

EFFECT OF POLAR AND NON-POLAR SOLVENTS ON THE ROTATORY
POWER AND DISPERSION OF *l*-BENZOIN, *l*-BENZOIN
METHYL ETHER, AND METHYL *l*-MANDELATE.

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I N T R O D U C T I O N .

Developments in the study of optical activity may be said to date from 1808. In that year, Malus made his classical discovery that a beam of light, after reflection at a certain angle from any transparent substance, was plane polarised.

It is not at all surprising then, that his two pupils, Arago and Biot, should have used this knowledge as a means of investigating the optical properties of inorganic and organic compounds. They were the actual discoverers of optically active substances.

In 1811, Arago had found the plane of polarisation of a plane polarised beam of light to be rotated when the beam was passed through a quartz plate, while Biot, two years later, was able to distinguish between two kinds of plates, the one contributing a dextro-twist, the other a laevo-twist.

The attempts of the pioneers to discover simple factors governing this interesting phenomenon, were highly successful. It was demonstrated that fused quartz exerted no rotatory effect whatsoever, thus it was made clear that the twisting power of quartz was a

property of the crystalline state and was due to the definite, spatial, configuration of the crystal.

However, in 1815, Biot had established the fact that some liquids, such as sugar solution, also produced rotation, or more properly exhibited "optical activity." As liquids were generally considered isotropic, the activity could not be assigned to the arrangement of the molecules. Thus the activity of liquids was realised to be due to an inherent molecular property, a definition of which was given by the chemist Pasteur. From a review of his work on tartaric acid and the tartrates, he was able to correlate optical activity with molecular dissymmetry and optical inactivity with molecular symmetry. Indeed he made a shrewd guess at the structure of an asymmetric molecule in remarking, apropos of the asymmetry of dextro-tartaric acid, "Are the atoms of the right acid grouped on the summits of an irregular tetrahedron."

Under the influence of suggestions of this nature, Van't Hoff and Le Bel advanced almost identical solutions of the problem. Though they still considered the asymmetry of the whole molecule as the crucial factor, they realised, nevertheless, that this state could, in general, be produced by assigning asymmetry to a particular atom in the molecule. In this hypothesis both adopted the idea of the quadrivalency of

carbon as advanced by Kekulé and stipulated an asymmetric distribution in space of the four groups attached to the atom.

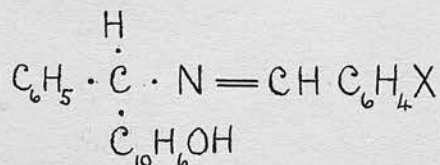
This work was soon followed by attempts to formulate a quantitative relationship between optical rotatory power and the properties of the groups attached to the asymmetric atom. The first of such attempts was by Guye, (Compt. Rend. 1890, 110.-1724; 1893; 116. 1378, 1451.) who tried to calculate the degree of asymmetry from the masses of the four radicals and the distances of the centres of gravity from the asymmetric atom. Under stringent tests the relationship failed. Crum Brown (Proc. Roy. Soc. Edin. 1890, 182) adopted a similar attitude but gave to each group a value K, which was a function of its composition and constitution. Unfortunately the evaluation of K was impossible nor could any physical conception be assigned to it, but, in the light of modern theories of polarity, it is clear that K is rather of electrical than of gravitational origin.

With the advance of time, a few fragmentary facts, indicating constitutional influences were observed. Thus the presence of a double or triple bond usually increased the rotations. Ring formation especially if the asymmetric atom be included in the

ring, had a similar effect. (Haller & Desfontaines, Compt. Rend., 1905, 140, 1205.) Further it had been shown by Frankland, that in a homologous series of optically active compounds, the rotatory power underwent a marked change, as the growing chain, attached to the asymmetric atom, reached a length of five or six atoms. This last mentioned type of work was greatly extended by Pickard and Kenyon (J.C.S. 1912 onwards, also Kenyon, Trans. Far. Soc., 1930, 439.) who showed that a similar effect resulted when the growing chain, attained a length of ten or eleven carbon atoms.

A more definite line of attack in correlating the magnitude of optical rotation with substituent influence was begun in 1907 by Betti, whose results were summarised in two papers, (Gazz. Chim. Ital., 1927, 51, 814; Trans. Far. Soc., 1930, 26, 337).

By condensing β -naphthol-benzylamine with benzaldehyde and substituted benzaldehydes, he obtained a series of optically active Schiff's bases of the type.



where X is a variable substituent.

When he arranged the bases in the decreasing order of rotatory power, the series so obtained showed

an excellent agreement with the dissociation constants of the benzoic acids corresponding to the aldehydes employed. The influence of a given substituent upon the rotatory power is therefore closely related to its influence upon the acid strength of the benzoic acid.

The following table I. containing Betti's results (Trans. Far. Soc., 1930, 26, 337) illustrates this point very clearly.

TABLE I./

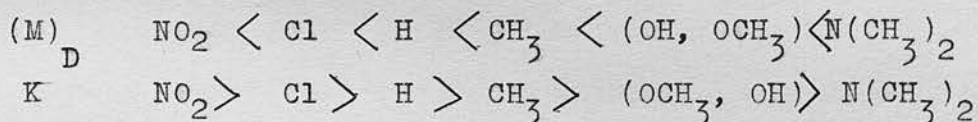
TABLE I.

(M)D	Aldehyde.	K x 10 ⁵ at 25°
+ 2670°	p-dimethylamino benzoic	0.94
+ 1049.5	p-hydroxy benzoic	2.6
+ 588.8	protocatechuic	3.3
+ 504.5	m-toluic	5.6
+ 373.1	benzoic	6.6
+ 362.6	m-hydroxybenzoic	8.3
+ 311.8	p-chlorobenzoic	9.3
+ 280.9	m-bromobenzoic	13.7
+ 255.9	m-chlorobenzoic	15.5
+ 167.6	m-nitrobenzoic	34.8
- 85.7	Salicylic	106
- 128.4	O-chlorobenzoic	132
- 308.2	O-bromobenzoic	145
- 990.7	O-nitro benzoic	657

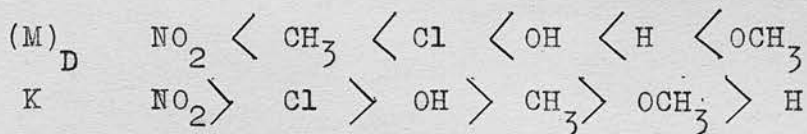
In discussing these interesting results, Rule has emphasised the polar character of the influence by comparing the changes produced by the introduction of different substituents into the same position in the aldehyde molecule. Thus when the mono-substituted

p - and o - derivatives are examined the changes are found to be as follows:-

Mono-para-substituted compounds.



Mono-ortho-substituted compounds.

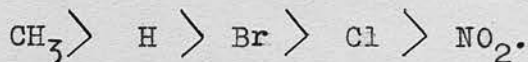


The agreement between rotatory power and dissociation constant is particularly good in the case of the para-compounds.

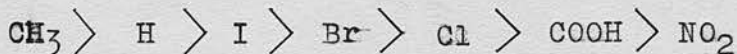
With mono-ortho-substituted compounds the correlation was not quite so good. It was suggested that the irregularities were probably due to "disturbances caused by the spatial proximity of the substituent to the asymmetric carbon atom." (Rule, *loc.cit.*) A sequence of substituent effect similar to that shown above in the case of p-substitution, had been observed by several investigators, while proceeding along quite different avenues of research. With only a few minor displacements, Flurschein (J.C.S., 1909, 95, 718) obtained the same series from a consideration of substituent influence on the dissociation constants of acids and bases. Results of a similar nature were

also obtained by Kellas (Zeit. Phys. Chem., 1897, 24, 227) from the rates of hydrolysis of esters of substituted benzoic acids.

Better still in this connection are the excellent data of Olivier, (Rec. Trav. Chem., 1914, 33, 244) illustrating the effect of substituents on the speed of formation of sulphones from p-bromobenzene-sulphonyl chloride and substituted benzenes. This author deduced the following sequence:-



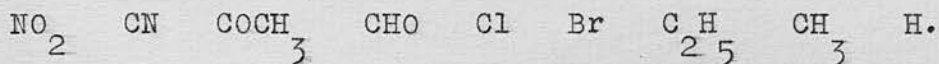
Moreover from an investigation of the rates of hydrolysis of p-substituted benzyl chlorides, he arrived at almost the same order, (Rec. Trav. Chem., 1923, 42, 516, 775) namely



This type of influence has been termed by Robinson (Ann. Rep. Chem. Soc., 1922, 98) the general "polar effect" and the radicals "polar groups."

The link connecting the polar effect and optical rotation was established by Rule and co-workers (J.C.S., 1924, 125, 1121, and later) who showed a close relationship to exist between the influence of substituents on the rotatory power of an active compound and on the dielectric constant of benzene, as deduced from derivatives of the type $\text{C}_6\text{H}_5\text{X}$. This contribut-

ion yielded a series showing excellent agreement with those obtained by previous investigators. The effect of groups on the dielectric constants of mono-substituted benzenes was given as follows:-



From then onwards, Rule and his co-workers have investigated in numerous cases the variations brought about in the optical rotation by the systematic insertion of polar groups into the optically active compounds. The results were highly interesting and only one instance need be cited illustrating the type of agreement obtained. Table II. contains the molecular rotations of a number of λ -menthyl esters of mono-substituted acetic acids, X CH₂COOH, the dissociation constants of the parent acids and the dipole moments of the groups. The dipole-moments are a measure of the polarity, characteristic of each substituent X.

TABLE II./

TABLE II.

Rule, Thomson, & Robertson, J.C.S., 1930, 1889.

X	$(M)_D^{20}$	$K_a \times 10^5$	$\mu \times 10^{18}$ e.s.u.
N(Et) ₂	-154.6 ⁰	} small	-
N(Me) ₂	-156.9		+1.4
H	-157.3	1.8	-
CH ₃	-160.2	1.4	+0.4
COOH	-160.2	160	-0.9(1.7)
OEt	-160.6	23	-
OMe	-165	33	-1.2
OH	-165(at 94 ⁰)	15	-1.7
Br	-169	138	-1.5
Cl	-171	155	-1.5
CN	-174	370	-3.8

This last contribution, indicating that the effect of a substituent depended primarily upon its dipole moment, gave good evidence that the influence was due to some fundamental electrical change in the molecular structure, and consequently, sympathetic variations in such properties as rate of hydrolysis and optical rotation were to be expected. The truth of Rule's prediction (loc.cit.), made six years earlier

and so aptly described by Lowry (Trans. Far. Soc., 1930, 266) as "the predominance of the polarity of substituent groups over their mere mass" was more clearly established.

The physicist, Sir J. J. Thomson (Phil. Mag. 1923, 497), suggested that the change in the electrical character of a molecule, as modified by a new substituent, could be explained as follows. He considered the introduction of a polar group into a hydrocarbon molecule as similar to the insertion of a small electrostatic doublet, which varied in strength and orientation with the nature of a substituent. The development of this problem is associated with the rapid progress in the study of valency in the field of inorganic chemistry. It was believed that for compound formation, the two components, forming an inorganic molecule, could be held together in either of two ways, (i) by an electron or group of electrons passing from one radical to the other, or (ii) through the mutual sharing of electrons by both radicals. Now, in general, the atoms in organic compounds were considered to be united to each other by co-valencies. When a polar group, therefore, was introduced into a hydrocarbon chain, the shared electrons did not take up such a position that the centre of the nuclear charges

coincided with that of electronic origin. Consequently, the insertion of a polar group caused the two resultant charges to be separated by a short distance. It was evident that the quantitative electrical effect depended conjointly on the magnitude of the resultant charges and the distance of their separation. The factor containing both quantities was termed the dipole moment and was measured as the product of one of the charges into the distance between them.

Thomson was the first to suggest a means of differentiating in a practical manner between the two types of radicals, electro-positive and electro-negative. In the first place, their relative magnitudes could be determined irrespective of sign, from a comparison of the molecule inductive capacity of organic compounds for long wave-lengths, where the compounds were of the type RX , R being the hydrocarbon residue and X the variable substituent. Secondly, the magnitudes were assumed to be vectorial, so that for disubstituted benzenes, the substituents of similar sign, if in the ortho position to each other, would enhance one another's effect. On the other hand, if the groups occupied the para positions, the effects would tend to neutralise one another. For groups of dis-similar type, results, the reverse of those stated

above, would be obtained.

A real impetus to the study of dipole moments, was given by Debye in 1912 (*Phys. Zeit.*, 1912, 13, 97). Debye devised a method whereby the value of the dipole moment could be calculated from a knowledge of the dielectric constant and the refractivity of the compound. Proceeding along similar lines, many investigations have been carried out in recent times by C. P. Smyth, J. W. Williams, K. Hojendahl, J. Errera and others; (*Chem. Revs.*, 1929, 549; *Chem. Revs.*, 1929, 589; Thesis, Copenhagen, 1928; *Leipziger Vortrage*, 1929). All these researches have indicated the dipole moment to be characteristic of the substituent, and, for mono-substituted hydrocarbons, largely independent of the hydrocarbon residue.

The substance of Debye's method for evaluating μ , the dipole moment, is as follows. Two factors must be considered, when polar molecules are under the influence of an electrostatic field. First, the molecules will tend to orientate themselves so as to oppose the exciting field. In this, they will conflict with the thermal agitation, which tends to orientate them equally in all directions. Hence an equilibrium is set up between these two forces, in which the number of opposing molecules is clearly dependent on their

polarity. Secondly, the external field has an inducing effect so that the electrons of the molecule are attracted to the positive region and the protons towards the negative region. Thus there is set up an induced polarity in distinction to that characteristic of the undistorted molecule.

Debye formulates P , the electric moment or total polarisation per gram molecule as

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho}$$

where ϵ is the dielectric constant

M " " molecular weight

of the dielectric

ρ " " density of the dielectric.

The total polarisation can be split into two parts, P_D , the polarisation due to distortion, and the polarisation due to orientation.

$$\text{i.e. } P = P_D + P_\mu$$

Thus P_μ is given as the difference of P and P_D , which are two quantities that can be easily determined.

P can be obtained from the above data, while P_D can be evaluated from the Lorenz-Lorentz equation

$$P_D = \frac{N^2 - 1}{N^2 + 2} \frac{M}{\rho}$$

where N is the refractive index of the dielectric and

M and ρ as defined above. Since there is atomic as well as electronic distortion, only light in the far infra-red should be used in determining N. Atomic distortion, however, is negligible in comparison with that of electronic origin, so that visible light, in which case N is dependent solely on electronic distortion, is employed. The connection between P_μ and μ is given by the following equation,

$$P_\mu = \frac{4\pi N\mu^2}{aKT}$$

where T = absolute temperature.

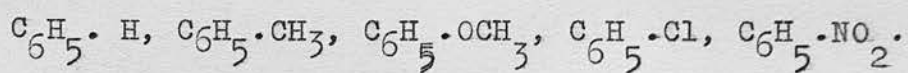
N = Avogadro's number

and K = the gas constant

whence μ can be evaluated.

It is imperative for a proper evaluation of P_μ and μ , that the conditions employed are such, that the polar molecules are far enough separated as to eliminate mutual interference, since polar molecules have a great tendency to associate, minimising their external field and thus altering the dipole moment. As a result, measurements are carried out with the dielectric either as a vapour, or in highly dilute solution in a non-polar solvent, such as benzene or hexane. Of these two methods, the latter is the more generally applicable.

It is apparent that by judicious selection, a series of solvents can be arranged, all of which are related to the same hydrocarbon compound, but, by having different substituents, are capable of showing a gradual transition from low to high polar properties, e.g.



EFFECT OF POLAR SOLVENTS ON OPTICAL ACTIVITY.

