycide phenyl ether, \( \alpha[^\theta]_D = -34.1^\circ, 1.8 \text{ gms.} \),

(-) \( \beta \) chlor \( \beta \) phenoxy-isopropyl alcohol, 0.7 gms.,
b.p. 143-145/20mm, \( \eta^\theta = 1.5378 \) was obtained having

\( \alpha[^\theta]_D = -2.3^\circ \)

(-) \( \beta \) chlor \( \beta \) phenoxy-isopropyl alcohol, 0.5 gms., was added to a warm solution of phthalic anhydride, 0.4 gms., in
pyridine, 0.24 gms., and toluene, 1 cc., the mixture was allowed to stand for two weeks and then the (-)hydrogen
phthalic ester isolated as before; yield: 0.56 gms., \( \alpha[^\theta]_D = -13.1^\circ \), i.e. within the limits of experimental error there was no
loss of activity during the conversion of the (-) \( \beta \) chlor
\(-\beta \) phenoxy-isopropyl hydrogen phthalate into the (-)gycide
phenyl ether, then into the (-) \( \beta \) chlor \( \beta \) phenoxy-isopropyl
alcohol and back to its hydrogen phthalic ester.
Preparation of (+) Sec. Butyl Cheryl Ether

The dry hydrogen bromide gas used in this experiment was generated by dropping bromine onto red phosphorus and water. The gas was purified (from bromine) by passing it through three U tubes containing moist red phosphorus spread on glass wool, and dried by passing successively through two U tubes containing granular calcium chloride, and a drying tower containing phosphorus pentoxide on glass wool.

(+)-Sec. Butyl alcohol, [α]D17 = +10.9°, 5 gms., was saturated with dry hydrogen bromide gas by passing the latter into the ice cold alcohol, contained in a long tube, until the liquid fumed continuously. The fuming liquid was then heated under reflux for about one hour, cooled, and washed with concentrated sulphuric acid, to remove any butene formed during the reaction, and then with sodium bicarbonate solution. The bromide was then dissolved in ether and the ethereal solution dried over sodium sulphate. Most of the ether was removed with the aid of a short fractionating column, and the bromide distilled, the fraction collected, 3 gms., had b.p. 86–87°, nD17 = 1.4235 (i.e. it contained some ether which it was not practicable to remove).
(+)-Sec-butyl bromide, 5 gms., as prepared above, was treated with freshly prepared sodium phenate, 2.75 gms., for twelve hours; the reaction mixture was then extracted with ether, washed with an excess of 3N caustic soda solution, and dried over powdered calcium chloride. The ether was then removed on a water bath and the (+)-sec-butyl phenyl ether distilled, the fraction collected had: -1.p. 74-76°C/16 mm. Yield: 0.65 gms., nD20 = 1.4276 [α]D +20.34 d410 = 0.9800
(Sprung and Tallis[12] give nD20 = 1.4086 & t.p. 144-146/16 mm.)

The rotatory dispersion of the (+)-sec-butyl phenyl ether was determined in the homogeneous state, and in solution in diethyl ether and di-propylene oxide. The rotatory powers are given in Table XV, the figures given therein have been corrected to the values which would have been obtained if optically pure (-)-sec-butyl alcohol had been used in this experiment (i.e. multiplied by -13.87/10.3) in order to facilitate comparison with other results.

Preparation of (-)-sec-Octyl Phenyl Ether

The method used was identical with that outlined above for the preparation of (+)-sec-butyl phenyl ether, the (-)-sec-octyl bromide could however be readily separated from the ether.

(-)-Sec-Octyl alcohol, [α]D = -9.39, 15 gms., yielded the (-)-sec-octyl bromide b.p. 150-170°C/2mm., 10 gms., having
\[ n_\text{D} = 1.4500 \] (Shriner and Young(93) give \[ n_\text{D} = 1.4600 \]).

\((-)\text{Sec.Octyl bromide}, 7 \text{ gms.}, \text{ as prepared above}, \text{ was heated at } 150^\circ \text{C with sodium phenate, } 4.7 \text{ gms.}, \text{ for twelve hours. The } (-)\text{sec.Octyl phenyl ether was then isolated in a manner analogous to that used for the } (+)\text{sec.Buyl phenyl ether (above), it had } -\text{b.p. } 137^\circ/16\text{mm.}, n_\text{D} = 1.4675, \]

\[ \alpha = -17.19^\circ \]

Yield 1.4 gms.

The figures given in Table XIV have been corrected to the values which should have been obtained if optically pure \((-)\text{sec.Octyl alcohol (}[\alpha]_D = -9.9^\circ)\) had been used in this experiment, (i.e. multiplied by 9.9/2.39).
Table VII

specific rotation powers of (-)-glycine benzyl ether in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>l c d j k</th>
<th>6703 5431 321 1720 556 480</th>
<th>Wavelength (A.0.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.1</td>
<td>12.9</td>
<td>107.7 17.1 15.7 25.6 35.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.5</td>
<td>15.1</td>
<td>- 31.3 23.5 31.1 31.1</td>
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<tr>
<td>1,4-Dioxan</td>
<td>1.7</td>
<td>11.8 25.9 25.7 10.3 11.4</td>
<td>- 11.8 1.53</td>
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<tr>
<td>Carbon tetrachloride</td>
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<tr>
<td>Freon 1</td>
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<td></td>
</tr>
<tr>
<td>Chloride</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Hesperidin</td>
<td>1.0</td>
<td>12.7 13.4 12.3 11.7 11.3 11.3 21.9 34.7 34.1 31.1 34.1 47.1 1.65</td>
<td></td>
</tr>
<tr>
<td>Cenzerin</td>
<td>1.0</td>
<td>14.1 18.3 18.3 43.5 31.9 28.3 38.7 34.1 34.1 31.1 34.1 47.1 1.65</td>
<td></td>
</tr>
<tr>
<td>Glycine</td>
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<td>18.3 18.3 21.7 21.7 26.4 37.3 34.7 34.7</td>
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</tr>
<tr>
<td>Methanol</td>
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</tr>
<tr>
<td>Ethanol</td>
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<td>13.1 13.3 13.3 13.3 13.3 13.3 13.3 23.1 13.3</td>
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</tr>
<tr>
<td>Methanol</td>
<td>0.5</td>
<td>14.1 17.8 17.8 17.8 17.8 17.8 17.8 27.1 17.8</td>
<td>- 17.8 1.33</td>
</tr>
<tr>
<td>Solvent</td>
<td>c</td>
<td>Temp °C</td>
<td>Wavelength (A.U.)</td>
</tr>
<tr>
<td>------------</td>
<td>---</td>
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<td>-------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6433 5893 5730 5461 5066 4800 4380</td>
</tr>
<tr>
<td>Tetrahydro</td>
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<td>12.0</td>
<td>33</td>
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<td>Ether</td>
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<td>12.0</td>
<td>17</td>
</tr>
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<td>8.0</td>
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</tr>
<tr>
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<td>10.0</td>
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<tr>
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<td>21</td>
</tr>
<tr>
<td>Ether</td>
<td>1.0</td>
<td>11.2</td>
<td>17</td>
</tr>
</tbody>
</table>
**Table IX**