The early efforts to connect variations in rotatory power with solvent influence met with little success. As early as 1901, Patterson attempted to correlate solvent effect with the internal pressure of the solution. This idea was rejected by Dawson (J.C.S. 1910, 97, 1041.) who suggested the responsible factor to be the formation of compound molecules of solvent and solute. This last hypothesis was in turn discarded by Scheuer (Zeit.Phys. Chem., 1910, 72, 513.) who found no evidence for it from a consideration of the rotatory powers of mixtures of diacetyltartrate and menthol in several inactive solvents.

Two reasons explaining the vacillating opinions on this subject, were the restricted number of solvents used and the diversity of their structural types. Not until 1926 was definite progress made when an extensive investigation on the rotatory powers of five mono-substituted octyl esters of acetic acid in different solvents, was undertaken by Rule and Mitchell (J.C.S., 1926, 3202). It was found that when solvents of the same type were employed, namely benzene and its mono-substituted derivatives, a distinct polar influence could be traced. The results obtained are shown

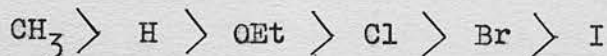
in Table III.

TABLE III.

Molecular Rotations $(M)_D^{20}$ of d-Octyl
Acetates in various 5% solutions.

Solvents	Acetate	Methoxy-Acetate	Chloro-Acetate	Bromo-Acetate	Iodo-Acetate
Homog.	+11.8	+16.3	+17.9	+30.3	+41.1
$C_6H_5CH_3$	-	+ 0.8	-	+10.8	-
C_6H_6	+ 1.4	- 1.0	+ 0.8	+10.1	+19.9
C_6H_5OEt	- 2.4	- 6.4	- 5.2	+ 4.9	+16.4
C_6H_5Cl	- 5.3	- 7.1	- 6.7	+ 2.5	+12.1
C_6H_5Br	-	- 7.0	- 8.8	+ 1.6	+ 9.1
C_6H_5I	-	-12.7	- 9.9	- 1.0	+ 2.5

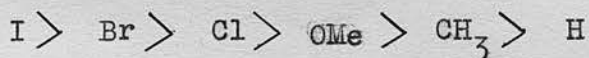
From these figures it is seen that a change of solvent produces similar variations in the rotatory power. The increase in dextro rotation brought about by a modification of X in the solvent C_6H_5X is represented by



and this series is independent of the particular ester used.

The authors note that when a substituent X

is introduced into the α -position in the active acetic ester the corresponding increase in the dextro-rotation is given by



a series almost exactly the reverse of that given above.

From a review of these and similar data, Rule (J.C.S., 1927, 58) suggested "that polar groups whether present in the asymmetric compound or in the solvent, also exert an influence on the neighbouring molecules leading to corresponding changes on the rotatory power."

With the evaluation of dipole moments, however, a numerical value could be assigned to a particular solvent, indicating its polar character and as a result, the closer relationship between the polarity of the solvent and the optical rotation as shown by Rule and McLean (J.C.S., 1931, 674) was only to be expected.

These authors employed the diester *l*-menthyl methyl naphthalate, which was found to be extremely sensitive to solvent action. Its behaviour was examined in some fifty solvents, which could be placed in four groups, as derivatives of methane, ethane, benzene or naphthalene respectively. The relationship for the benzene series of solvents is illustrated in Table IV.

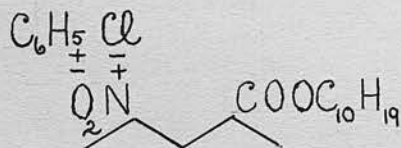
TABLE IV.

TABLE IV.

Solvent	20 (M) ₅₄₆₁	18 x 10 e.s.u.
C_6H_5CN	-372	3.85
$C_6H_5NO_2$	-423	3.98
C_6H_5CHO	-432	2.75
$O-C_6H_4Cl_2$	-433	2.24
C_6H_5Cl	-463	1.62
C_6H_5I	-465	1.50
C_6H_5Br	-466	1.50
C_6H_5OMe	-466	1.25
C_6H_6	-543	0
$C_6H_5CH_3$	-546	0
S - $C_6H_3(CH_3)_3$	-583	0
Cyclohexane	-688	0

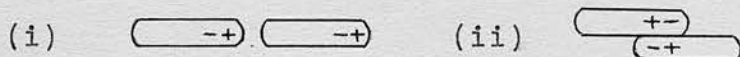
The explanation advanced by the authors for this sympathetic variation is that there arises a change in the internal field of the active molecule through deformation or dipole association with the solvent. Association of this type would tend to neutralise the influence of the polar substituents in the active molecule and thus to diminish their contribution towards

the molecular rotation.



It was soon realised that secondary disturbing influences would arise causing displacements in the series. These irregularities have been investigated and explained with striking success by Rule and co-workers.

For example in dealing with a polar liquid, association of the type solute-solvent may not be the only kind present. It may be accompanied by association of the solvent molecules themselves, giving solvent-solvent complexes, capable of orientating in either of two ways



In the first instance, the dipole moment would be greater than that of a single molecule, but in the second it would be zero.

Optical evidence for the existence of these two types has been advanced by Rule and McLean (loc. cit.). They used a method of analysis similar to that of Debye (Polare Molekeln p.48), by which he deduced the polarisation - dissociation diagram for a polar liquid on dilution with a non-polar solvent such as

benzene or hexane. By employing the same mixtures and plotting the rotation, contributed by the polar component of the mixture, along the polarisability axis, a curve, in most cases, the inverse of that of Debye, was obtained. Thus for nitrobenzene, the curves obtained both by Debye and Rule indicated association of type (ii). With alcohols, however, such as N-propyl, N- and iso-butyl, iso - and tert - amyl, the curves agreed on the existence of complexes, orientated as shown in figure (i), at certain concentrations of the mixtures.

In the systems of mixtures previously discussed, we have considered two classes of molecular association (a) solvent-solute type and (b) solvent-solvent type. There is still a third class which calls for some consideration, i.e. (c) solute-solute type.

EFFECT OF CONCENTRATION ON OPTICAL ACTIVITY.

From the work of Rule and co-workers (J.C.S., 1933, 376, Dunbar, Thesis, Edinburgh; Cunningham, Thesis, Edinburgh.), there is evidently a connection between the variations in rotation due to concentration changes and those produced by alteration in the polarity of the medium.

It was concluded that if once the direction of change due to a highly polar solvent was known, then the variations in rotatory power with changing concentration in a non-polar medium could be foretold. In the former instance, the change was attributed to dipole association of the solvent-solute type, due to the intense polar character of the solvent. In the latter case, by increasing the concentration, the solute molecules were brought into closer proximity and minimised their external fields by formation of solute-solute complexes, these affecting rotatory power in the same direction as the solvent-solute complexes discussed above.

From the data obtained in these studies, it was suggested that optically active solutes could be divided into four main classes according to the nature of the substituent groups present and their reaction

towards the solvents.

Class I. Non Polar Solutes.

The chief representatives are saturated hydrocarbons, which may be regarded as assuming an entirely random orientation towards one another, whether in the homogeneous state or dissolved in a polar or non-polar liquid. Little or no variation in the rotatory power is probable when the compound passes from the homogeneous state into solution.

Class II. Weakly Polar Solutes.

Herein are contained compounds with low dipole moments, such as the majority of un-saturated hydrocarbons, ethers, alcohols, esters and halogen derivatives. Owing to the weakness of intra-molecular forces, when such compounds are diluted with a non-polar solvent the molecules are largely separated by the diluent, so that the internal field is no longer diminished by mutual orientation and its full influence is exerted on the rotatory power. In dilute solutions therefore, the rotatory power should be closely related to the dipole moment of the solvent. This prediction has been fulfilled by a large number of widely selected active compounds, all of which come under the heading of this

group.

Class III. Strongly polar solutes.

In this group are included compounds such as nitro, cyano carboxy and ketonic derivatives, which exhibit a strong tendency to undergo association even when dissolved in solvents of low or zero polarity. With such compounds the changes following dilution with a solvent depend on the extent to which the latter is capable of breaking up these association complexes. Two compounds from among several of this class are d- β -nitro-octane (J.C.S., 1933, 380.) and methylene tartaric acid (Cunningham, Thesis, Edinburgh).

Class IV. This group contains compounds which when brought into contact with certain solvents, suffer electronic rearrangement, due to compound formation, co-ordination, ionisation etc. The irregular changes found for octyl alcohol (J.C.S., 1933, 377) in hexane on progressive dilution, may be traced to a similar origin.

EFFECT OF TEMPERATURE ON OPTICAL ACTIVITY.

Until recently, scant attention has been paid to the explanation of variations in slope of the temperature-rotation curves of an active compound in various solvents. The first generalisation advanced by Patterson and co-workers (J.C.S., 1932, 1715; see also J.C.S., 1908, 1843; J.C.S., 1909, 321.) was of a pure empirical nature. Chiefly from a comprehensive investigation of a large number of tartaric derivatives, they suggested that "in solvents which confer high rotations, the rotation should diminish or else increase slowly with rise of temperature, whereas in solvents of depressing influence the rotation should increase fairly rapidly." In this connection, as was pointed out by Rule (J.C.S., 1933, 1222.), the theory of dipoles allowed a prediction to be made as to the relative slopes of the temperature-rotation curves for solvents of the two extreme types, where a definite relationship was traceable between the influence of the solvent and its polar character.

A rise in temperature was considered to operate chiefly in two ways. First, the configuration or mean resting position of the molecule was altered with the increase in the free rotation of groups

around single bonds. Such a modification would occur with those molecules momentarily free from solvent influence. Secondly, considering a polar solvent, the extent of solute-solvent association would diminish as the mobility of the molecules increased at higher temperatures.

In comparison with a solution in a non-polar medium, it followed that the optical displacement due to a polar solvent was more accentuated at low than at high temperatures so that the temperature-rotation curve for a polar medium should converge towards that of a non-polar medium as the temperature rose. Since the polarity of optically active compounds was generally less than that of strongly polar solvents, e.g. nitrobenzene, in general the temperature-rotation curve for the homogeneous compound would lie in position and direction between those obtained for solutions in solvents of the two extreme types.

These conclusions have been substantiated in the few cases as yet considered. From the results of Patterson's work on ethyl tartrate (J.C.S., 1908, 93, 1849.), Rule (loc. cit.) illustrated the above hypothesis in the following table

$$(\text{M})_{\text{D}}/$$

$(M)_D$

	$C_6H_5NO_2$ P = 2	Homog.	Mesitylene P = 10
20°	79.1	16.7	3.71
100°	58.7	28	22.8
80°	-20.4	+11.3	+19.1

For a rise of 80° the high values for nitrobenzene fell by 20.4°, and the lower values for mesitylene increased by 19.1°, while the homogeneous substance occupied an intermediate position.

Further instances will be discussed later in this thesis, in which there is also an attempt to correlate solvent influences with changes of temperature and concentration, employing five different wavelengths ranging from the hydrogen red to the mercury violet, and using *l*-benzoin, *l*-benzoin methyl ether, and methyl *l*-mandelate as the active components.

EXPERIMENTAL.PREPARATIVE.PREPARATION OF *l*-BENZOIN.

The preparation was conducted in two stages according to the method of Smith (Ber., 1931, 64, 427). From a solution of amygdalin, as supplied by British Drug Houses, Ltd., d-mandelonitrile was first isolated, this being later converted into *l*-benzoin. l

(a) Preparation of d-Mandelonitrile.

To a solution of 60 gms. of amygdalin in 180 cc. of water, 64 cc. of conc. sulphuric acid was added, drop by drop with constant stirring. After the addition of the acid, the mixture was heated at 90° on a water-bath for about 60 minutes. The solution was then cooled, diluted with water, and the nitrile extracted three times from the aqueous layer, with benzene. The extracts were added together, washed with water and dried over anhydrous sodium sulphate for three days. In the first experiments partial decolorisation was effected by the use of animal charcoal. This was later discarded, as the nitrile obtained in a dark-coloured semi-solid condition was found to be sufficiently pure for the conversion into *l*-benzoin. The greater

part of the benzene was distilled over under reduced pressure at about 35° and the last traces removed by leaving the dark viscous oil over paraffin wax in a vacuum desiccator.

A yield corresponding to 25% of the theory was obtained in the first experiment. Later this was increased to an average of 54%, this being rather less than that obtained by Smith, who quoted 50% - 70% of the theoretical yield.

(b) Preparation of *l*-Benzoin.

Owing to the varying quantities of d-mandelonitrile obtained, each conversion required a different amount of Grignard reagent to be prepared. The requisite quantities were calculated proportionally from those given by Smith (loc.cit.), which are reproduced below in the method of preparation as adopted by that author.

Pure d-mandelonitrile, 3.75 gms., was subjected to the action of Grignard reagent prepared from 13.3 gms. of bromobenzene. The reagent was prepared according to the method advanced by Gilman and co-workers (J.A.C.S., 1929, 51, 1579.) in the hope of obtaining the minimum proportion of diphenyl. The nitrile was dissolved in its own weight of ether and added as rapidly as possible to the reagent. When

the reaction had somewhat slackened, the mixture was heated for 15 minutes on a water-bath. After cooling and pouring into 30 c.c. conc. sulphuric acid and 180 gms. of ice, the intermediate compound was decomposed as speedily as possible by brisk stirring and the ether layer immediately separated. On standing for some time, crude β -benzoin precipitated itself from the aqueous solution. l

The initial experiment was conducted with semi-solid nitrile containing a considerable portion of liquid product and gave a poor yield, 6.9 gms. giving only 1.3 gms. of crude β -benzoin. The second experiment conducted with semi-solid nitrile gave a better yield, 5.29 gms. of β -benzoin being obtained from 6.7 gms. of nitrile. Thereafter the yields were always comparable with those of Smith (loc. cit.) who obtained 6.12 gms. of crude β -benzoin from 7.5 gms. of dark-coloured oily d-mandelonitrile. l

The crude material was recrystallised from absolute alcohol, until optical purity was obtained.

M.p., 131-132.5° (McKenzie & Wren, J.C.S., 1908, 93, 313.)

M.p., 131-132° (present investigation.)

$\frac{16}{D}$ = 119.4° in acetone c. = 2.5005 (Smith loc. cit.)

$\frac{20}{D}$ = 119.2° " " c. = 2.764 (present investigation.)

PREPARATION OF *l*-BENZOIN METHYL ETHER.

This compound was prepared according to the method used by Wren (J.C.S., 1909, 95, 1584). The experiment was carried out several times, the quantities stated by Wren being used each time.

Dry silver oxide (21 gms.) was added to a solution of *l*-benzoin (7.3 gms.) and methyl iodide (43.9 gms.) in 100 cc. of acetone. (The crude *l*-benzoin obtained from the previous preparation was only once recrystallised for the present purpose, the product being then sufficiently pure for conversion into the methyl derivative, (c.f. Wren J.C.S., 1909, 95, 1597). On warming the methylating mixture gentle boiling set in, which continued for about 10 minutes. The mixture was subsequently boiled gently with frequent shaking during two hours, after which time the precipitate of silver oxide and silver iodide was filtered and well washed with acetone.

The bulk of the acetone was distilled over, under reduced pressure at room temperature, and the last traces finally removed in a vacuum desiccator. In one or two cases the crude residual oil had to be left overnight, when it solidified to a mass of yellow crystals. However, in later experiments, after the removal of the acetone, the bubbling of a stream of

air, from a fine jet, through the thick viscous oil caused crystallisation to set in almost immediately. The average yield of crude compound was 7.1 gms. After one recrystallisation from light petroleum, 25 gms. of crude material yielded 21 gms. of partially purified compound. This was recrystallised a second time giving a crop of 18.6 gms. of prismatic crystals, the optical rotation of which for $c = 3.028$ was $[\alpha]_D^{18.5} = + 46.5^\circ$ in benzene. The polarimeter carrier would not accommodate a 4 dcm. tube, thus a direct comparison with Wren's result for $c = 0.6428$ & $l = 4$ could not be obtained. The compound was recrystallised other two times, the yield now being only 12.5 gms. The rotation had increased very slightly from the second recrystallisation, the value now being $[\alpha]_D^{20} = + 46.9^\circ$ for $c = 4.022$ in benzene. The melting point was very sharp and it was thought that the ether would be optically pure, a conclusion which was later confirmed from the concentration-rotation diagram for benzene, which proved the rotatory power to vary strongly with change of concentration.

$$[\alpha]_D^{20} = + 46.9^\circ \quad c = 4.022 \text{ in benzene}$$

Wren (loc. cit.) quotes $[\alpha]_D^{11} = + 50.9^\circ \text{C} = 0.6428$ in benzene.

$$\text{M.p.} = 51^\circ - 52^\circ \text{ (corr.)}$$

$$\text{(Wren) M.p.} = 53^\circ - 54^\circ$$

THE DETERMINATION OF ROTATORY POWER.

All the angles of rotation in this thesis were determined with the same polarimeter, except in one instance. The polarimeter, of Schmidt and Haensch design, could be relied upon to give a limiting error of 0.02° , and was fitted with a "Doppel-Monochromator". This enables the experimenter to examine optical behaviour over as wide a range as desired in the visible region. Only five wave-lengths, however, about equally distributed from the red to the violet end of the spectrum, were employed in this research, as the object was not to conduct an extensive investigation on the dispersion of the various solutions. The exception mentioned above, a very dilute solution of *l*-benzoin in cyclohexane, was examined in a four decimetre tube on a Hilger polarimeter, capable of reading to $.01^{\circ}$ and fitted with a Kelvin, Bottomley and Baird mercury-vapour lamp. Thus only two determinations were taken with this instrument, one for the mercury green line and the other for the mercury violet. A two decimetre tube was mainly used. For the examination of temperature effects, a one decimetre water-jacketted tube was employed, the bulb of a thermometer dipping into the solution under investigation. Water from the

main pipes gave a temperature of approximately 10° , steam gave one in the vicinity of 100° and intermediate temperatures were obtained from two thermostats which could be regulated at any fixed points between (i) 20° and 50° and (ii) 50° and 90° . Water from the thermostats was driven through the jacket of the tube by two small turbine pumps. For each determination from the lowest to the highest temperatures, the water or steam was circulated for a reasonable period until temperature-equilibrium had been established.

The heating of the room was regulated to give a temperature of $20^{\circ} + 1^{\circ}$. For all the values taken with the five wave-lengths at this temperature, the rotatory powers were expressed as specific rotations, this being the more usual form when dealing with dispersion curves. However, for illustrating solvent influence the molecular rotations of the active solutes for the mercury green line were listed against the dipole moment for the solvent as in the past researches in this subject.

For the evaluation of rotatory powers with changing temperature, care had to be exercised in determining the densities of the two solutions of α -benzoïn in toluene which tended to deposit solid at $40^{\circ} - 50^{\circ}$, and also in a lesser degree with the

l.

homogeneous methyl ether of *l*-benzoin. During the weighing at room temperature, the *l*-benzoin crystallised out from the toluene, so that for each determination, the pyknometer had to be heated up in the usual manner and kept at the desired temperature not only until the solid had redissolved but until it had long enough to disperse equally all through the solution. In many of the temperature-rotation tables the limiting error is given, calculated on the basis of an error of $.03^{\circ}$ on the observed angle of rotation. This figure, however, is probably well outside the ordinary error of reading.

PURIFICATION OF SOLVENTS.

The purest available solvents were used as starting materials and were then further purified by the following methods:

Nitromethane.

The B.D.H. product was washed, dried over anhydrous calcium chloride and fractionated. It was obtained colourless.

B.p. 100.8° - 101.1°

Acetonitrile.

Aytoun, Scott and Co.'s acetonitrile was dried over calcium chloride and fractionated, giving a colourless product.

B.p. 80.7° - 81.4° .

Acetaldehyde.

Aytoun, Scott and Co.'s acetaldehyde was dried over calcium chloride, boiled over succinic acid to remove traces of basic impurity and fractionated.

B.p. 20.8° .

Methyl Iodide.

Aytoun Scott and Co.'s purified methyl iodide was washed with sodium carbonate solution and water, dried over calcium chloride and fractionated. A colourless fraction of b.p. 42.7° - 43° was collected. It was kept in a dark bottle over a small quantity of clean mercury.

Acetic Acid.

Kahlbaum's 100% acid was cooled until about two-thirds frozen. The liquid portion was then decanted off and the crystalline mass dried and fractionated.

M.p. 16° . B.p. 118° - $118^{\circ}.2^{\circ}$.

Methylene Dichloride.

Methylene dichloride (B.D.H.) was washed with water, dried over calcium chloride and fractionated.

A colourless middle fraction of b.p. 40.4° - 40.6° was employed.

Acetone.

Acetone, "bisulphite purified" (B.D.H.) was well-dried over anhydrous calcium chloride and fractionated.

B.p. 55° - 56° .

Methyl Alcohol.

"Absolute" methyl alcohol was purified by the method of Bjerrum and Zechmeister (Ber., 1923, 56, 897).

One litre of the alcohol was mixed with about 10 grams of clean magnesium turnings (previously washed with ether and thoroughly dried), and allowed to stand in an all-glass distillation apparatus. The reaction was vigorous and when all the metal had disappeared the liquid was refluxed for several hours and then distilled in a current of dry air, the first and last fractions being rejected. A middle fraction was collected in a receiver from which moist air was excluded by means of a calcium chloride tube.

B.p. 65° .

Chloroform.

The product of Macfarlane and Co. was dried and fractionated. A middle portion of b.p. 61° - 61.1° was collected.

Carbon Disulphide.

Aytoun, Scott and Co's redistilled carbon disulphide was shaken with mercury to remove sulphur, dried over calcium chloride, filtered and fractionated.

B.p. 46° - $46^{\circ}.2^{\circ}$.

Carbon Tetrachloride.

The sample available had already been carefully purified. It was dried and fractionated.

B.p. 77.6° - 77.8° .

Cyclohexane.

The sample of B.D.H. cyclohexane for spectroscopic purposes required no further purification.

Benzonitrile.

The B.D.H. product was dried over freshly ignited sodium sulphate, filtered and partially frozen out. The crystalline portion was melted, dried and distilled under diminished pressure in a Wittmar flask. A middle portion of b.p. 68° / 10 mm. was collected as a colourless liquid.

Nitrobenzene.

Nitrobenzene (B.D.H.) was fractionated and the middle fraction was partially frozen out. The crystalline portion was melted, dried and fractionated under reduced pressure.

M.p. 5.6° - 5.7° ; b.p. 90° - 91° / 15 mm.

Benzaldehyde.

The B.D.H. product was washed with sodium carbonate solution, dried over sodium sulphate and fractionated under reduced pressure, care being taken to prevent exposure to the air as far as possible. This product was freshly fractionated for each rotation in which it was employed as solvent.

B.p. 179° - 179.2°

Aniline.

Kahlbaum's aniline "from sulphate" was dried and fractionated. A colourless liquid was obtained.

B.p. 182.9° - 183° .

Anisole.

Anisole (B.D.H.) was dried and fractionated. A middle portion was obtained colourless and gave no phenol reaction.

B.p. 153.8° .

Chlorobenzene.

The B.D.H. product was washed with alkali and with water, dried over anhydrous calcium chloride and fractionated.

B.p. 131.6° - 132° .

Bromobenzene.

The B.D.H. product was treated in the same manner as chlorobenzene.

B.p. 154.8° - 155.2° .

Iodobenzene.

Iodobenzene (B.D.H.) was treated in the same manner as chlorobenzene. B.p. 72.5° - 73° / 14 mm.

Benzene.

"Extra pure" benzene (B.D.H.) was dried over calcium chloride, filtered and partially frozen out. The crystalline portion was redried and fractionated.

M.p. 5.5° ; b.p. 80° - 81.1° .

Toluene.

The B.D.H. product was dried with metallic sodium wire for 3 days. The liquid was then decanted, fresh sodium wire added, and the whole refluxed for 40 minutes. The liquid was then directly fractionated and a middle portion collected.

B.p. 110° .

Mesitylene.

Morck's mesitylene was dried over calcium chloride and fractionated. /e

B.p. 164° - 165° .

o. Dichlorobenzene.

On cooling B.D.H. o. dichlorobenzene to -20° , a small amount of crystalline substance (probably p.dichlorobenzene) deposited and was rapidly filtered off at the pump. The liquid was then dried over calcium chloride and fractionated under reduced pressure.

B.p. 60° - 61° / 11 mm.

Influence of Solvents on the RotatoryPowers of *l*-Benzoin.TABLE I. *l*-Benzoin.Methane Type Solvents. $l = 2 \text{ dcm.}$ $t = 20^{\circ} + 1^{\circ}$ in each case.

Solvent	c	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
CH_3CHO	2.328	-3.78°	-4.96°	-6.07°	-8.68°	-12.86°
CH_3COCH_3	2.764	5.07	6.59	-8.18	11.84	17.90
CH_3CN	2.262	5.53	7.14	-8.82	12.64	18.85
CH_3NO_2	2.306	5.76	7.47	9.29	13.33	20.05
$\cdot\text{X}\cdot\text{CH}_3\text{OH}$	1.012	2.55	3.3	4.08	5.86	8.68
CH_2Cl_2	2.288	7.41	9.56	11.77	16.72	24.62
CH_3Cl	2.212	7.18	9.39	11.55	16.43	24.03
CH_3COOH	1.010	3.57	4.56	5.57	7.86	11.41
CH_3I	2.216	8.30	10.66	13.08	18.53	27.01
C Cl_4	.220	0.84	1.09	1.32	1.86	2.73
CS_2	.522	3.32	4.28	5.24	7.44	10.75

$\cdot\text{X}\cdot (\alpha_{6200} = -2.90^{\circ}, \alpha_{5353} = -4.33^{\circ}.)$

TABLE II. *l*-Benzoin.

Solvent	$[\alpha]_{6563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{4861}^{20}$	$[\alpha]_{4358}^{20}$	$\mu \times 10^{18}$
CH ₃ CHO	-81.1 ^a	-106 ^o	-130 ^o	-186 ^o	-276 ^o	2.7
CH ₃ COCH ₃	91.6	119.2	148	214	324	2.8
CH ₃ CN	122	158	195	280	417	3.21
CH ₃ NO ₂	125	162	201	289	435	3.05
CH ₃ OH	126	163	202	290	429	1.68
CH ₂ Cl ₂	162	209	257	366	538	1.51
CH ₃ Cl	162	212	261	371	543	1.05
CH ₃ COOH	177	226	276	389	565	1.73
CH ₃ I	187	240.5	295	418	609.5	1.35
C Cl ₄	191	247	299	422	619	0
CS ₂	318	410	502	713	1030	0

$$[\alpha]_{6200}^{20} = -143^{\circ}, \quad [\alpha]_{5353}^{20} = -214^{\circ}$$

All attempts to examine the optical behaviour of *l*-benzoin under similar conditions of concentration were unsuccessful. In general, as the above results indicate (Table I.) the solubility of the compound varied with the polarity of the solvent. In solvents of intense polar character e.g. nitromethane, the

solubility was fairly high; such was also the case with the halogenated derivatives, chloroform, methylene chloride and methyl iodide, which are of intermediate polarity. However, with the intermediate polar solvents, methyl alcohol and acetic acid moderate solubility was exhibited. Only very dilute solutions could be obtained with the non-polar solvents, carbon disulphide and carbon tetrachloride.

The following table III. contains the requisite data for drawing a comparison between the polarity of the methane type of solvents and the corresponding effect on the rotatory power of ℓ -benzoin for one wavelength only, i.e. the mercury-green, $\lambda = 5461$. Solvents are arranged in the order of increasing negative rotation.

TABLE III. ℓ -Benzoin./

TABLE III. *l*-Benzoin. $l = 2$ dcm. $t = 20_{\pm 1}^{\circ}$ in each case.

Solvent	conc.	α_{5461}	$\mu \times 10^{18}$	$[M]_{5461}^{20}$
CH_3CHO	2.328	-6.07	2.7	-276 ^o
CH_3COCH_3	2.754	8.18	2.8	-314
CH_3CN	2.262	8.82	3.21	-413
CH_3NO_2	2.306	9.29	3.05	-427
CH_3OH	1.012	4.08	1.68	-427
CH_2Cl_2	2.288	11.77	1.51	-545
CHCl_3	2.212	11.55	1.05	-553.5
CH_3COOH	1.010	5.57	1.73	-585
CH_3I	2.216	13.08	1.35	-626
CCl_4	.220	1.32	0	-633
CS_2	.522	5.24	0	-1064

TABLE IV. *l*-Benzoin./

TABLE IV. *l*-Benzoin.

Benzene Type of Solvent.

For cyclohexane $l = 4$ dcm.

" nitrobenzene
 " bromobenzene } $l = 1$ dcm.
 " mesitylene }

" other solvents $l = 2$ dcm.

$t = 20_{+1}^{\circ}$ in every case; except nitrobenzene
 for which $t = 21.5^{\circ}$

Solvent	conc.	α 6563	α 5893	α 5461	α 4861	α 4358
$C_6H_5COCH_3$	2.036 ^d	-5.53 ^o	-7.15 ^o	-8.83 ^o	-12.57 ^o	-18.57 ^o
$C_6H_5NO_2$	1.037	1.38	1.80	2.26	3.27	-
C_6H_{12}	(i) 0.047 (ii) 0.056	-	-	.42 .49	-	.950 1.13
C_6H_5CHO	2.314	6.87	9.01	11.19	16.10	24.03
C_6H_5CN	2.324	7.28	9.40	11.61	16.52	24.35
$S-C_6H_3(CH_3)_3$	0.9665	1.54	1.99	2.51	3.54	5.19
$C_6H_5CH_3$	0.81	2.72	3.54	4.34	6.16	9.03
C_6H_6	1.012	3.37	4.43	5.44	7.69	11.24
C_6H_5Br	0.9865	1.80	2.33	2.88	4.14	6.1
C_6H_5Cl	2.068	7.70	9.95	12.24	17.35	25.37
$O-C_6H_4Cl_2$	2.052	7.73	9.96	12.26	17.36	25.47
$C_6H_5OCH_3$	2.082	7.98	10.36	12.75	17.97	26.23
C_6H_5I	2.058	8.59	11.05	13.60	19.19	28.23

TABLE V. *l*-Benzoin.

Solvent	20 [α]6563	20 [α]5893	20 [α]5461	20 [α]4861	20 [α]4358	$\mu \times 10^{18}$
$C_6H_5COCH_3$	-136°	-176°	-217°	-309°	-456°	2.94
$C_6H_5NO_2$	133	174	218	315		3.90
C_6H_{12}	(i)		223		505	
	(ii)		219		505	0
C_6H_5CHO	148.5	194.5	242	348	519	2.75
C_6H_5CN	156.5	202	250	355.5	524	3.8
$S-C_6H_3(CH_3)_3$	159	206	259	366	537	0
$C_6H_5CH_3$	168	218	268	380.5	557.5	.4
C_6H_6	167	219	269	380	555	0
$C_6H_5Br.$	182	236	292	420	618	1.50
C_6H_5Cl	186	240.5	296	419	613	1.52
$O-C_6H_4Cl_2$	188.5	243	299	423	620.5	2.25
$C_6H_5OCH_3$	192	249	305.5	432	630	1.20
C_6H_5I	209	268.5	330.5	466	686	1.25

The concentrations in the above solvents are somewhat irregular. The strongly polar solvents were examined first, the non-polar being considered last. All the solutions were of moderate solubility until the

non-polar group was reached. Benzene and toluene only gave very dilute solutions and so mesitylene, benzene and toluene were examined in dilute solutions of almost similar values. Since temperature work was to be carried out later with nitrobenzene and bromobenzene, it was thought advisable to make up solutions in the last two solvents of the same concentration as was used with mesitylene so as to give a proper comparison of the temperature-rotation diagrams for the three solvents. It was only with the greatest difficulty that an exceedingly dilute solution with cyclohexane could be obtained; in which determination a four decimetre tube had to be adopted with a polarimeter used in conjunction with a mercury vapour lamp. The experimental error was, however, very high, the limits for the specific rotation being of the order ($\pm 20^{\circ}$)

TABLE VI. *l*-Benzoin./

TABLE VI. *l*-Benzoin.