Specific Rotatory Powers of (-)-Glycidyl Phenyl Ether

in the Homogeneous State

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>[α] (°)</th>
</tr>
</thead>
<tbody>
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<td>6700</td>
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<tr>
<td>6438</td>
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<tr>
<td>4800</td>
<td>37.3</td>
</tr>
<tr>
<td>4678</td>
<td>35.6</td>
</tr>
<tr>
<td>4500</td>
<td>45.5</td>
</tr>
</tbody>
</table>

**Ultra-violet Region**

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>[α] (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4540</td>
<td>40.6</td>
</tr>
<tr>
<td>4360</td>
<td>35.3</td>
</tr>
<tr>
<td>3873</td>
<td>37.7</td>
</tr>
<tr>
<td>3600</td>
<td>60.6</td>
</tr>
<tr>
<td>3483</td>
<td>73.7</td>
</tr>
<tr>
<td>3304</td>
<td>76.5</td>
</tr>
<tr>
<td>3292</td>
<td>64.1</td>
</tr>
<tr>
<td>3180</td>
<td>61.7</td>
</tr>
</tbody>
</table>

**Intermediate Region**

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>[α] (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4737</td>
<td>38.9</td>
</tr>
<tr>
<td>4647</td>
<td>39.1</td>
</tr>
<tr>
<td>4570</td>
<td>39.8</td>
</tr>
<tr>
<td>4504</td>
<td>40.4</td>
</tr>
<tr>
<td>4452</td>
<td>41.3</td>
</tr>
<tr>
<td>4402</td>
<td>42.6</td>
</tr>
<tr>
<td>4459</td>
<td>43.9</td>
</tr>
<tr>
<td>4476</td>
<td>44.1</td>
</tr>
</tbody>
</table>

Limit of transmission.
## Table X

**Specific Rotatory Powers of (−)-Glycine Phenyl Ether in Methyl Ether Solution**

<table>
<thead>
<tr>
<th>Visible Region</th>
<th>Ultra-Violet Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 19.6°C</td>
<td>T = 19.6°C</td>
</tr>
<tr>
<td>c = 10.32</td>
<td>c = 10.32</td>
</tr>
<tr>
<td>l = 1.0</td>
<td>l = 0.6</td>
</tr>
<tr>
<td>λ A.</td>
<td>[α]</td>
</tr>
<tr>
<td>3425</td>
<td>7.2</td>
</tr>
<tr>
<td>5595</td>
<td>8.3</td>
</tr>
<tr>
<td>6760</td>
<td>8.7</td>
</tr>
<tr>
<td>5461</td>
<td>9.6</td>
</tr>
<tr>
<td>5086</td>
<td>10.1</td>
</tr>
<tr>
<td>4600</td>
<td>11.1</td>
</tr>
<tr>
<td>4378</td>
<td>-</td>
</tr>
<tr>
<td>4355</td>
<td>13.3</td>
</tr>
<tr>
<td>3907</td>
<td>13.0</td>
</tr>
<tr>
<td>3883</td>
<td>14.3</td>
</tr>
<tr>
<td>3907</td>
<td>16.0</td>
</tr>
<tr>
<td>3907</td>
<td>17.4</td>
</tr>
<tr>
<td>3943</td>
<td>18.55</td>
</tr>
<tr>
<td>3943</td>
<td>19.4</td>
</tr>
<tr>
<td>3756</td>
<td>24.5</td>
</tr>
<tr>
<td>3690</td>
<td>30.5</td>
</tr>
<tr>
<td>3545</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Limit of Transmission.
Table XI

The Effect of Temperature on the Specific Rotatory Power
of Homogeneous (-)-Glycine Phenyl Ether

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Specific Rotatory Power for Different Wavelengths (A. U.)</th>
<th>Density δ/1000</th>
<th>ι</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>19.0 51.0 26.0 31.1 58.0 41.5 1.000 1.101</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>16.7 30.6 23.5 37.6 47.2 1.000 1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.0</td>
<td>14.4 17.8 10.8 22.8 31.0 1.000 1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>11.9 15.9 16.7 13.6 21.0 36.0 1.000 1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90.0</td>
<td>13.1 18.7 14.3 16.4 18.4 21.8 1.000 1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>141</td>
<td>- 7.9 6.3 - 11.9 1.02 1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>174</td>
<td>- 6.5 5.5 - 0.6 1.04 0.195</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table VII

The Effect of Temperature on the Specific Rotatory Power of (-)-Glycite Pheny1 Ether in n-Butyl Ether Solution

c = 0.4  l = 1.0

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>-5.3 -5.9 -7.8 -7.7 -4.4</td>
<td>1.188</td>
</tr>
<tr>
<td>41</td>
<td>-3.6 -3.8 -4.3 -5.2 -4.1</td>
<td>0.993</td>
</tr>
<tr>
<td>81</td>
<td>-2.1 -2.1 -2.3 -4.1 -41.9</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>-1.3 -0.7 +0.3 -41.8</td>
<td>11.8</td>
</tr>
</tbody>
</table>
Table XIII

The Ultra-violet Absorption Spectrum of Glyoxylic Pheryl Ether

(Determined by Dr. G.A. Feenan)

Instrument: Beckman photo-electric quartz spectrophotometer with a hydrogen discharge lamp as the source.