For one wave-length only, mercury green,
 $\lambda = 5461$. The other specifications are identical
 with those set out for table IV.

Solvent.	conc.	α 5461	$\mu \times 10^{18}$	$[M]_{5461}^{20}$
$C_6H_5COCH_3$	2.036	-8.83 ^o	2.94	-460 ^o
$C_6H_5NO_2$	1.037	2.26	3.90	-462 ^o
C_6H_{12}	(i).047) (ii).056)	.42) .49)	0	-473) -464)
C_6H_5CHO	2.314	11.19	2.75	-513
C_6H_5CN	2.324	11.61	3.8	-530
$S-C_6H_3(CH_3)_3$	0.9665	2.51	0	-549.5
$C_6H_5CH_3$	0.81	4.34	.4	-568
C_6H_6	1.012	5.44	0	-571
$C_6H_5Br.$	0.9865	2.88	1.50	-619
C_6H_5Cl	2.068	12.24	1.52	-627
$O-C_6H_4Cl_2$	2.052	12.26	2.25	-632
$C_6H_5OCH_3$	2.082	12.75	1.20	-649
C_6H_5I	2.058	13.60	1.25	-700

Influence of Solvents on the RotatoryPower of *l*-Benzoin Methyl Ether.

The solvents are arranged in the order of diminishing negative or increasing positive rotations.

TABLE VII. *l*-Benzoin Methyl Ether.Methane Type of Solvents.

$$l = 2 \text{ dcm.}$$

$$t = 20_{\pm}^{\circ} 1^{\circ} \text{ in each case.}$$

Solvent	conc.	α 6563	α 5893	α 5461	α 4861	α 4358
CH_3OH	4.022	-7.68 ^o	-10.10 ^o	-12.53 ^o	-17.97 ^o	-27.05 ^o
CH_3COOH	4.020	-7.53	-9.91	-12.25	-17.29	-25.36
CH_3NO_2	4.014	-5.39	-7.20	-9.04	-13.36	-20.75
CH_3CHO	4.020	-5.35	-7.05	-8.66	-12.28	-17.95
CH_3CN	4.006	-4.97	-6.65	-8.38	-12.32	-19.22
CH_3Cl	4.020	-4.84	-6.24	-7.63	-10.75	-15.45
CH_2Cl_2	4.018	-3.91	-5.14	-6.32	- 8.88	-12.84
CH_3COCH_3	4.030	-2.18	-2.89	-3.65	- 5.46	- 8.51
CH_3I	4.036	+0.35	+0.62	+0.98	+ 2.06	+ 5.14
C Cl_4	4.026	+6.46	+8.82	+11.25	+17.46	+30.23
CS_2	4.012	+7.58	+10.25	+13.15	+20.34	+35.07

TABLE VIII. *l*-Benzoin Methyl Ether.

Solvent	$[\alpha]_{6563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{4861}^{20}$	$[\alpha]_{4358}^{20}$	$\mu \times 10^{18}$
CH ₃ OH	-95.5 ^o	-125.5 ^o	-156 ^o	-223 ^o	-336 ^o	1.68
CH ₃ COOH	-93.7	-123	-152	-215	-315	1.73
CH ₃ NO ₂	-66.9	-89.4	-112	-166	-258	3.05
CH ₃ CHO	-66.6	-87.7	-108	-153	-223	2.7
CH ₃ CN	-62.0	-83.0	-105	-154	-240	3.21
CH ₃ Cl	-60.2	-77.6	-94.9	-134	-192	1.05
CH ₂ Cl ₂	-48.8	-64.0	-78.7	-110.5	-160	1.51
CH ₃ COCH ₃	-27.1	-35.9	-45.3	-67.8	-105.5	2.8
CH ₃ I	+4.34	+7.93	+12.1	+25.5	+63.7	1.35
C ₂ Cl ₄	+80.2	+109.5	+140	+217	+375	0
CS ₂	+99.0	+128	+164	+253	+437	0

No difficulty was experienced in getting similar concentrations, as the ether was comparatively readily soluble in all the solvents used.

As in the case of *l*-benzoin in the two types of solvents, the following table IX was compiled from the data in tables VII and VIII to facilitate discussion of the results.



TABLE IX. *l*-Benzoin Methyl Ether.

$$l = 2 \text{ dcm.}$$

$$t = 20^{\circ} + 1^{\circ}$$

$$\lambda = 5461 \text{ \AA}^{\circ}.$$

Solvent	c	α_{5461}	$\mu \times 10^{18}$	$[M]_{5461}^{20}$
CH_3OH	4.022	-12.53 ⁰	1.68	-352 ⁰
CH_3COOH	4.020	-12.25	1.73	-344
CH_3NO_2	4.014	-9.04	3.05	-320
CH_3CHO	4.020	-8.66	2.7	-243.5
CH_3CN	4.006	-8.38	3.21	-236
CHCl_3	4.020	-7.63	1.05	-214.5
CH_2Cl_2	4.018	-6.32	1.51	-178
* $(\text{CH}_3\text{COCH}_3)$	(4.030)	(-3.65)	(2.8)	(-102)
CH_3I	4.036	+0.98	1.35	+27.4
CCl_4	4.026	+11.25	0	+316
CS_2	4.012	+13.15	0	+370

* This solvent does not properly belong to the simple methane type but was used in order to obtain solutions of lower negative rotation.

TABLE X. ℓ -Benzoin Methyl Ether.Benzene Type of solvents.

For nitrobenzene }
 " bromobenzene } $\ell = 1$ dcm.
 " mesitylene }

All other solvents $\ell = 2$ dcm.

$t = 20^{\circ} + 1^{\circ}$ except for bromobenzene $t = 18.25^{\circ}$

Solvent	conc	α 6563	α 5893	α 5461	α 4861	α 4358
C_6H_5CN	4.064	-3.21 ^o	-4.23 ^o	-5.26 ^o	-7.64 ^o	-11.57 ^o
C_6H_5CHO	4.010	-2.79	-3.65	-4.45	-6.36	-9.08
$C_6H_5NO_2$	4.018	-1.25	-1.67	-2.07	-2.96	-
$C_6H_5COCH_3$	4.016	-2.17	-3.16	-3.88	-5.98	-7.97
$O-C_6H_4Cl_2$	10.036	-0.90	-0.91	-0.80	+0.03	+3.88
$C_6H_5OCH_3$	4.008	+0.05	+0.11	+0.23	+0.79	+2.53
C_6H_5Br	3.984	+0.25	+0.37	+0.58	+1.17	+2.80
C_6H_5Cl	4.020	+0.58	+0.89	+1.26	+2.35	+5.35
C_6H_5I	4.026	+ .71	+1.06	+1.53	+2.94	+6.76
C_6H_6	4.022	+2.81	+3.78	+4.91	+7.84	+14.34
$C_6H_5CH_3$	4.022	+3.82	+5.24	+6.76	+10.52	+18.49
$S-C_6H_3(CH_3)_3$	4.021	+2.77	+3.75	+4.84	+7.39	+12.57
C_6H_{12}	4.022	+7.68	+10.32	+13.29	+20.18	+34.31

TABLE XI. *l*-Benzoin Methyl Ether.

Solvent	$[\alpha]_{6563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{4861}^{20}$	$[\alpha]_{4358}^{20}$	$\mu \times 10^{18}$
C_6H_5CN	-39.5 ^o	-52.0 ^o	-64.7 ^o	-93.9 ^o	-142 ^o	3.80
C_6H_5CHO	-34.8	-45.5	-55.5	-79.3	-113	2.75
$C_6H_5NO_2$	-31.1	-41.6	-51.5	-73.7	-	3.90
$C_6H_5COCH_3$	-27.0	-39.3	-48.3	-74.5	-99.2	2.94
$O-C_6H_4Cl_2$	-4.48	-4.54	-3.99	+0.1495	+19.3	2.25
$C_6H_5OCH_3$	+0.624	+1.37	+2.87	+9.86	+31.6	1.20
C_6H_5Br	+6.27	+9.29	+14.5	+29.4	+70.3	1.50
C_6H_5Cl	+7.21	+11.1	+15.7	+29.2	+56.55	1.52
C_6H_5I	+8.82	+13.2	+19.0	+36.5	+83.95	1.25
C_6H_6	+34.9	+47.0	+61.0	+97.45	+178	0
$C_6H_5CH_3$	+47.5	+65.1	+84.0	+131	+230	0.4
$S-C_6H_3(CH_3)_3$	+68.9	+93.2	+120	+184	+313	0
C_6H_{12}	+95.5	+128	+165	+251	+426.5	0

The ether was extremely soluble in all the above solvents. An unusually high concentration was employed with *o*-dichlorobenzene, since the observed angles of rotation were very small. This also served to accentuate the manner in which the dispersion curve crossed the zero axis with changing wave-length (see p.112).

TABLE XII. *l*-Benzoin Methyl Ether.*l* = 1 dcm. for nitrobenzene

" bromobenzene

" mesitylene

l = 2 dcm. in other cases.*t* = 20° ± 1°

Solvent	conc.	α 5461	$\mu \times 10^{18}$	$[M]_{5461}^{20}$
C_6H_5CN	4.064	-5.26°	3.80	-146°
C_6H_5CHO	4.016	-4.45	2.75	-125
* $C_6H_5NO_2$	4.018		3.90	-117
$C_6H_5COCH_3$	4.016	-3.88	2.94	-109
$O-C_6H_4Cl_2$	10.036	-0.80	2.25	-8.02
$C_6H_5OCH_3$	4.008	+0.23	1.20	+6.64
C_6H_5Br *	3.984		1.50	+35
C_6H_5Cl	4.026	+1.26	1.52	+35.4
C_6H_5I	4.026	+1.53	1.25	+42.9
C_6H_6	4.022	+4.91	0	+138
$C_6H_5CH_3$	4.022	+6.76	0.4	+190
$S-C_6H_3(CH_3)_3$	4.021	+4.84	0	+269
C_6H_{12}	4.022	+12.29	0	+373
$C_6H_5NH_2$	4.022	-13.31		-374
Homog. *				-99°

* interpolated values from temperature-rotation diagrams.

INFLUENCE OF CONCENTRATION ON ROTATORY
POWER OF ℓ -BENZOIN.

Owing to the insolubility of ℓ -benzoin in aliphatic and aromatic non-polar solvents, it was impossible to make an extensive investigation of the influence of concentration on its optical rotatory power at ordinary temperatures. In an attempt, however, to overcome this obstacle, it was decided to determine the rotation at higher concentrations, within those temperature limits which kept the solute in solution. Thus two higher concentrations were used, the one solution being approximately saturated at 35° and the other at 50°.

In this way it was hoped that the positions of the three temperature-rotation curves would indicate the effect of increased concentration. Toluene was chosen as the solvent in preference to benzene, owing to its relatively higher boiling point.

A second point requiring much caution was the making up of the solution. The quantities of solute and solvent were weighed at ordinary temperatures, and tightly stoppered in a 10 cc. flask. This was carefully heated in a bath up to 35° or 50° until all the ℓ -benzoin had dissolved, the contents being

slightly agitated by twisting the flask neck between the thumb and forefinger.

Water at the specified temperature was in the meantime running through the jacketted polarimeter tube. As quickly as possible the hot solution was transferred from the flask to the tube and the experiment thereafter conducted in the usual manner. The manner, in which the density of the solution, corresponding to the temperatures at which angles of rotation were observed, was determined, will be discussed in a latter section. Only the mercury-green line was used in this case.

TABLE I. ℓ -Benzoin.

Toluene.

$$\ell = 1 \text{ dcm.}$$

$$p = 0.9423 \text{ gms. per 100 gms. of solution.}$$

t	21°	40.5°	58.5°	77.5°
D_4^t	0.8646	0.8470	0.8299	0.8128

t	D_4^t	α_{5461}	$[M]_{5461}^t$
21°	0.8650	-2.18°	-568°
56	0.8325	1.95	-527
71.5	0.8183	1.84	-507
98.5	0.7935	1.65	-468

Error in $[M]_{5461}^t$ for $t = 21^\circ$ is $+ 7.8^\circ$
 " $t = 98.5^\circ$ is $+ 8.5^\circ$.

TABLE II. ℓ -Benzoin.

Toluene.

 $\ell = 1$ dcm.

$p = 2.905$ gms. per
 100 gms. of solution.

t	56.25°	67.5°	77°	84°
D_4^t	0.8381	0.8279	0.8185	0.8116

t	D_4^t	α_{5461}	$[M]_{5461}^t$
54.75°	0.8392	-5.98°	-520°
83°	0.8132	5.53	-496
96.75°	0.8005	5.29	-482

Error in $[M]_{5461}^t$ for $t = 54.75^\circ$ is $+ 2.6^\circ$
 " $t = 96.75^\circ$ is $+ 2.7^\circ$

TABLE III. ℓ -Benzoin./

TABLE III. *l*-Benzoin.Toluene $l = 1 \text{ dcm.}$ $p = 4.978 \text{ gms. per } 100$
gms. of solution.

t	75°	82.5°	90°
D_4^t	0.8250	0.8185	0.8127

t	D_4^t	α_{5461}	$[M]_{5461}^t$
54.5°	0.8440	-10.39	-524°
82.5	0.8207	9.76	-506
97.5	0.8047	9.38	-496

Error in $[M]_{5461}^t$ for $t = 54.5^{\circ}$ is $\pm 1.5^{\circ}$
 " $t = 97.5^{\circ}$ is $\pm 1.5^{\circ}$

TABLE IV. *l*-Benzoin./

TABLE IV. *l*-Benzoin.Toluene

$$l = 1 \text{ dcm.}$$

p = .9423		p = 2.905		p = 4.978	
t	$[M]_{5461}^t$	t	$[M]_{5461}^t$	t	$[M]_{5461}^t$
21°	-568°	-	-	-	-
56	-527	54.75°	-520°	54.5°	-524
71.5	-507	83	496	82.5	506
98.5	-468	96.75	482	97.5	496

As can be seen from the temperature-rotation diagram (p. 91.) the above results, instead of being parallel to one another, intersected at certain points. In addition, no direct readings could be obtained for the two highest concentrations using temperatures below 54.5°, owing to the precipitation of the solute.

Hence as a point of interest and if possible, as a check against the above data for toluene, which represent conditions at relatively high temperatures, it was decided to investigate the temperature-rotation diagrams for two solutions of benzene over the range 20° - 60°.

TABLE V. *l*-Benzoin.Benzene. $l = 1$ dcm. $p = 1.145$ gms. per 100
gms. of solution.

t	21.5°	47°	59°
D_4^t	0.8794	0.8525	0.8403
t	D_4^t	α_{5461}	$[M]_{5461}^t$
20.5	0.8803	-2.72°	-572°
42	0.8575	2.57	553
55.5	0.8434	2.44	534

Error in $[M]_{5461}^t$ for $t = 20.5^{\circ}$ is $\pm 6.3^{\circ}$
 " $t = 55.6^{\circ}$ is $\pm 6.6^{\circ}$

TABLE VI. *l*-Benzoin.Benzene. $l = 1$ dcm. $p = 2.831$ gms. per 100
gms. of solution.

t	20°	41.5°	59.75°
D_4^t	0.8851	0.8630	0.8441

t	D_4^t	α_{5461}	$[M]_{5461}^t$
21.5°	0.8835	-6.57°	-557°
46	0.8584	6.21	541
63	0.8408	5.91	526

Error in $[M]_{5461}^t$ for $t = 21.5^\circ$ is $\pm 2.5^\circ$
 " $t = 63^\circ$ is $\pm 2.7^\circ$

The two results for benzene were repeated using a new sample of extra pure quality benzene (British Drug Houses, Ltd.)

TABLE VII. l-Benzoin.

Benzene

$l = 1$ decm.

$p = 1.148$ gms. per 100
gms. of solution.

t	25°	45.5°	60.25°
D_4^t	0.8762	0.8546	0.8390

t	D_4^t	α_{5461}	$[M]_{5461}^t$
19°	0.8825	-2.74	-572
41	0.8593	2.59	555.5
65	0.8334	2.35	520

TABLE VIII. l-Benzoin.Benzene. $l = 1 \text{ dcm.}$ $p = 2.827 \text{ gms. per } 100$
gms. of solution.

t	21.5°	47.25°	62°
D_4^t	0.8836	0.8569	0.8412
t	D_4^t	α_{5461}	$[M]_{5461}^t$
19.25	0.8868	-6.63	-560
50	0.8542	-6.11	536
65.5	0.8383	-5.92	529

Influence of Concentration on the Rotatory
Power of ℓ -Benzoin Methyl Ether.

In view of the difference between the value obtained by Wren for the rotatory power of ℓ -benzoin methyl ether in benzene at a concentration of 0.6428 per cent and that obtained in the present investigation at a concentration of 4.022 per cent, it was decided to employ benzene as the non polar solvent and examine the behaviour of the ether at different concentrations.

Also by extrapolating back to lower concentrations and keeping in mind that Wren's determination of the rotatory power was made at a temperature of 15° , it was possible to ascertain with some degree of accuracy that the ether employed was optically pure.

TABLE IX. ℓ -Benzoin Methyl Ether.

Benzene.

$$l = 2 \text{ dcm} \quad t = 20^{\circ} \pm 1^{\circ}.$$

c	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
4.022	+2.81	+3.78	+4.91	+7.84	+14.34
12.02	6.80	9.39	12.27	19.99	36.88
25.05	9.60	13.40	17.76	29.64	57.13

TABLE X. ℓ -Benzoin Methyl Ether.

c	$[\alpha]_{6563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5641}^{20}$	$[\alpha]_{4861}^{20}$	$[\alpha]_{4358}^{20}$
4.022	34.9	47.0	61.0	97.5	178
12.020	28.3	39.1	51.0	83.2	153
25.052	19.16	26.75	35.46	59.17	114

TABLE XI. ℓ -Benzoin Methyl Ether.

c	$[\alpha]_{5893}^{20}$	$[M]_{5461}^{20}$
⊙ 0.6	+50.9°	-
4.022	+47.0	+138°
12.020	+39.1	+115°
25.052	+26.75	+80.1
* Homog.	-35.4°	-99°

⊙ Wren's result for which $t = 15^\circ$.

* Extrapolated values from the temperature-rotation diagram for homogeneous ℓ -benzoin methyl ether.

INFLUENCE OF TEMPERATURE.

In order to test the recent hypothesis mentioned in the Introduction (p, 27.) concerning the relative slopes of the temperature-rotation curves for solvents of polar and non-polar characters respectively, the three solvents nitrobenzene, bromobenzene, and mesitylene were employed. These were taken as representatives of strongly polar, weakly polar and non-polar types. The determinations were conducted as previously indicated. The density values for the solutions at approximately 20° , 40° , 60° and 80° were plotted against the temperatures, and the relationship was found to be linear in every case considered. By interpolation of these graphs, the requisite values were noted corresponding to the temperatures at which the angles of rotation were observed. Only the mercury-green line was used.

Influence of Temperature on the RotatoryPower of ℓ -Benzoin.TABLE XII. ℓ -Benzoin.Nitrobenzene.

$$\ell = 1 \text{ dcm.}$$

$$p = 0.8640 \text{ gms. per}$$

$$100 \text{ gms. of solution.}$$

t	26.5°	40°	59.5°	80.5°
D_4^t	1.1950	1.1820	1.1640	1.1450

t	D_4^t	α_{5461}	$[M]_{5461}^t$
12°	1.209	-2.32	-471°
21.5	1.200	2.26	-462
50	1.173	2.09	-437
74.5	1.150	1.94	-414
97.75	1.129	1.79	-389

TABLE XIII. l-Benzoin.Bromobenzene. $l = 1$ dcm.p = 0.6619 gms. per
100 gms of solution.

t	21.75°	40.5°	62.75°	80.5°
D_4^t	1.490	1.466	1.436	1.414

t	D_4^t	α_{5461}	$[M]_{5461}^t$
10.5°	1.504	-2.95	-629°
21	1.491	2.88	-619
38	1.469	2.80	-611
45.5	1.460	2.76	-605
51	1.452	2.70	-596
73	1.424	2.51	-565
96.5	1.393	2.30	-529

TABLE XIV. *l*-Benzoin.

Mesitylene.

$$l = 1 \text{ dcm.}$$

$$p = 1.117 \text{ gms. per 100} \\ \text{gms. of solution.}$$

t	22°	41°	61.5°	81.5°
D ₄ ^t	0.8646	0.8498	0.8333	0.8172

t	D ₄ ^t	α_{5461}	[M] ₅₄₆₁ ^t
11°	.8737	-2.54°	-552°
20.5	.8655	2.51	-549.5
49.5	.8427	2.36	-532
55.5	.8379	2.31	-523
69.5	.8267	2.21	-508
72.5	.8245	2.18	-502
96.5	.8052	2.02	-477

TABLE XV. *l*-Benzoin./

TABLE XV. *l*-Benzoin.

$\text{C}_6\text{H}_5\text{NO}_2$ $p = 0.8640$		$\text{C}_6\text{H}_5\text{Br.}$ $p = 0.6619$		$\text{S-C}_6\text{H}_3(\text{CH}_3)_3$ $p = 1.117$	
t	$[\text{M}]_{5461}^t$	t	$[\text{M}]_{5461}^t$	t	$[\text{M}]_{5461}^t$
12°	-471°	10.5°	-629°	11°	-552°
21.5	-462	21	-619	20.5	-549.5
50	-437	38	-611	49.5	-532
74.5	-414	45.5	-605	55.5	-523
97.75	-389	51	-596	69.5	-508
		73	-565	72.5	-502
		96.5	-529	96.5	-477

$\text{C}_6\text{H}_5\text{NO}_2$ Error in $[\text{M}]_{5461}$ for $t = 12^\circ$ is $+ 6.0^\circ$

" $t = 97.75^\circ$ is $+ 6.5^\circ$

$\text{C}_6\text{H}_5\text{Br.}$ Error in $[\text{M}]_{5461}$ for $t = 10.5^\circ$ is $+ 6.3^\circ$

" $t = 96.5^\circ$ is $+ 6.9^\circ$

$\text{S-C}_6\text{H}_3(\text{CH}_3)_3$ Error in $[\text{M}]_{5461}$ for $t = 11^\circ$ is $+ 6.5^\circ$

" $t = 96.5^\circ$ is $+ 7.0^\circ$

Influence of Temperature on the Rotatory

Power of *l*-Benzoin Methyl Ether.

In solution.

The three solvents, nitrobenzene, bromobenzene and mesitylene were again employed. Owing to

the change from negative to positive rotations on passing from nitrobenzene to mesitylene, it was deemed advisable to investigate if the dispersion curves for the active compound gave any interesting results with varying temperature. Hence the rotatory power was determined for the five stipulated wave-lengths and for at least four different temperatures.

TABLE XVI. *l*-Benzoin Methyl Ether.

Nitrobenzene.

$l = 1 \text{ dcm.}$

$p = 3.354$

t	24.5°	42.75°	61.25°	80.75°
D_4^t	1.196	1.176	1.161	1.142

t	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
10.5°	-1.44°	-1.91°	-2.40°	-3.55°	errors too large owing to yellow colour of solution
21	1.25	1.67	2.07	2.96	
35.5	-	-	1.72	-	
47.25	0.79	1.09	1.32	1.78	
75.5	-	-	0.92	-	
94.5	0.47	0.59	0.68	0.79	

t	D_4^t	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4861}$
10.5°	1.209°	-35.5°	-47.1°	-59.2°	-87.6°
21	1.198	31.1	41.6	51.5	73.7
35.5	1.187			43.2	
47.25	1.174	20.1	27.7	33.6	45.2
75.5	1.147			23.9	
94.5	1.128	12.4	15.6	18.0	20.9

TABLE XVII. *l*-Benzoin Methyl Ether.

Bromobenzene.

$l = 1 \text{ cm.}$

$p = 2.699.$

t	23°	43.75°	63.75°	82.25°
D_4^t	1.472	1.466	1.421	1.398

t	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
10.25°	+0.13°	+0.25°	+0.39°	+0.89°	+2.18°
18.25	0.25	0.37	0.58	+1.17	+2.80
35.5	0.42	0.59	0.83	1.57	3.31
52.25	0.50	0.73	1.00	1.75	3.67
73.5	0.58	0.83	1.13	1.96	4.01
97.25	0.62	0.91	1.22	2.06	4.18

t	D_4^t	$[\alpha]_{6563}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4861}$	$[\alpha]_{4358}$
10.25°	1.488	+3.24°	+6.22°	+9.71°	+22.7°	+54.3°
18.25	1.476	6.275	9.29	14.55	29.4	70.2
35.5	1.456	10.7	15.0	21.1	39.95	84.2
52.25	1.435	12.9	18.85	25.8	45.2	92.6
73.5	1.409	15.25	21.8	29.7	51.6	105.
97.25	1.379	16.3	24.4	32.8	55.35	112.

TABLE XVIII. *l*-Benzoin Methyl Ether.Mesitylene.

= 1 dcm.

p = 4.604

t	21°	47.25°	68°	92°
D_4^t	0.8734	0.8523	0.8362	0.8156

t	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
9.5°	+2.92°	+3.93°	+5.00°	+7.67°	
20.5	2.76	3.71	4.79	7.30	+12.44°
34.5	2.59	3.46	4.43	6.84	11.61
52	2.35	3.15	4.08	6.27	10.73
75	2.08	2.76	3.51	5.51	9.62
97.25	1.84	2.44	3.13	4.83	8.63

t	D_4^t	$[\alpha]_{6563}^t$	$[\alpha]_{5893}^t$	$[\alpha]_{5461}^t$	$[\alpha]_{4861}^t$	$[\alpha]_{4358}^t$
9.5	.8825	+80.1°	+108°	+137°	+210.5°	
20.5	.8735	76.5	103	133	202	+ 345°
34.5	.8625	72.7	97.2	124	192	326
52	.8480	67.1	89.95	116.5	179	306
75	.8295	60.7	80.6	102	161	281
97.25	.8110	54.9	72.9	93.5	144	258

TABLE XIX. *l*-Benzoin Methyl Ether.

$C_6H_5NO_2$ p = 3.354		$C_6H_5Br.$ p = 2.699		$S-C_6H_3(CH_3)_3$ p = 4.604	
t	$[M]_{5461}^t$	t	$[M]_{5461}^t$	t	$[M]_{5461}^t$
10.5°	-132°	10.25°	+21.95°	9.5°	+278°
21	-116	18.25	+32.9	20.5	+269
33.5	-97.6	35.5	+47.7	34.5	+252
47.25	-75.65	52.25	+58.35	52	+236
75.5	-54.6	73.5	+67.2	75	+208
94.5	-40.6	97.25	+74.1	97.25	+189

$C_6H_5NO_2$ Error in $[M]_{5461}$ for t = 10.5° is $\pm 1.2^\circ$.
 " t = 94.5° is $\pm 1.7^\circ$.

$C_6H_5Br.$ Error in $[M]_{5461}$ for t = 10.25° is $\pm 1.7^\circ$.
 " t = 97.25° is $\pm 1.8^\circ$.

$S-C_6H_3(CH_3)_3$ Error in $[M]_{5461}$ for t = 9.5° is $\pm 1.6^\circ$.
 " t = 97.25° is $\pm 1.8^\circ$.

TABLE XX.

Homogeneous Methyl Ether of *l*-Benzoin.

Since the melting point of *l*-benzoin methyl ether is 51° - 52° , the temperature-rotation diagram for the range approximately 54° - 100° was alone determined. Unfortunately the ether crystallised too rapidly below its melting point for it to be used in the supercooled condition. The anomalous behaviour of the ether was fully examined in the short region investigated and the slopes of the graphs for each wave-length indicated that the ether would behave more normally with respect to the variations in the wave-length of the light employed as the temperature decreased.

$$l = \frac{1}{2} \text{ cm.}$$

t	66.8°	75°	83.25°
$\frac{D^t}{4}$	1.085	1.078	1.072

t	α 6563	α 5893	α 5461	α 4861	α 4358
54.25°	-7.64°	-9.64°	-11.48°	-15.18°	-15.71°
69.25	-5.07	-6.18	- 7.07	- 7.91	- 4.39
85.00	-3.00	-3.43	- 3.54	- 2.37	+4.47
99.25	-1.58	-1.43	- 0.94	+ 1.63	+9.62 & (13.12

t	D_4^t	$[\alpha]_{6563}^t$	$[\alpha]_{5893}^t$	$[\alpha]_{5461}^t$	$[\alpha]_{4861}^t$	$[\alpha]_{4358}^t$
54.25°	1.094	-13.95°	-17.6°	-21.0°	-27.7°	-28.7°
69.25	1.083	- 9.36	-11.4	-13.05	-14.6	- 8.11
85	1.070	- 5.61	- 6.41	- 6.62	- 4.43	+ 8.35
99.25	1.059	- 2.98	- 2.70	- 1.775	+ 3.08	

Homog. Ether.			
t	$[M]_{5893}^t$	t	$[M]_{5461}^t$
54.25°	-39.8°	54.25°	-47.4°
69.25	-25.8	69.25	-29.5
85.	-14.5	85	-14.95
99.25	- 7.105	99.25	-4.01

Error in $[M]_{5461}$ for t = 54.25° is $\pm .12^\circ$

" t = 99.25° is $\pm .12^\circ$

Error in $[M]_{5893}$ for t = 54.25° is $\pm .12^\circ$

" t = 99.25° is $\pm .14^\circ$

Determination of the Molecular Weight
of ℓ -Benzoin in Solution.

The values for the molecular weights were determined in two or three non-polar solvents using the Differential Thermometer Apparatus devised by Menzies & Wright (J.A.C.S., 1921, 2309).

ℓ = Benzoin, M.W. = 212.

In Benzene.

Vol. = 27.9 c.c. B.p. = 80^o K = 32.

Wt. of Solute.	c^*	ΔT	M
0.1356 gms.	0.4860	0.07543 ^o	206
0.2739 "	0.9817	0.1501	209
0.4688 "	1.68	0.2506	214
0.6570 "	2.355	0.3375	223

ΔT = Elevation of boiling point.

* C = conc. per 100 c.c. solvent.

In Carbon Tetrachloride.

Vol. = 29.1 c.c. B.p. = 76.3^o K = 32.4

Wt. of Solute	C	ΔT	M
0.0786 gms.	0.2701	0.04443	196
0.1761 "	0.6050	0.0990	198
0.2863 "	0.9840	0.1563	204
0.3790 "	1.302	0.2018	209

In Cyclohexane.

$$D_4^{81.3} = 0.7193 \text{ (calc.) vol.} = 28.4 \text{ c.c. B.p.} = 81.3^\circ *K = 27.5.$$

Wt. of Solute.	C.	$\Delta T.$	M.
0.1053 gms.	0.3708	0.05932 ^o	238
0.1992 "	0.7015	0.1091	246
0.2946 "	1.037	0.1471	274

* (Mascarelli & Musatty, Gazz., 1911. 41. I. 73).

In Carbon Disulphide.

$$\text{Vol.} = 27.5 \text{ c.c. B.p.} = 45.6^\circ K = 19.4.$$

Wt. of Solute.	C.	$\Delta T.$	M.
0.1784 gms.	0.6503	0.05744 ^o	219
0.2437 "	0.8861	0.07847	219
0.3204 "	1.165	0.1033	215

The results in the above four solvents were repeatable to within 2 - 5%, except in the case of carbon disulphide. In this solvent a higher concentration would have given better accuracy, since the low boiling point meant that a difference in reading of one-tenth of a millimetre for the concentrations used gave a variation in the molecular weight of about 2 - 3%. This however was not possible owing to the low solubility of the compound. The following results for the methyl ether were very much more dependable owing to the greater solubility of the ether.