1. In mixed octane

<table>
<thead>
<tr>
<th>λ&lt;sub&gt;max&lt;/sub&gt; Å</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt;</th>
<th>( \log_{10} \varepsilon ) ( \varepsilon ) ( \mathrm{max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3770</td>
<td>1520</td>
<td>5.130</td>
</tr>
<tr>
<td>3700</td>
<td>1550</td>
<td>5.361</td>
</tr>
<tr>
<td>3650</td>
<td>1230</td>
<td>3.390</td>
</tr>
<tr>
<td>3190</td>
<td>7400</td>
<td>3.674</td>
</tr>
</tbody>
</table>

2. Homogeneous Substance

No selective absorption down to 2940 Å. For a layer of 0.10 cm, the optical density rises smoothly from 0.05 at 3100 Å to 0.72 at 2940 Å.
### Table XIV

Specific Rotary Powers of (-)3a,6a-Dihydro Dihydro Chrysanthemum

in the Nonpolar State

\( T = 28.0^\circ C \quad \alpha_1 = 0.000 \)

<table>
<thead>
<tr>
<th>Visible Region</th>
<th>( \lambda ) (( \text{A} ))</th>
<th>( [\alpha] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6706</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>6486</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>6106</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td>5886</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td>5706</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>6411</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>6086</td>
<td>23.1</td>
<td></td>
</tr>
<tr>
<td>5806</td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>4976</td>
<td>32.1</td>
<td></td>
</tr>
<tr>
<td>4591</td>
<td>35.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultra-violet Region</th>
<th>( \lambda ) (( \text{A} ))</th>
<th>( [\alpha] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4031</td>
<td>58.6</td>
<td></td>
</tr>
<tr>
<td>4301</td>
<td>57.8</td>
<td></td>
</tr>
<tr>
<td>4031</td>
<td>58.9</td>
<td></td>
</tr>
<tr>
<td>4006</td>
<td>58.1</td>
<td></td>
</tr>
<tr>
<td>3945</td>
<td>74.8</td>
<td></td>
</tr>
<tr>
<td>3840</td>
<td>74.5</td>
<td></td>
</tr>
<tr>
<td>3710</td>
<td>79.0</td>
<td></td>
</tr>
</tbody>
</table>

Limit of

Transmission.
### Table XV

**Specific Rotatory Powers of (-)Sec. Butyl Phenyl Ether in the Homogeneous State and in Solution in Various Solvents**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>l</th>
<th>c</th>
<th>95</th>
<th>6433</th>
<th>5893</th>
<th>5780</th>
<th>5461</th>
<th>5086</th>
<th>4893</th>
<th>4678</th>
<th>4358</th>
<th>d4358</th>
<th>25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Homogeneous)</td>
<td>1.25</td>
<td>33.5</td>
<td>13</td>
<td>29.3</td>
<td>36.0</td>
<td>37.7</td>
<td>42.1</td>
<td>51.0</td>
<td>59.1</td>
<td>66.3</td>
<td>74.8</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>1.6</td>
<td>8.1</td>
<td>19</td>
<td>26.3</td>
<td>34.3</td>
<td>36.2</td>
<td>41.2</td>
<td>53.1</td>
<td>57.2</td>
<td>61.3</td>
<td>75.2</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.6</td>
<td>5.1</td>
<td>16</td>
<td>22.2</td>
<td>35.3</td>
<td>36.4</td>
<td>43.4</td>
<td>56.7</td>
<td>-</td>
<td>-</td>
<td>77.4</td>
<td>1.78</td>
<td></td>
</tr>
</tbody>
</table>

### Table XVI

**Specific Rotatory Powers of β-Chloro β'-Phenoxy-Isopropyl Alcohol in the Homogeneous State and in Solution in Various Solvents**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>l</th>
<th>c</th>
<th>95</th>
<th>6433</th>
<th>5893</th>
<th>5780</th>
<th>5461</th>
<th>5086</th>
<th>4893</th>
<th>4678</th>
<th>4358</th>
<th>d4358</th>
<th>25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Homogeneous)</td>
<td>1.25</td>
<td>120.9</td>
<td>19</td>
<td>-1.6</td>
<td>-2.1</td>
<td>-2.2</td>
<td>-2.5</td>
<td>-3.1</td>
<td>-3.4</td>
<td>-4.2</td>
<td>-4.2</td>
<td>1.72</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>1.6</td>
<td>5.8</td>
<td>18</td>
<td>-4.7</td>
<td>-5.4</td>
<td>-6.4</td>
<td>-7.2</td>
<td>-8.2</td>
<td>-9.0</td>
<td>-12.0</td>
<td>-12.0</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>1.6</td>
<td>5.6</td>
<td>21</td>
<td>1.3</td>
<td>-1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
<td>2.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.6</td>
<td>6.7</td>
<td>18</td>
<td>-1.6</td>
<td>-5.2</td>
<td>-5.8</td>
<td>-6.9</td>
<td>-8.4</td>
<td>-9.7</td>
<td>-11.4</td>
<td>-11.4</td>
<td>1.68</td>
<td></td>
</tr>
</tbody>
</table>
### Table VIII

Specific Rotatory Powers of (-)β-Chloro-β-methoxy-isopropyl hydrogen phosphonate in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1 cm</th>
<th>3 cm</th>
<th>5 cm</th>
<th>7 cm</th>
<th>9 cm</th>
<th>11 cm</th>
<th>13 cm</th>
<th>15 cm</th>
<th>17 cm</th>
<th>19 cm</th>
<th>21 cm</th>
<th>23 cm</th>
<th>25 cm</th>
<th>27 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
<td>2.2</td>
<td>2.4</td>
<td>2.6</td>
<td>2.8</td>
<td>3.0</td>
<td>3.2</td>
<td>3.4</td>
<td>3.6</td>
<td>3.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.7</td>
<td>0.8</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.4</td>
<td>1.5</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
<td>2.1</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
<td>1.6</td>
<td>1.7</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

All rotatory powers.