Determination of Molecular Weight of *l*-Benzoin
Methyl Ether in Solution.

l-Benzoin Methyl Ether M.W. = 226.

In Benzene.

Vol. = 29 c.c. B.p. = 79.6° K = 32.

Wt. of Solute	C.	$\Delta T.$	M.
0.2361 gms.	0.8141	0.1156°	225
0.3334 "	1.149	0.1673	220
0.4371 "	1.508	0.2164	223
0.5462 "	1.884	0.2668	226

In Cyclohexane.

Vol. = 28 c.c. B.p. = 80° K = 27.5

W. = 20.14 gms.

Wt. of Solute	C.	$\Delta T.$	M.
0.2656 gms.	0.9705	0.1492°	243
0.4179 "	1.492	0.2273	251
0.5547 "	1.981	0.2967	255

DISCUSSION.

In discussing the behaviour of *l*-benzoin in the various solvents, three points must be observed.

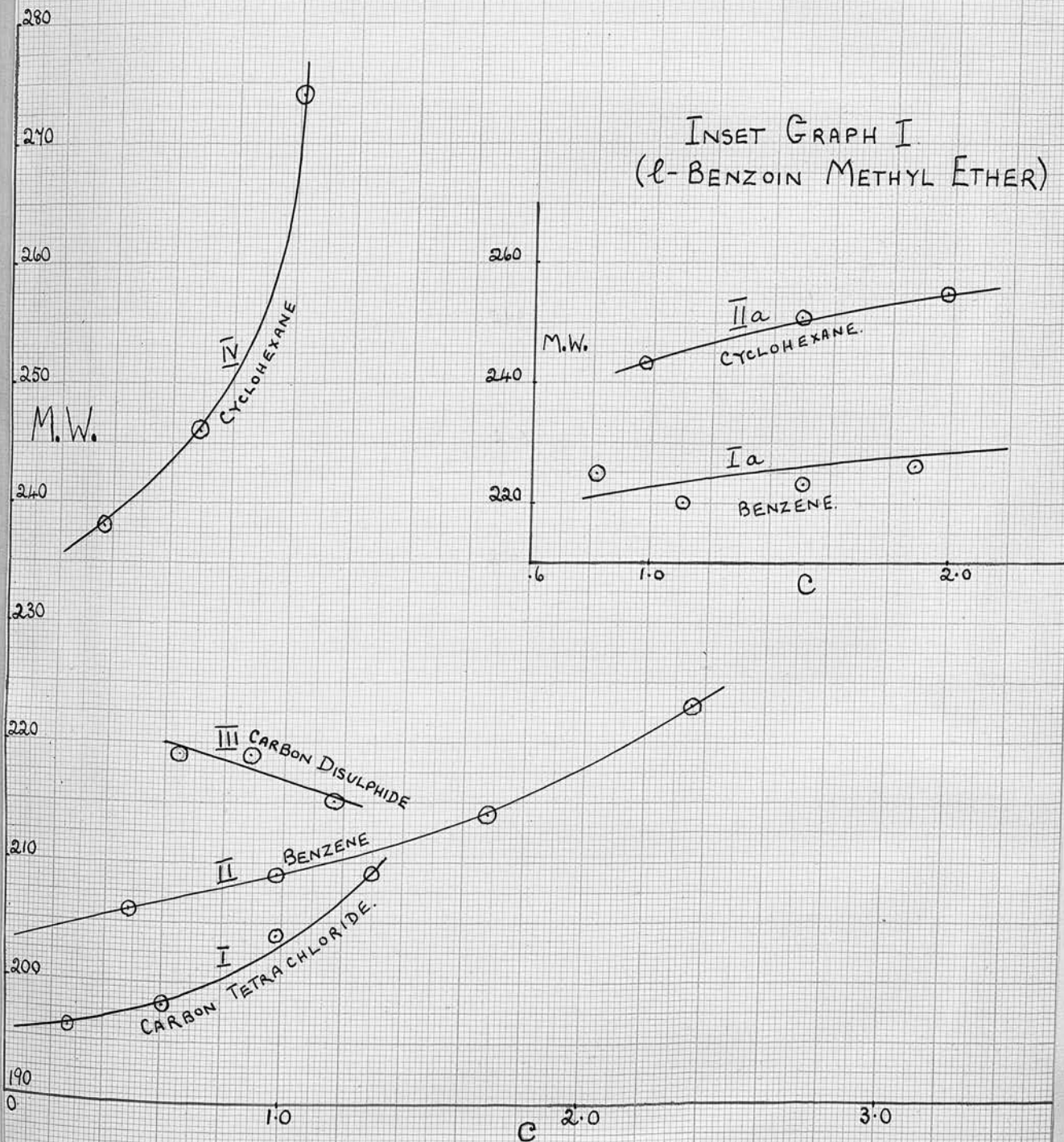
I. The dipole moment of benzoin is relatively high, $\mu = 3.46 \times 10^{-18}$ e.s.u., (Hassel & Naeshagen, Z.P.C., 1929, B. 6, 152).

II. *l*-Benzoin is a secondary alcohol.

III. In juxta-position to the hydroxyl group is a Ketonic group.

I. The high polarity of the benzoin molecule indicated that the compound will have a strong tendency to undergo association in solution. A similar case which has been more completely studied by Hildebrand is given by the behaviour of the polar compound, benzoic acid in different solvents. In discussing these results, Glasstone (Physical Chemistry, p.379) mentions the greater solubility of benzoic acid in the more polar solvents, a peculiarity which is also shown by *l*-benzoin. Such a relationship between increasing solubility and the polarity of the medium is to be expected in view of the polarity of benzoic acid. The interpretation of this relationship indicates that for a mixture of two components, A & B, if A is the more polar then there is a specific attraction between its molecules tending to minimise their external fields. Thus a

GRAPH I


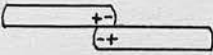
MOLECULAR WEIGHT DETERMINATIONS
OF *l*-BENZOIN

non-polar substance will generally be insoluble in a polar liquid since the molecules of the latter tend to aggregate and push out the former. For the same reason, a polar compound such as benzoic acid or benzoin, is usually only sparingly soluble in non-polar solvents, (Glasstone, Phys. Chem., p.369). In the extreme case of attraction between polar molecules, definite association into complex molecules results, giving further derivations from Raoult's Law.

In the accompanying diagram (graph I. p.80) the results for the molecular weight determinations from the experimental section p.76 are shown graphically. Along the ordinate are plotted the molecular weight values and the abscissa contains the percentage concentration of solute. Owing to the arbitrary way in which the constants used for the calculation of the molecular weights have to be selected, it is unsafe to make comparisons based upon relatively small differences in the deduced molecular weight values. In such cases it appears safer to compare the slopes of the graphs i.e. the manner in which the calculated molecular weight increases with rise of concentration. On this basis the somewhat untrustworthy results (cf. p.80) for carbon disulphide in curve III would indicate, if not complete dissociation, at all events a small degree of association. In benzene and still more in carbon tetrachloride there is definite association. For the

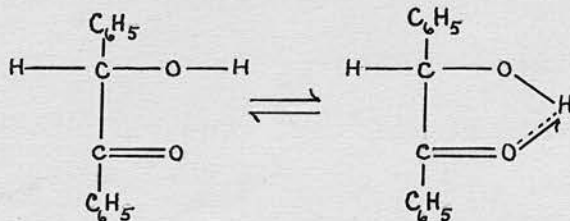
solvent cyclohexane, curve IV, the degree of association rises enormously with increased concentration so that even at the very dilute concentration employed for a polarimetric determination, we are quite justified in assuming a considerable degree of association in cyclohexane.

The inset graph I p.80 compiled from the source mentioned previously shows the behaviour of -benzoin methyl ether in the two solvents, benzene (curve Ia) and cyclohexane (curve IIa). There appears to be no association of the ether in benzene and only a slight amount in cyclohexane.

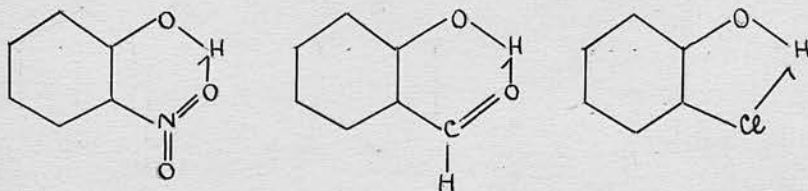
II. Alcohols have a tendency to orientate in either of two ways as shown in the Introduction (p.22). The actual type of orientation depends on the location of the hydroxyl group in the molecule. When the doublets are at the end of a long hydrocarbon chain and remote from any branch in the chain, an orientation of type I. is supposed to predominate  type I. But when the hydroxy groups are attached to a tertiary carbon atom they are so screened that association of type II. predominates  type II. Since, however, the rigidity of the chain and the shape of the molecule depend upon the positions of the hydroxyl group and the branching chain, the relation of orientation to structural formula is very complex

(cf. C.P. Smyth, Dielectric Constant and Molecular Structure, 1931, p.187). The variations in polarisation with concentration and more especially with temperature will be discussed later with respect to the slopes of the temperature-rotation diagrams of α -benzoin at different concentrations in benzene and toluene.

III. There is a probability of the hydrogen of the hydroxyl group becoming bivalent by accepting the two extra electrons which the oxygen of the ketonic group can give in the capacity of donor atom.



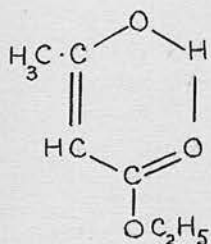
Sidgwick, (The Co-ordinate Link in Chemistry 1933) has put forward much evidence in support of this internal coupling from boiling point data relating to the ortho-substituted phenols.



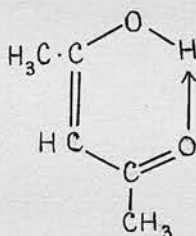
The O-substituted nitro and aldehydic phenols give rise to six-membered rings and the chloro-derivative to a five-membered ring.

This same author from a consideration of solubility data also deduced co-ordinated formulae for

the enolic forms for Acetoacetic ester and Acetyl Acetone.

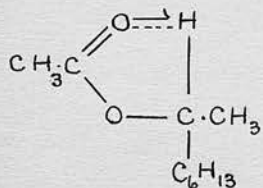


Acetoacetic ester
(enolic form)

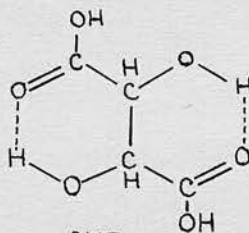


Acetyl Acetone
(enolic form)

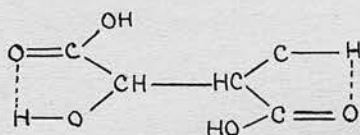
From a consideration of the coupling forces between "donor" and "acceptor" atoms, which are assumed to be sufficiently strong to prevent free rotation round single bonds, Lowry and Lloyd (J.C.S., 1929, 1781) have attempted to explain the variations in the types of dispersions for such substances as octyl acetate with changing conditions of temperature and solvent. Moreover, Lowry (see Trans. Far. Soc., 1930, p.417) has explained the anomalous behaviour of tartaric acid as arising from dynamic isomerism due to variations in the coupling forces between different substituents in the acid molecule.



Octyl Acetate.



AND



Tartaric Acid.

These cases appear to be strictly comparable

to that of benzoin, leading to the co-ordinate formula given on the previous page.

TABLE III. (p.45.) *l*-Benzoin.

(All tables taken from Experimental Section.)

Solvent.	c.	$[M]_{5461}^{20}$	$\mu \times 10^{-18}$
CH_3CHO	2.328	-276	2.7
CH_3COCH_3	2.764	314	2.8
CH_3CN	2.262	413	3.21
CH_3NO_2	2.306	427	3.05
CH_3OH	1.012	427	1.68
C_6H_{12}	0.056	464	0
CH_2Cl_2	2.288	534	1.51
CHCl_3	2.212	545	1.05
CH_3COOH	1.010	585	1.73
CH_3I	2.216	625.5	1.35
CCl_4	0.220	633	0
CS_2	0.522	1064	0

The use of hexane was not possible owing to the sparing solubility of *l*-benzoin. However, a very dilute solution was obtained in cyclohexane, which resembles hexane in its properties.

There is evidently a general agreement between the optical rotation of the solute and the polarity of the solvent. The minor discrepancies due to acetaldehyde and acetone were more or less expected. By

whatever mechanism the displacement is effected by these two solvents, the action of the ketonic group would be less pronounced with acetone owing to the greater shielding influence of the two methyl residues. Evidence for this is noticeable in the relative magnitudes of the two displacements. At the non-polar end of the table the optical properties have undergone a marked change on passing from carbon tetrachloride to carbon disulphide. One contributory reason for this difference which is supported by molecular weight determinations is that the solute molecules associate with one another in carbon tetrachloride to a somewhat greater extent than in carbon disulphide, thus leading to a lower rotation in the former solvent. * On this view the depression in rotatory power caused by self-association of the benzoin in carbon tetrachloride is approximately the same as that due to association between benzoin and the weakly polar methyl iodide in the latter solution.

In agreement with the observed optical rotatory powers, the molecular weight data (see graph p.80) appear to show that benzoin undergoes very little association in carbon disulphide solution, but that the degree of association increases as we pass from this

* The concentration changes in benzene and toluene solution described later show that the association of benzoin lowers the rotatory power.

solvent to carbon tetrachloride, while in cyclohexane the association becomes quite pronounced. As has already been pointed out, this interpretation of the molecular weight data is based not only on the actual value of the deduced molecular weight, but also upon the slope of the graph with increasing concentration. It will be observed that the rotation in cyclohexane is what would be anticipated on the assumption of extensive self-association of the benzoin molecules. The position of acetic acid with respect to methyl alcohol is rather unusual. That acetic acid is abnormal in its behaviour has long been known. There is a great deal of evidence supporting the view that even in dilute solutions of benzene, the acid molecules are associated in pairs, the carboxyl groups being arranged in such a manner as to give partial or complete cancellation of their polar properties. X-ray investigations have shown the molecules of higher fatty acids in the solid state to be paired with their carboxyl groups in contact, and a similar conclusion has been drawn for the liquid state (Smyth, loc. cit. p.173). At ordinary temperatures then, and if the presence of the solute has no undue effect on the association acetic acid would to an appreciable extent exhibit non-polar properties and on this assumption the large rotation of -benzoin in this solvent is readily understood. A similar displacement in the same sense was observed by Rule and McLean for menthyl methyl naphthalate in acetic acid (J.C.S., 1931, 676).

TABLE VI. (p.49.) *l*-Benzoin.

Solvent	c.	$[\text{M}]_{5461}^{20}$	$\mu_x \times 10^{18}$
$\text{C}_6\text{H}_5\text{COCH}_3$	2.036	-460	2.94
$\text{C}_6\text{H}_5\text{NO}_2$	1.037	462	3.90
	(i)0.047	(i)473	
C_6H_{12}	(ii)0.056	(ii)464	0
$\text{C}_6\text{H}_5\text{CHO}$	2.314	513	2.75
$\text{C}_6\text{H}_5\text{CN}$	2.324	530	3.8
$\text{S-C}_6\text{H}_3(\text{CH}_3)_3$	0.9665	549.5	0
$\text{C}_6\text{H}_5\text{CH}_3$	0.81	568	0.4
C_6H_6	1.012	571	0
$\text{C}_6\text{H}_5\text{Br.}$	0.9865	619	1.5
$\text{C}_6\text{H}_5\text{Cl}$	2.068	627	1.52
$\text{O-C}_6\text{H}_4\text{Cl}_2$	2.052	632	2.25
$\text{C}_6\text{H}_5\text{OCH}_3$	2.082	649	1.20
$\text{C}_6\text{H}_5\text{I}$	2.058	700	1.25

O-Dichlorobenzene is a disubstituted derivative and thus, strictly speaking, ought not to be included in the above table.