*Note: Values are approximate and refer to specific rotation at different centimeter lengths.*/
Methods Available for the Investigation of Optical Rotatory Dispersion in the Ultra-Violet Region of the Spectrum

As has been pointed out earlier it is essential that measurements of the rotatory dispersion should be extended into the ultra-violet region, if the results are to be of fundamental value. It is therefore proposed to give a short survey of the methods at present available for measuring the rotatory dispersion in this region.

The normal method for the determination of the optical rotatory power of a liquid substance, or solution, is to observe visually through a column of liquid of known length placed in a two or three field polarimeter. The reading is obtained by matching the two or three fields. Theoretically the three field polarimeter should be the easiest to use and the most accurate. In practice, however, this is not always the case since the colour of the two outside fields is seldom exactly the same so that only one of these can be matched with the central field at once. From the practical point of view therefore, it seems that no increase in accuracy is obtained by the use of the three field polarimeter in the visible region. In the ultra-violet region, however, it is almost essential to use a three field instrument, since otherwise there is no check on the evenness of the illumination of the field of the instrument. The photographs
on page 111 show how difficult it is to read an extinction when the field is unevenly illuminated, and how easy it would be to make an incorrect estimation of the extinction position with a two field instrument. In the visible region, rendering of the light source is usually observable immediately and can be corrected. In the ultra-violet region the illumination may be uneven, though it appears to the eye to be even. Therefore the first requirement of an instrument for measurement in the ultra-violet region is that it should have three fields.

Several methods of measuring in the ultra-violet region of the spectrum have been devised. They may be divided into two types according to the means of recording:

(a) Those which employ a photoelectric cell.

(b) Those utilizing a photographic plate.

The recent trend in spectrophotometric work is towards the use of direct reading photoelectric spectrophotometers, the photoelectric cell being more uniformly sensitive to light of different wavelengths than a photographic plate. This is, however, not so important in polarimetric measurements since they depend on the variation in intensity of a particular spectral line, and not on the comparison of the intensities of different lines.

The photographic method has the advantage that it provides a permanent record, and the accuracy obtainable is higher, in
the region of complete transmission; in the region of absorption the accuracy is much reduced in either case and exact comparison is difficult to make since, in the case of the photographic apparatus, the accuracy depends upon the length of time which can be devoted to the measurement (see method (1) page 113).

The criterion which should be used in assessing the merits of a particular apparatus for use in the ultra-violet region, is its performance when the substance under investigation has a low rotary power and a high absorption.

The most critical parameter is "path length". For a given wavelength, complete absorption takes place when the path length of the light in the liquid exceeds a certain value, and a very large increase in exposure produces no significant increase in the range of observation. This "path length" is the factor which determines the extent of the penetration into the ultra-violet, more than the brightness of the source, or the half-shadow angle used, since the effect of these may be counterbalanced by alteration of the exposure.

In general, therefore, the technique should be to use as low a half-shadow angle as possible, as bright and as constant a source as possible, and as short a path length as the accuracy of the instrument allows.
The example on page 116 shows that to attain the foot of the first characteristic absorption band at $a = 2600$ Å., in glycine phenyl ether, would require the use of a layer of liquid $0.03$ cm. thick with $\alpha = 0.26^\circ$. It is therefore desirable that the polarimeter should be able to read to $0.001^\circ$. The Lorry polarimeter has a scale which reads to $0.001^\circ$, but the instrument, as used by the author, did not seem capable of an accuracy greater than $0.03^\circ$. If the instrument could be made to read to $0.001^\circ$, then using the method of "pin-pointing" (page 118) an accuracy of one part in 200 should be attainable with a substance with $\alpha = 0.06^\circ$, for wavelengths in the region of absorption. This compares favourably with the accuracy of one part in 500 claimed by Franck(14) for his photoelectric polarimeter when used in the region of transparency with $\alpha = 48^\circ$.

The method of Cotton and Perreault(94) deserves special consideration as it provides, in one operation, a record of the rotary power for a complete spectrum. Perreault estimates the error at $0.02^\circ$, which compares well with that actually found in the Lorry instrument, especially when it is remembered that the method of Cotton and Perreault is much less tedious than that of Lorry; it has, however, two major disadvantages:
(a) It involves continuously moving parts, which raises difficulties when utmost accuracy is required.

(b) It only allows the use of a small aperture.

The photoelectric method, though it has been continuously improved by Bruhat (et al.) has not yet achieved the accuracy of the photographic methods (for slope). Lowry's method, if improved as outlined on page 114, would prove a very useful tool in the systematic investigation of the rotary dispersion of simple organic molecules, a process which, as yet, has hardly been attempted.

A detailed review of the methods of ultra-violet polarimetry has been given by Lowry (14).
Explanations of the Method of Use of the Lowne Ultra-Violet

Through the courtesy of Professor R.G.W. Norrish F.R.S., it is possible to use the late Professor T.H. Lowry's instrument.

A description of the methods employed, together with the results obtained for the rotary dispersion of quartz has been given by Lowry and Gooch-Adams (11). The present short account of the method of working the instrument is given mainly from practical points of operation.

Figure 5

Diagram of the Apparatus

The instrument consists of:

A Iron Arc

B a quartz lens

D a three field polariser, consisting of one large and two small Foucault prisms containing air films instead of the Canada balsam usual in the Glan-throck prism, which are used in the visible and near ultra-violet regions.

Aperture of large prism, inc. approximately.
C  Slit - Fully open for use in the ultra-violet.
D  Long trough - made primarily for Lowry's c. cm. quartz bar.
E  Analyzer, one large conoscalt prism.
F  Quartz-calcite lens combination, $l_2$, which focuses an
    image of the aperture at $G$ on the slit, $S$, of the spectro-
    graph.
G  Fine slit of Hilger Medium Spectrograph.

The various parts of the polarimeter are mounted on a
wooden optical bench, and the spectrograph on a separate table.
The focal length of the lens, $l_2$, is about 50 inches, so that
the operator can examine the field visually at $P$, and see
that the image of $G$ is correctly focused on $C$, and also that
even illumination is provided by the arc. If necessary
the lens, $l_2$, can be replaced by a prismatic eyepiece
without disturbing the spectrograph.

Procedure

(1) Using the visual eyepiece, set the polarimeter at its
    approximate extinction position with the empty polarimeter
    tube in position.

(2) Replace the eyepiece by the lens, $l_2$, and photograph
    the zero setting using the spectrograph. Alter the
    analyzer setting a few fractions of a degree to one
    side of the extinction photograph, - repeat for several
    different settings of the analyzer. Now repeat the
    procedure on the other side of the visual zero. This
provides evidence of the position of the zero of the instrument and polarimeter tube combined, for various wavelengths. From this a zero calibration curve is constructed. The instrument itself shows very little rotary dispersion above 2500 Å.

3 Fill the polarimeter tube with the substance, and set the analyser to the approximate value of determined visually for 4258 Å. Photograph — close the small shutter over slit G, then increase the analyser setting and alter the plate setting. The field is photographed for the new setting by reopening the small shutter at G.

The first photographic plate should contain:

(a) Some 5 or 6 photographs of zero settings (see (2) above).
(b) 4 or 5 well spaced readings, covering as far as possible the whole range of probable... up to the region of absorption or slittle beyond.

N.P. for this reason the ultra-violet absorption spectrum of the compound should first be determined.

This procedure enables further settings of the analyser to be planned so as to cover... suitable intervals, all the rotations up to the region of absorption.

4 There are two ways in which the polarimeter may be used.

(a) First Method

The polarimeter is set at definite values of... in (3) above. The extinctions are determined as follows:-
The diagram illustrates methods (a) & (b) of locating extinction positions.

N.B. (1) In the diagram the extinction position is shown moving from one line to the next in successive photographs (an ideal case).
(2) The settings of the analyzer used for method (a) usually render it impossible to use method (b) simultaneously.
(3) The method of reading the photographs of the zero settings is similar to that employed in the visible region unless the instrument or polarimeter tube shows rotatory dispersion, when the extinctions must be estimated as shown, and a calibration curve constructed to give the zero for any wavelength.
(4) In the above figure the variations are in the thickness of the line rather than in its intensity, this is also the case in positive prints, but the reverse is the case in the negative.
The eye is run along the photograph (for a particular setting of the analyser) until it reaches a spectral line in which the inner and two outer portions are evenly illuminated. The wavelength of this line is read off from the standard wavelength chart, thus giving the wavelength corresponding to extinction for a particular event.

This is the method most commonly used as it quickly covers the desired region of the spectrum.

The accuracy depends on the half-shadow angle used, the density of the negative at the extinction position, and the number of lines available in that region.

(1) Second Method

The rotation corresponding to a given spectral line is estimated or determined experimentally as in (3) and (4)(c) above, and then the analyser is set to fractions of a degree either side of the expected extinction position, thus obtaining a series of photographs in which the line appears, on the prints, as a white line, in one photograph darker in the middle than on the outside, in the next of the same density throughout the line (extinction position), and in the next darker on the outside than in the middle. In this method the eye runs up and down a given spectral line in the series of photographs, selecting that in which the line appears evenly illuminated, the analyser setting corresponding to the photograph gives \( \lambda \) for that line. (Methods (a) & (1)
are illustrated by Figure 4, page 110). This method corresponds to that normally used in the visible region, and for a given half-angle angle it gives greater accuracy than that obtainable visually. It is, however, very tedious; it is generally described as "pin pointing".

(5) An extinction is most readily observed when the lines in that region are only just visible on the negative. The usual method of observation is visual inspection using a low power travelling microscope. Projection methods may be used (particularly for (b) above) when the negatives are of medium density. A photoelectric densitometer would be very useful at this stage, since as the lines have individual characteristics it is impossible to make several estimations of the extinction within a short space of time without being biased as to its position.

(6) For accurate work a knowledge of the probable strength of the lines is desirable so that exposures can be timed to give a suitably dense negative at the extinction position. A dense negative makes accurate work impossible. A negative of suitable density for measuring extinctions gives a very poor print.

(7) If the investigation is to reach short wavelengths with
strongly absorbing substances, then a short cell (say 0.5 cm.) should be used and the accuracy maintained by using a lower half-shadow angle and longer exposure. The 10° half-shadow angle used in these experiments is too great to allow an accuracy of much more than 1° and in dense regions the accuracy drops to about 3°.

(c) The long distance between the polariser and the analyser in this particular instrument, whilst ensuring that only parallel light passes through, means the centre of the arc more critical and very difficult to maintain.

(d) The chief difficulty in the use of this instrument is the mental and physical fatigue occasioned by the long exposures in the dark. The arc sometimes runs satisfactorily for several hours, but usually requires frequent attention in order to keep the beam centralised on the analyser. In any future development of the instrument an automatic method of centring the arc will be desirable. The instrument would then require only occasional attention, for the alteration of the analyser settings and when the arc failed.
Notes on the Measurements in the Ultra-Violet Region

Homogeneous (–)Glycine Phenyl Ether

(1) Using 0.25 cm. cell and glass end plates it was only possible to proceed down to 2800 A. with an exposure of 1 hour.

(2) Using 0.05 cm. fused quartz cell the limit of transmission was 3100 A. (exposure 1 hour). Only a very small correction is required for the rotatory dispersion of this cell.

(3) Absorption data indicate that it is not possible to proceed much below 3100 A since:– (see page 96)

\[
\begin{array}{ccc}
\text{wavelength (A)} & \text{optical density} & \text{correction} \\
3140 & 0.1 & 0.05 \\
3160 & 0.5 & 0.03 \\
\end{array}
\]

\[\text{correction approx.} 0.03\]

: 0.25 is the maximum density which will permit a reading on the photographic plate of the polarimeter.