As in the previous table, the rotatory powers in aromatic liquids are arranged approximately accordingly to their polar properties, highly polar liquids again yielding solutions of high negative rotations. In this case also the non-polar solvents are displaced

towards the polar end of the table, an irregularity which is to be expected from the association of benzoin in these media. Reference to the graph shows that the degree of association in benzene is much less than that in cyclohexane and in agreement with this the rotation is much lower in the latter solvent than in the former. A similar displacement in the effect of non-polar solvents upon rotatory power has already been discussed by Rule, Smith & Harrower (J.C.S., 1933, 376) in the case of the strongly associating compound, d - β -nitro-octane.

d - β -nitro-octane.

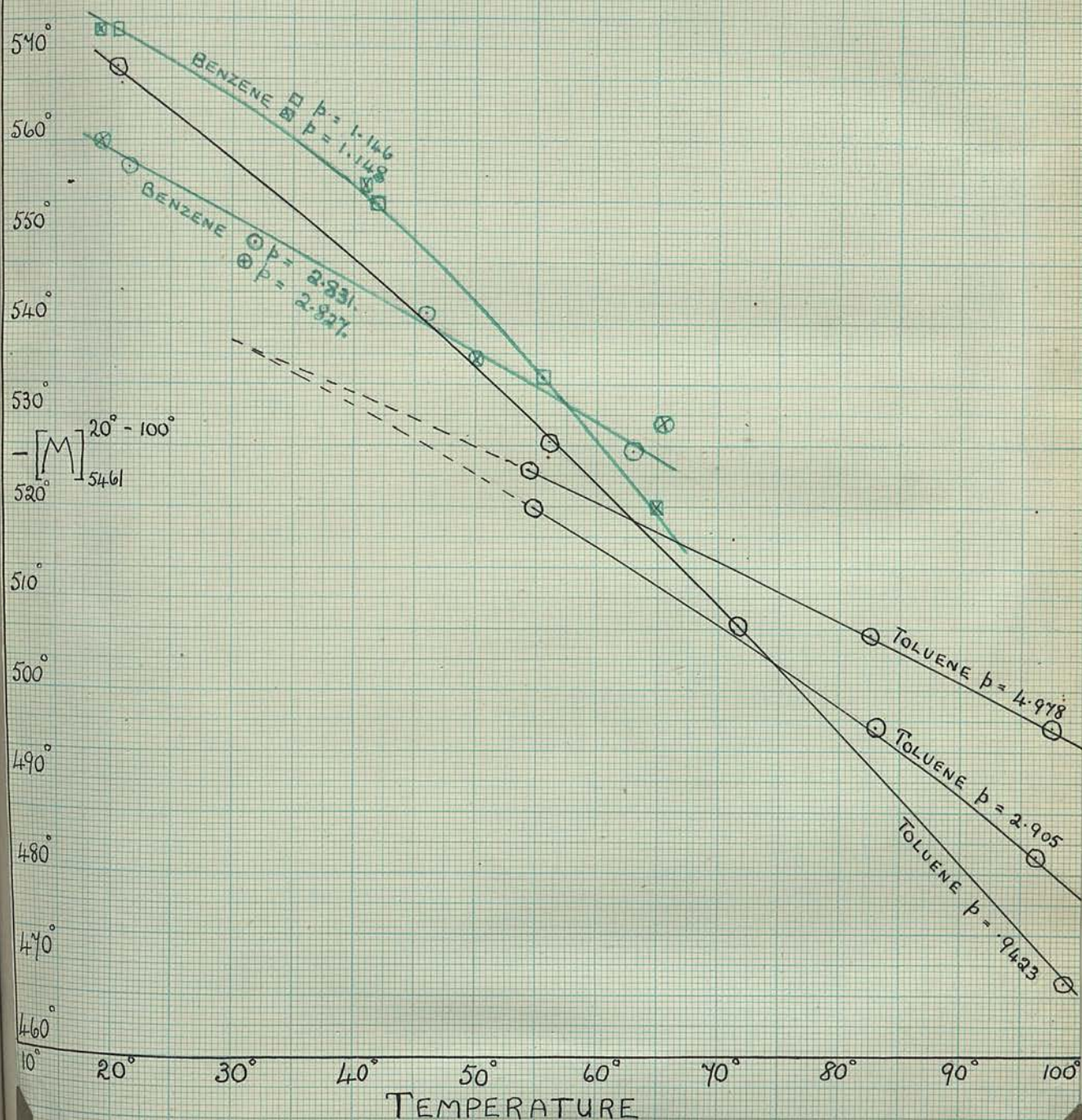
Solvent	C ₆ H ₅ OCH ₃	C ₆ H ₅ Cl	C ₆ H ₆	C ₆ H ₅ NO ₂	C ₆ H ₁₄	Homog.
M 5461	35.5°	31.5°	31.1°	27.2°	26.9°	26.7°
$\times 10^{18}$	1.25	1.52	0	3.90	0	0

A corresponding explanation can be advanced for the apparent irregularities with l -benzoin, which shows an almost identical sequence for solvent influence. On this view the weakly polar iodobenzene and anisole disrupt the benzoin complexes, but by dipole association with the solute depress the rotation to some extent. The more polar chlorobenzene and bromobenzene will depress the rotation still further. On the other hand, benzene, toluene and mesitylene only break up the benzoin complexes to a very small extent, and the low rotations in these solvents are due to the fact that the highly polar active molecules are here strongly

associated with themselves. Benzene, with its capacity of acquiring a weak induced polarity in the presence of a polar solute has apparently a stronger dissociating power than mesitylene, in which the three methyl groups partially screen the benzene nucleus. Cyclohexane in the case of *l*-benzoin and hexane in the case of nitro-octane behave as though they had very little influence in dissociating the solute aggregates. As in the aliphatic series ketonic solvents show minor displacements.

GRAPH II

T-R DIAGRAM FOR *l*-BENZOIN IN
BENZENE AND TOLUENE AT DIFFERENT
CONCENTRATIONS.

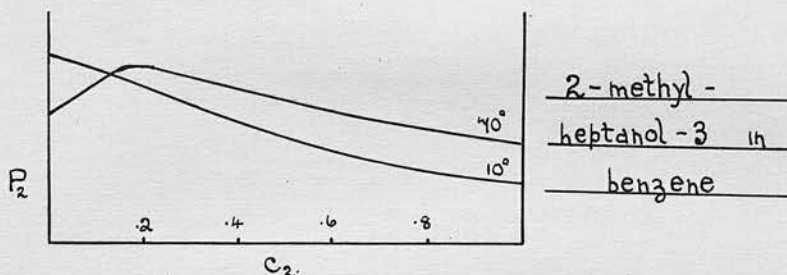


CONCENTRATION EFFECT.

Since highly polar solvents by association with *l*-benzoin lower the laevo-rotation of the latter, it was to be expected that an increased concentration should also decrease the rotation in a non-polar solvent, as indicated in the Introduction p.23. This is found to be the case for the two concentrations examined in benzene for temperatures below approximately 55°, also by extrapolating the values in toluene to 20°. The three concentrations behave as expected at room temperatures, i.e. an increased concentration decreases the rotation in a non-polar solvent (graph II. p.91). That the order is reversed at higher temperatures appears rather strange. There are two possible explanations for this reversal, one of which will be discussed later when a comparison of the influence of polar solvents on the rotation of *l*-benzoin and its methyl ether will be made.

The first suggestion is connected with the two different modes of association of alcohols mentioned previously. It is found with practically all alcohols as yet investigated that in the region of dilute solution ($C_2 = 0$ to $C_2 = 0.2$ molar) there is an inversion in the polarisation-concentration curves. This inversion has been traced for different temperatures and is illustrated by the case of 2-methyl-heptanol-3 in benzene at 10° and 70° respectively (Smyth, loc.

cit. pp.180-184).

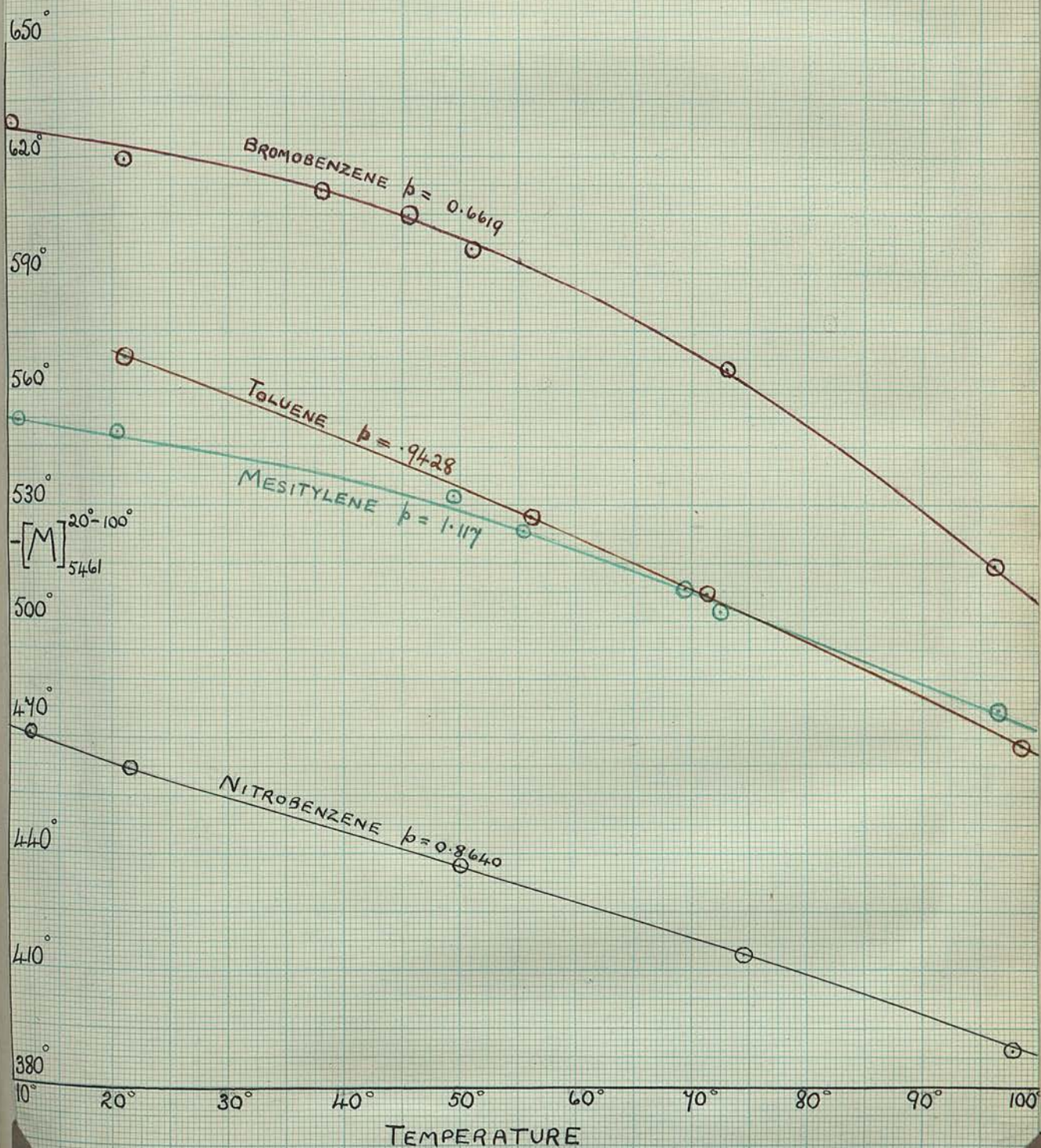


The interpretation of these diagrams as advanced by Debye has already been discussed (p.22). It may be noted, however, that at 70° the polarisation changes with rise of concentration from 0 to approximately 0.2 molar, are in the opposite sense to those above 0.2 molar. At 10° only the normal type of change representing a falling of the polarisation with rise of concentration is observed. It may be well observed, therefore, that an optically active alcohol of this type might show at 70°, concentration-rotation effects in opposite directions above and below $C = 0.2$ molar respectively, and it is possible that this kind of behaviour is being observed in the case of *l*-benzoin.

TEMPERATURE EFFECTS.

In the Introduction, p.27., it has been predicted from the dipole theory that the T - R curves for an active compound in a strongly polar and a non-polar solvent respectively should tend to meet with rise of temperature. As has already been stated this prediction depends upon the solute being comparatively non-associated in the non-polar media. Owing, however, to the strong association of *l*-benzoin in the latter

GRAPH III

T-R DIAGRAMS FOR *l*-BENZOIN
IN SOLUTION

solvents, it was not found possible to test this prediction with certainty. The same conclusion as to the convergence of the T - R curves should nevertheless hold for solutions in strongly polar and in weakly polar solvents respectively and this point has been tested experimentally using nitrobenzene ($\mu = 3.90$) and bromobenzene ($\mu = 1.50$). The results are shown graphically in graph III. p.94 and it is clearly seen that the curves for bromobenzene and nitrobenzene become closer together at higher temperatures, in agreement with theory. The T - R curves for toluene and mesitylene are also drawn for comparison. It will be observed that these also follow the general trend of the graphs for bromobenzene and nitrobenzene. They are, however, displaced, and instead of lying well above the other two graphs, they occupy an intermediate position, the depressed rotations in these solvents being caused by the association of the solute.

TABLE IX & XII (pp. 52 & 55) *l*-Benzoin Methyl Ether.

Solvent.	c.	$[\text{M}]_{5461}^{20}$	$\mu \times 10^{18}$
CH_3OH	4.022	-352 ⁰	1.68
CH_3COOH	4.020	-344	1.73
CH_3NO_2	4.014	-320	3.05
CH_3CHO	4.020	-243.5	2.70
CH_2CN	4.006	-236	3.21
CH_3Cl	4.020	-214.5	1.05
CH_2Cl_2	4.018	-178	1.51
$(\text{CH}_3\text{COCH}_3)$	(4.030)	(-102)	(2.8)
CH_3I	4.036	+27.4	1.35
C_6Cl_4	4.026	+316	0
CS_2	4.012	+370	0
C_6H_{12}	4.022	+376	0
$\text{C}_6\text{H}_5\text{NH}_2$	4.022	-374	1.56
$\text{C}_6\text{H}_5\text{CN}$	4.064	-146	3.80
$\text{C}_6\text{H}_5\text{CHO}$	4.010	-125	2.75
$\text{C}_6\text{H}_5\text{NO}_2$	4.018	-117	3.90
$\text{C}_6\text{H}_5\text{COCH}_3$	4.016	-109	2.94
* Homog.	-	- 99	-
$\text{O}-\text{C}_6\text{H}_4\text{Cl}_2$	10.036	-8.02	2.25
$\text{C}_6\text{H}_5\text{OCH}_3$	4.008	+6.64	1.20
$\text{C}_6\text{H}_5\text{Br}$	3.984	+35	1.50
$\text{C}_6\text{H}_5\text{Cl}$	4.020	+35.4	1.52
$\text{C}_6\text{H}_5\text{I}$	4.026	+42.9	1.25
C_6H_6	4.022	+138	0
$\text{C}_6\text{H}_5\text{CH}_3$	4.022	+190	0.4
$\text{C}_6\text{H}_3(\text{CH}_3)_3$	4.021	+269	0
C_6H_4	4.022	+376	0

✱ By extrapolation of T - R diagram.