Corresponding data:

This to reach 3040 A a layer 0.03 cm. is required 0.05 3060 0.10 0.04

These figures serve to show why no attempt was made to proceed with the investigation of the rotatory dispersion below 3100 A.

(–)Glycine Phenyl Ether in Solution in Diethyl Ether

Limit of transmission in 0.5 cm. tube 3545 A (exposure half an hour). Balanced quartz and plates used, zero correction determined for one wavelength and the correction for other wavelengths calculated from the Brühl equation for quartz. (This is necessary because the "balance" of the end plates is destroyed then they are screwed up in the polarimeter tube).

(–)Norephine Phenyl Ether

0.5 cm. fused quartz cell used (low zero correction). Limit of transmission 3500 A (exposure 15 minutes). Unfortunately this was not available at Cambridge for an extension of the investigation by using longer exposures.
Appendix

Evaluation of Drude Equations for the Rotatory Dispersion of Glycide Phenyl Ether

1. Attempted evaluation of a two-term from the rotatory dispersion curve alone (see page 43).

2. Evaluation of equations partly from known absorption frequencies in glycide phenyl ether, and partly from the rotatory dispersion curve (see page 44). A two-term equation calculated by this method needs only two experimental observations of rotatory power for its solution, whilst a three-term equation requires three, i.e. it is "tied" to the experimental curve at a further point. The corresponding numbers of observations required for evaluation from the rotatory dispersion curve alone being four or six respectively. Thus the method of calculation here used is inclined to demand additional terms over and above those required for a direct determination solely from the rotatory dispersion curve.

On the other hand, it shows the difficulty of drawing conclusions from the rotatory dispersion curve alone, since several combinations of different absorption bands may be made to fit the rotatory dispersion curve in the visible and near ultra-violet regions.
Method of Calculation

(a) Two-term equation using two values of \( \lambda_1 \) and \( \lambda_2 \) selected from possible absorption bands. The evaluation resolves itself into the solution of the equations:

\[
\begin{align*}
[\alpha_i] & = 2 \lambda \frac{\alpha_i}{\lambda_i - \lambda_0} + 2 \lambda \frac{\alpha_i}{\lambda_i - \lambda_0} \\
[\alpha_j] & = 2 \lambda \frac{\alpha_j}{\lambda_j - \lambda_0} + 2 \lambda \frac{\alpha_j}{\lambda_j - \lambda_0}
\end{align*}
\]

(b) Three-term equation method similar to that used for a two-term equation except that the solution involves three simultaneous equations representing three different sets of values.

(c) Direct evaluation of a single-term equation from the rotatory dispersion curve by equating:

\[
[\alpha_i] = \frac{2 \lambda \alpha_i}{\lambda_i - \lambda_0} \quad \text{and} \quad [\alpha_j] = \frac{2 \lambda \alpha_j}{\lambda_j - \lambda_0}.
\]

(d) Evaluation of a three-term equation for the rotatory dispersion of glycidyl phenyl ether in ethereal solution. The results obtained for a two-term equation are not good enough to merit comparison.
Glycycle Phenyl Ether

(1) Attempted Evaluation of a Two-Term Equation from the Experimental Rotatory Dispersion Curve

The method employed is that suggested by Loewy (14). The values used were chosen from a smooth curve through the experimental points. "y" is the specific rotatory power corresponding to a wavelength "x".

\[ x_1 = 67.67.66 \quad x_2 = 5466.73 \quad x_5 = 4428.34 \quad x_4 = 3392.999 \]
\[ y_1 = +12.49 \quad y_2 = +26.30 \quad y_3 = +41.60 \quad y_4 = +41.40 \]

The sign of the rotations is that of (+)glycycle phenyl ether.

<table>
<thead>
<tr>
<th>( x_1y_1 )</th>
<th>( x_2y_2 )</th>
<th>( x_3y_3 )</th>
<th>( x_4y_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>153,552,166</td>
<td>168,740,324</td>
<td>277,698,525</td>
<td>270,640,724</td>
</tr>
</tbody>
</table>

\[ k_1 = -39,565,866 \quad k_2 = -74,711,970 \quad k_3 = -135,667,688 \]

where \( k_1 = x_1y_1 - x_2y_2 \) etc.

\[ l_1 = x_1 - x_3 = +1247.15 \quad l_2 = x_1 - x_5 = +2342.52 \quad l_3 = x_1 - x_4 = +545.96 \]

\[ m_1 = y_1 - y_2 = -9.71 \quad m_2 = y_1 - y_3 = -27.11 \quad m_3 = y_1 - y_4 = -95.81 \]

\[ n_1 = x_2y_1 - x_3y_2 \]

where \( n_1 = x_2y_1 - x_3y_2 \) etc.

\[ m_{10} = 2,541,033,466 \quad n_{10} = -116,616,615,168 \quad l_{10} = -134,114,636,600 \]
\[ n_{10} = 2,540,944,712 \quad n_{10} = -110,386,504,567 \quad l_{10} = -129,124,147,472 \]

\[ k_{10} = -37,924,806 \quad k_{10} = -76,921,924 \quad k_{10} = -27,924,149 \]

\[ n_1 = x_1y_1 - x_5y_2 \]

\[ k_1 = +1,865,451,897 \quad k_1 = +2,928,614,951 \quad k_1 = +2,812,614,897 \]

\[ n_{10} = 2,541,670,765,463,325 \]

\[ m_1k_1 = +4,171,335,948 \quad k_1l_1 = -235,156,513 \]
\[ m_1k_1 = +4,171,335,948 \quad k_1l_1 = -235,156,513 \]
\[ D = -76,924,149 \quad S = +106,831,971 \]
\[ l_2l_3 = -923,002,922,000 \quad n_1 = -1,038,885,503 \]
\[ -l_2l_3 = -6,736,666,153,000 \quad n_1 = -911,564,491,891,162 \]
\[ n_k \phi = + \quad 5,255,666,586,000. \]
\[ n_3 \phi = + \quad 6,813,680,846,000. \]
\[ \phi = - \quad 947,921,861,000. \]
\[ n_1 \phi = + \quad 9,834,316,337,310. \]
\[ n_1 \phi = -1182,161,416,569,000. \]

**Calculation of "A"**

<table>
<thead>
<tr>
<th>Top line</th>
<th>Bottom line</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l_1 \alpha = + ) \quad 638,526,928.</td>
<td>( l_1 \alpha = - ) \quad 933,668,986.</td>
</tr>
<tr>
<td>( n_1 \gamma = + ) \quad 95,713,836,222.</td>
<td>( n_1 \gamma = - ) \quad 1,030,525,107.</td>
</tr>
<tr>
<td>( \text{Sum} = + ) \quad 10,583,383,822.</td>
<td>( \text{Sum} = - ) \quad 1,571,337,468.</td>
</tr>
<tr>
<td>( n_1 \beta = -751,281,741,160. )</td>
<td>( n_1 \beta = + ) \quad 156,164,375.</td>
</tr>
<tr>
<td>( \text{Sum} = -755,663,558,288. )</td>
<td>( \text{Sum} = -1,764,135,000. )</td>
</tr>
</tbody>
</table>

\[ A = - \left( \frac{755,663,558,288}{-1,764,135,000} \right) = -435,333,449.9 \]

**Calculation of "T"**

<table>
<thead>
<tr>
<th>Top line</th>
<th>Bottom line same as &quot;A&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \alpha = - ) \quad 14,683,266,287.</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( n_1 \gamma = - ) \quad 9,745,830,451,182.</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( \text{Sum} = -9,741,337,713,433. )</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( n_1 \beta = + ) \quad 9,343,714,357,710.</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( \text{Sum} = +2,160,306,648,510. )</td>
<td>( \text{Same as } A )</td>
</tr>
</tbody>
</table>

**Calculation of "G"**

<table>
<thead>
<tr>
<th>Top line</th>
<th>Bottom line same as &quot;A&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_1 \phi = - ) \quad 1,102,191,416,868,000.</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( n_1 \gamma = - ) \quad 95,616,364,484,107.</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( \text{Sum} = -1,103,746,510,766,110. )</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( \beta = + ) \quad 2,351,352,765,435,000.</td>
<td>( \text{Same as } A )</td>
</tr>
<tr>
<td>( \text{Sum} = +1,417,604,806,674,378. )</td>
<td>( \text{Same as } A )</td>
</tr>
</tbody>
</table>

\[ A^3 = a^3 + 3ab^2 \quad C = ab \]

\[ \therefore \quad a - b = \sqrt{A^3 - 4C} = \sqrt{156,957,467,000} \]

\[ = 351,335. \]

Since this involves the determination of the square root of a negative number, no solution is obtainable by this method.
(2) Comparison of Various Drug Equations
(calculated partly from absorption bands)

<table>
<thead>
<tr>
<th>No. of 1°</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of absorpt.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ion bands</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$\alpha$</th>
<th>Diff</th>
<th>Diff</th>
<th>Diff</th>
<th>Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>obs. calc.</td>
<td>calc.</td>
<td>calc.</td>
<td>calc.</td>
<td>calc.</td>
<td>calc.</td>
</tr>
</tbody>
</table>

| 6766 | 17.8 | 17.6 | -0.2 | 16.7 | -0.9 | 16.1 | -0.7 |
| 6766 | 35.2 | 35.0 | 0.2 | 34.3 | 0.7 | 33.9 | 0.3 |
| 6766 | 35.2 | 34.9 | -0.3 | 34.6 | -0.7 | 35.3 | 0.3 |
| 6766 | 35.2 | 34.9 | +0.3 | 34.6 | +0.7 | 35.3 | 0.3 |

Other Two-Term Equations

<table>
<thead>
<tr>
<th>wavelength</th>
<th>$\alpha$</th>
<th>Diff</th>
<th>Diff</th>
<th>Diff</th>
<th>Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>obs. calc.</td>
<td>calc.</td>
<td>calc.</td>
<td>calc.</td>
<td>calc.</td>
<td>calc.</td>
</tr>
</tbody>
</table>

| 6766 | 17.8 | 17.9 | -0.1 | 16.8 | -1.0 | 15.7 | -1.1 |
| 6766 | 35.2 | 35.1 | 0.1 | 34.3 | 0.7 | 35.3 | 0.3 |
| 6766 | 35.2 | 34.9 | +0.3 | 34.6 | +0.7 | 35.3 | 0.3 |

* from the dispersion curve alone
The constants of the equations compared on page 120 are:

Two-Term (a)

\[
[\alpha] = \frac{0.1093}{\lambda - 0.0541} - \frac{8.073}{\lambda - 0.0306}
\]

(1)

\[
[\alpha] = \frac{0.3297}{\lambda - 0.0541} - \frac{6.149}{\lambda - 0.0235}
\]

Three-Term

\[
[\alpha] = \frac{-1.854,074}{\lambda - 0.0735} + \frac{2.047,224}{\lambda - 0.0739} + \frac{-5.772,339}{\lambda - 0.0169}
\]

Glycide Lateral Ether in Etheral Solution

It was found impossible to obtain a two-term equation which would give a satisfactory representation of the rotary dispersion, but:

\[
[\alpha] = \frac{-10.129,039}{\lambda - 0.0735} + \frac{50.921,547}{\lambda - 0.0739} - \frac{14.459,630}{\lambda - 0.0169}
\]

gives the following:

<table>
<thead>
<tr>
<th>\lambda</th>
<th>( [\alpha] )</th>
<th>( [\alpha] )</th>
<th>( [\alpha] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6432</td>
<td>7.3</td>
<td>7.2</td>
<td>0.6</td>
</tr>
<tr>
<td>6461</td>
<td>9.6</td>
<td>9.1</td>
<td>-2.8</td>
</tr>
<tr>
<td>4312</td>
<td>13.2</td>
<td>12.2</td>
<td>0.0</td>
</tr>
<tr>
<td>3338</td>
<td>15.0</td>
<td>15.3</td>
<td>+0.3</td>
</tr>
<tr>
<td>3352</td>
<td>14.5</td>
<td>15.5</td>
<td>+1.0</td>
</tr>
<tr>
<td>3367</td>
<td>15.0</td>
<td>15.5</td>
<td>+0.3</td>
</tr>
<tr>
<td>3327</td>
<td>17.4</td>
<td>17.9</td>
<td>-0.5</td>
</tr>
<tr>
<td>3318</td>
<td>19.0</td>
<td>19.3</td>
<td>-1.0</td>
</tr>
<tr>
<td>3221</td>
<td>22.3</td>
<td>19.5</td>
<td>-4.8</td>
</tr>
<tr>
<td>3218</td>
<td>24.6</td>
<td>21.6</td>
<td>-3.2</td>
</tr>
<tr>
<td>3156</td>
<td>26.6</td>
<td>24.2</td>
<td>-1.7</td>
</tr>
<tr>
<td>3165</td>
<td>30.0</td>
<td>28.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The differences are relatively large, but an examination of Graph 17 will show that, owing to the shape of the curve, they are of the order of the experimental error (since this occurs in the estimation of the wavelength rather than the rotation.)
References

1. Jullin, Rev. Soc. Arcueil 1882, 8, 142-158.
2. Fresnel, Cuvres (1), 744.
9. Kuhn (Kerner), P. E. 1, 1910, 22, 292.
15. Scour, Aladdin Club Reprints, 14, p. 53.
17. Van't Hoff, Chemistry in Europe, Dutch Edition 1874.
30. Turner and Harvey, Quarterly Review 1927, 1, 4, 292.
32. Fresnel, Cuvres (1), xxviii, 707.
34. Allen, J. F. R. 1887, 17, 147.
38. Popp, Rev. der Physik 1910, 45, 177.
41. Green, Ann. der Physik 1918, 41, 1.
42. Gray, Phys. Rev. 1918, 7, 472.
41. Tschugaeff, T., C. 1914, 12, 70.
42. Tschugaeff and Goro Artsikoff, Z. ph. C. 1913, 45, 567.
43. (a) Lorry and Walker, Nature 1924, 113, 208.
(b) Lorry, Nature 1924, 111, 508.
44. Lorry and Hunter, J. 1925, 112, 434-444.
46. Arndt, Annalen de Chimie et de Physique, 1856, 11, 14-43.
48. Lorry, Reton and Barker, J. 1902, 1, 445.
51. Lorry, and Kenyon and Nickard, J. 1914, 109, 45-121.
54. Beckmann and Soner, J. 1926, 1, 764, 41; 1930, 2, 168.
55. Rule and Chambers, G. 1937, 141.
56. Tylee and Rule, J. 1936, 649.
59. Patterson, J. 1916, 109, 1376-1386.
Key to The References

C.R. = Comptes rendus de l'Academie des Sciences.
J. = Journal (or Transactions) of the Chemical Society.
J.A.C.S. = Journal of the American Chemical Society.
J.C.P. = Journal of Chemical Physics.
P.R.S. = Proceedings of the Royal Society.

Acknowledgements

The work described in this thesis was carried out by the author at Battersea Polytechnic under the direction of
Dr. J. Kenyon P.R.S.. The author would like to thank
Dr. Kenyon for his kindness and advice, Dr. M. P. Falbe for
his helpful criticism and suggestions, and Dr. J. H. Ieven
for the determination of the ultra-violet absorption spectrum
of glycine-phenyl ether. Thanks are also due to Professor
G. V. N. Sherratt F.R.S. for permission to use the ultra-violet
polarimeter; to Dr.決め M. Simpson for advice on the
interpretation of the photographs; and to Mr. M. Geody for
drawing the graph.
GRAPH 3
(-) Glycidol Phenyl Ether in Various Solvents (Å/Å)

I. No Solvent (Vesicular)
II. In Solution - Pyridine
III. In Solution - Carbon Disulphide
IV. In Solution - Benzene
V. In Solution - Methyl Alcohol
Graph 5

(-) Glycidyl Phenyl Ether in Ethereal Solvents

\[ \frac{[\alpha]}{\lambda} \]

Solvent
I. Diethyl Ether
II. Di-\(n\)-propyl Ether
III. Di-isopropyl Ether
IV. Di-\(n\)-butyl Ether
V. Di-\(n\)-Amyl Ether
Graph 7

(-) Glycyl phenyl Ether in m-butyl ether solution.

[Diagram showing a graph with data points and a scale for absorption at different wavelengths.]
Armstrong and Walker Diagram
(-) Glycidyl Phenyl Ether in the Homogeneous
State + in Various Solvents.
GRAPH II

Patterson Diagram for C-1 \( \beta \) Chloro \( \beta \) Phenoxymethyl Alcohol.
HOMOGENEOUS L-GLYCINE PHENYLETHER
Comparison of Various Drude Equations

\[ \sigma = \frac{K_1}{\lambda^2 - \lambda_1^2} + \frac{K_2}{\lambda - \lambda_2} \]

- \( K_1, K_2, \lambda_1, \lambda_2 \)

- Triangle: +3.97 ± 11.36 2700 2250
- Square: +4.50 ± 12.33 2250 1800
- Circle: +0.76 ± 8.45 2520 1800
- Diamond: Observed Dispersion Curve

← A.U. x 10^-2
GRAPH 15

(-) HYDROGEN PHTHALATE of BChloroP'Phenoxy Alcohol

$10^0/\alpha$

SOLVENT:

I. Dioxane
II. Acetone
III. Chloroform
IV. Carbon Disulfide
(-)-3-Chloro-3'-Phenyl isopropyl alcohol

In Various Solvents.
(-) Glycine Phenyl Ether in Diethyl Ether Solution: $[\alpha]_D / \lambda$

- Observed Rotatory Dispersion Curve
- Curve Calculated from the Drude Equation (Page 121)
GRAPH 18 Absorption Spectrum of GLYCIDE PHENYL ETHER

AS 119-120°C/20 mm.
Solvent Nujol Octane.