By methylating the hydroxyl group in *l*-benzoin this strongly associating group has been converted into the relatively non-associating methoxyl group. This structural change is reflected in the practically normal molecular weight values obtained for the ether in benzene and cyclohexane. In agreement with these conclusions it is found that the rotatory powers of *l*-benzoin methyl ether in solvents of the methane and benzene type correspond closely to the polarity of the medium. It will be seen that in both series the non-polar solvents are grouped together at one end of the table, yielding solutions of high dextro-rotation. Strongly polar solvents on the other hand give laevo-rotatory solutions. This behaviour is in strong contrast to that of *l*-benzoin in which secondary effects are produced by the self-association of the solute. Further, it may be noted that in both types of solvents, the arrangement of non-polar solvents in the case of benzoin methyl ether is in close agreement with their dielectric constants, viz. cyclohexane, carbon disulphide, carbon tetrachloride, and also cyclohexane, mesitylene, toluene and benzene. In each series also, the lowest dextro-rotation observed in a non-polar solvent is considerably higher than the rotation found for the succeeding solvent of weak polarity.

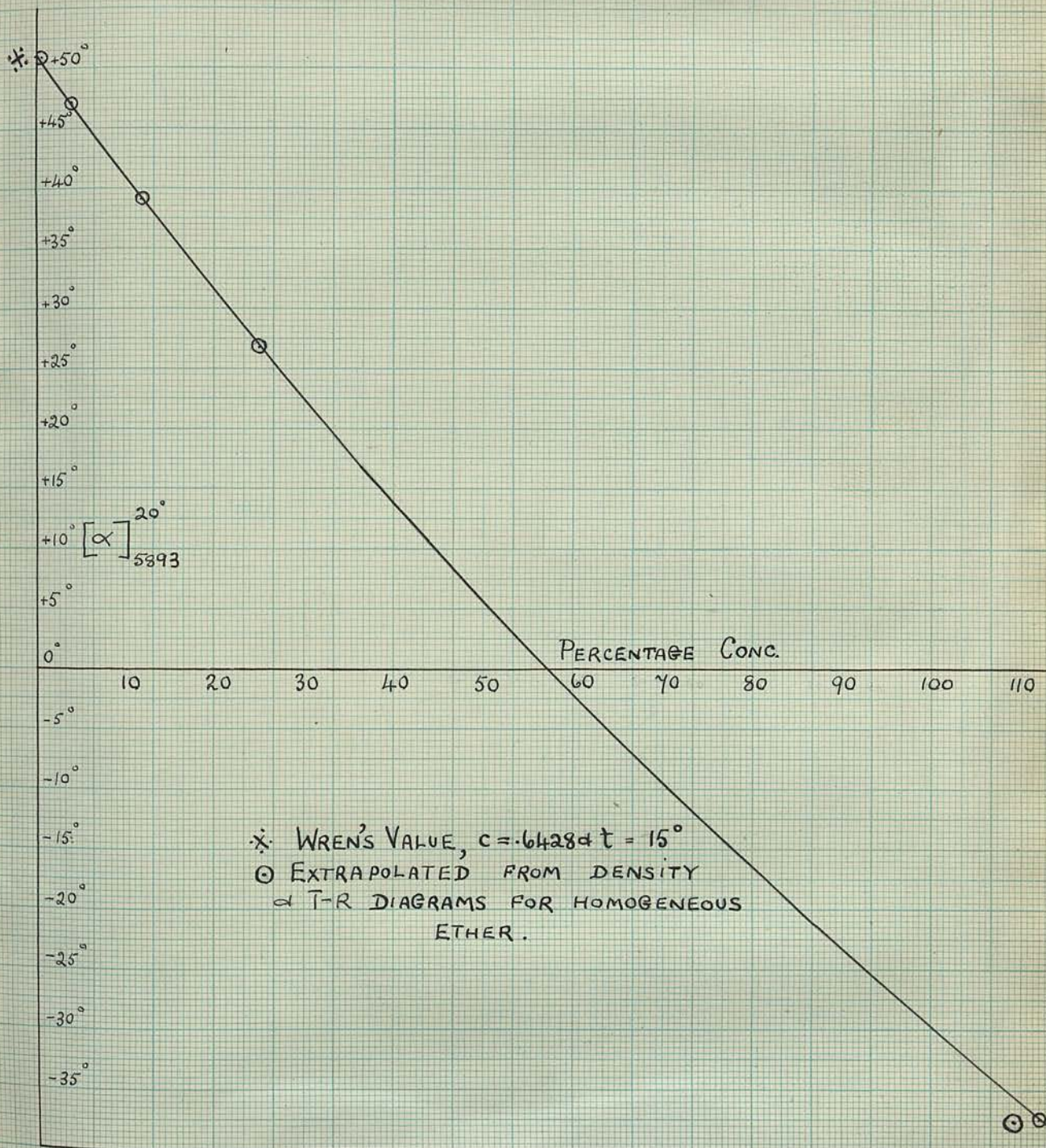
Several minor displacements are recorded in

the agreement between polar and optical properties. In the aliphatic group methyl alcohol and acetic acid yield unusually high laevo-rotations in comparison with their dipole moments. This point is discussed in more detail later (p.107). Acetone is a homologue of acetaldehyde, and strictly speaking is not comparable with the remaining simple methane derivatives; for this reason the values for this solvent are enclosed in brackets. Among aromatic derivatives aniline is the only noteworthy exception. This may arise from the same cause as the unusual behaviour of methyl alcohol, in view of the similar chemical properties of the hydroxyl and amino groups. Or the high rotation in aniline may be due to its tendency to enter into reaction with the ketonic group of the methyl ether - since evidence for this was obtained in the form of mutarotation. The following results were obtained using the sodium line, as the aniline solution acquired a brownish tint on prolonged standing. The concentration of the solution is mentioned on p-55.

Time.			$[\alpha]_{5893}^{20}$
0	2 dcm.	10.72 ⁰	301.1 ⁰
4 hrs.	"	10.67	299.7
28 "	"	10.67	299.7
46 "	"	10.50	294.9
118 "	"	10.26	229
4 months.	$\frac{1}{4}$	0.46	103

GRAPH IV

ROTATORY POWER OF *l*-BENZOIN METHYL ETHER
AT DIFFERENT CONCENTRATIONS IN BENZENE.



the subsequent fall in rotatory power in aniline solution may on the other hand be due to slowly racemisation in the weakly basic medium. The sensitivity of benzoin derivatives towards traces of alkali has been established by Wren (J.C.S., 1909, 95, 1583). A similar loss of activity was observed by Wren (loc. cit.) in attempting to obtain the anilide of *l*-benzoin.

The rotation of the homogeneous benzoin methyl ether falls into position in the middle of the aromatic table, in agreement with its low powers of association and its medium polar properties.

CONCENTRATION EFFECT.

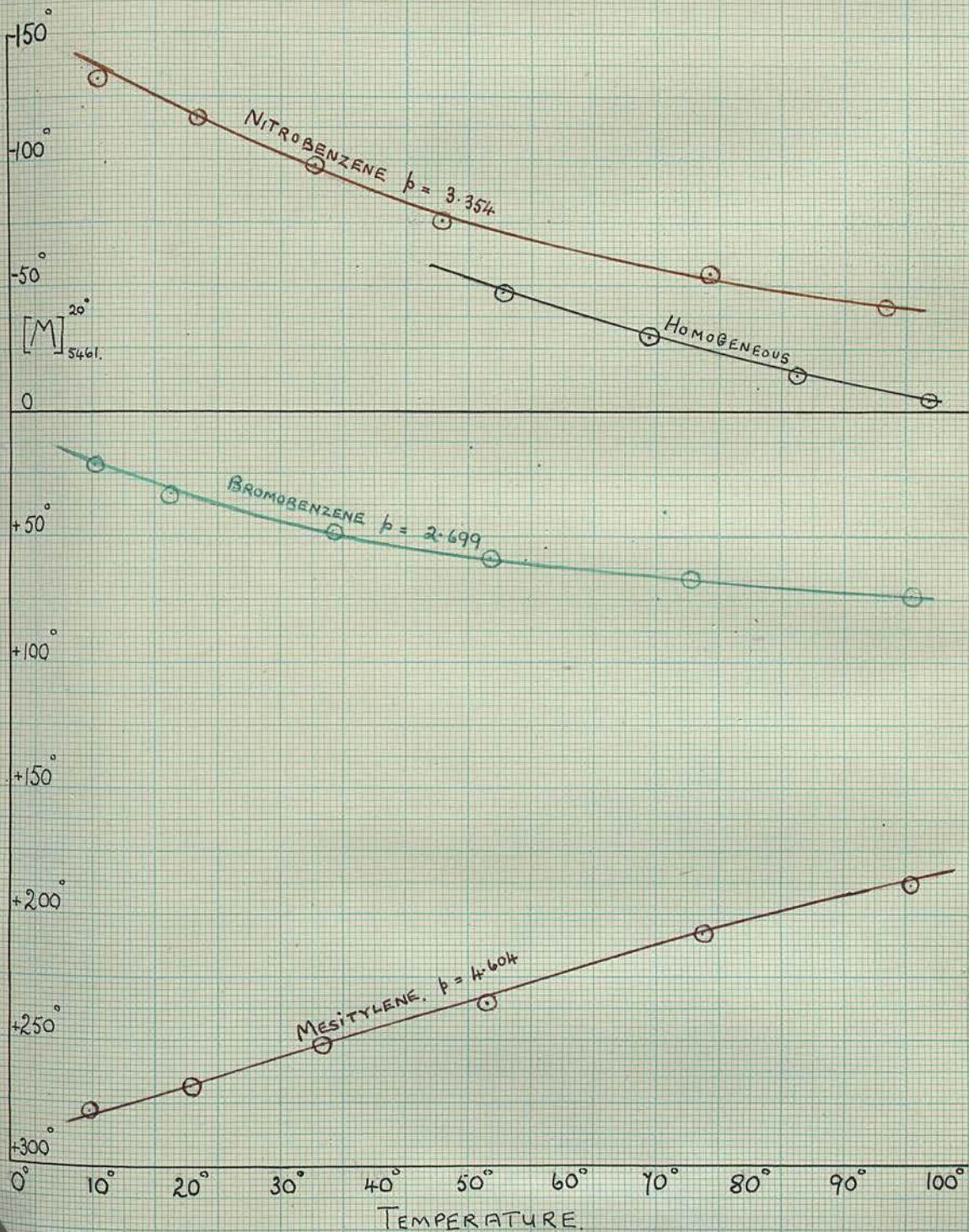
In the accompanying diagram (graph IV. p.99) it is seen that the dextro-rotation of the ether in benzene decreases as the concentration of the solute increases and finally swings over into the negative region towards the value for the homogeneous substance in the supercooled state. This last value is rather inaccurate, due to two reasons, (i) the T - R diagram had to be extrapolated from 50° back to 20°, which is rather far for accurate estimation; (ii) the short straight line connecting the densities from approximately 55° to 80° had to be extended down to 20° to enable the percentage composition of the homogeneous substance to be determined at this temperature.

The behaviour of the ether is in full agreement with the prediction of the dipole hypothesis.

Highly polar solvents have been shown to displace the rotation from a positive to a negative direction, a change which is attributed to increased association between solute and solvent. Consequently an increased concentration in a non-polar solvent, which really means an increased degree of self-association of the solute, ought to and in this instance actually does produce a change in the rotation in the same direction. The value for the most dilute solution, $C = 0.5428$, is that obtained by Wren, taken at a temperature of 15° and thus the diagram also confirms the purity of the compound with respect to that used by Wren (*loc.cit.*).

GRAPH V

T-R DIAGRAMS FOR *l*-BENZOIN METHYL
ETHER IN SOLUTION



TEMPERATURE EFFECTS.

The T-R diagrams (graph V. p. 102.) illustrate the effect of temperature on the rotatory powers of *l*-benzoin methyl ether in the three solutions, nitrobenzene, bromobenzene and mesitylene. The behaviour of the homogeneous ether itself over the short range 50° - 100° is also shown. From a consideration of the molecular weight data, previously discussed, it is seen that there is very little self-association in the cyclohexane and less still in the benzene solutions of the methyl ether. Hence in considering the T-R diagrams for the ether there is no doubt that the mesitylene solution will represent to a close approximation the ideal behaviour of the ether in the dissociated state. The four curves tend towards a common region, apparently on the positive side of the axis. With diminishing temperature the rotation in mesitylene increases in the positive direction. Relative to this the positive rotation in the more polar bromobenzene decreases with decrease in temperature and becomes negative a little below 0°C. This can be attributed to the increasing dipole association at lower temperatures between the bromobenzene and the solute, which diminishes the positive rotation (c.f. table 17). With the highly polar nitrobenzene solution the curve, which lies in the negative region becomes more and more negative at lower temperatures due to the increasing formation of nitrobenzene-ether

complexes. Further, the nitrobenzene curve is actually steeper than that for the less polar bromobenzene towards lower temperatures, as would be expected on theoretical grounds. The homogeneous substance which will probably have a dipole moment less than that for benzoin or nitrobenzene, but greater than for bromobenzene, gives a curve lying between those for nitrobenzene and bromobenzene. On passing from 100° to 55° , the melting point of the ether being $51^{\circ} - 52^{\circ}$, the forces between the molecules tending to produce crystallisation and thus the association of the substance will, in all probability, be increasing at a much greater rate per degree fall than in the case of the solvent-solute complexes in nitrobenzene, so that the variations in the rotatory power of the homogeneous substance over this range should be more noticeable than those found in nitrobenzene solution. This is evident in the steeper slope of the curve for the homogeneous ether in comparison with that for the nitrobenzene solution at the lower temperatures.

It is thus seen that *l*-benzoin methyl ether which undergoes very little self-association in dilute non-polar solvents, not only shows a regular change in rotatory power when dissolved in solvents of increasing polarity, but also exhibits the temperature effect predicted from the theory of dipoles, i.e. the T - R curves in polar and non-polar media respectively converge with increase of temperature.

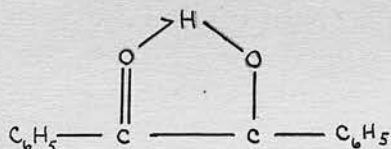
Comparison of Solvent Influences on *l*-Benzoin
and *l*-Benzoin Methyl Ether.

On changing the type of solvent from weakly polar to highly polar, the rotatory power of *l*-benzoin changes from a high laevo-rotation to a lower laevo-rotation, i.e. the optical displacement is in the dextro sense. With *l*-benzoin methyl ether, on the other hand, the change is from a high dextro rotation into a laevo-rotation, and the optical displacement is thus in the laevo sense. These two closely related substances are therefore affected in opposite directions by similar variations in the polarity of the solvent. Such a fundamental difference in behaviour cannot be explained by assuming a difference in the configurations of the two compounds, since the ether is prepared from the hydroxy derivative by direct methylation with silver oxide and methyl iodide. Methylating by this process has been concluded by other investigators in this field not to involve a Walden inversion, a point which is referred to in more detail in discussing the dispersion of these compounds.

Among the cases of a similar kind which have been examined in solvent series of this type are *d*-octyl alcohol, *d*-amyl alcohol and their methyl ethers (Rule, Smith & Harrower, J.C.S., 1933, 376). The alcohols were converted into their ethers by treatment with potassium and methyl iodide, a method which would also appear to preclude the possibility of a Walden inversion. The

authors found that the dextro-rotations of d-octanol and its methyl ether were both diminished as the polarity of the solvent increased, the displacements thus being in the same sense for alcohol and ether. With d-amyl alcohol, however, the laevo-rotation falls in strongly polar solvents, whereas the dextro-rotation of d-amyl methyl ether swings over into the negative region. Hence for these related compounds, the optical displacements are in opposite senses. Of the two cases quoted, octanol would appear to be the more comparable with benzoin, because in each of these compounds the hydroxyl group is directly united to the asymmetric carbon atom. In view of the work of Kuhn and Freudenberg, however, showing the powerful and characteristic influence of a phenyl group on the optical character of a compound, it would appear unsafe to compare the aromatic compounds with octanol and its ether. A very specific optical influence must, moreover, also be exerted by the ketonic group in benzoin and its ether.

A point of theoretical interest in this connection is the possibility that the ketonic and hydroxyl groups may tend to combine to form a chelate ring in benzoin. According to Sidgwick's views the evidence



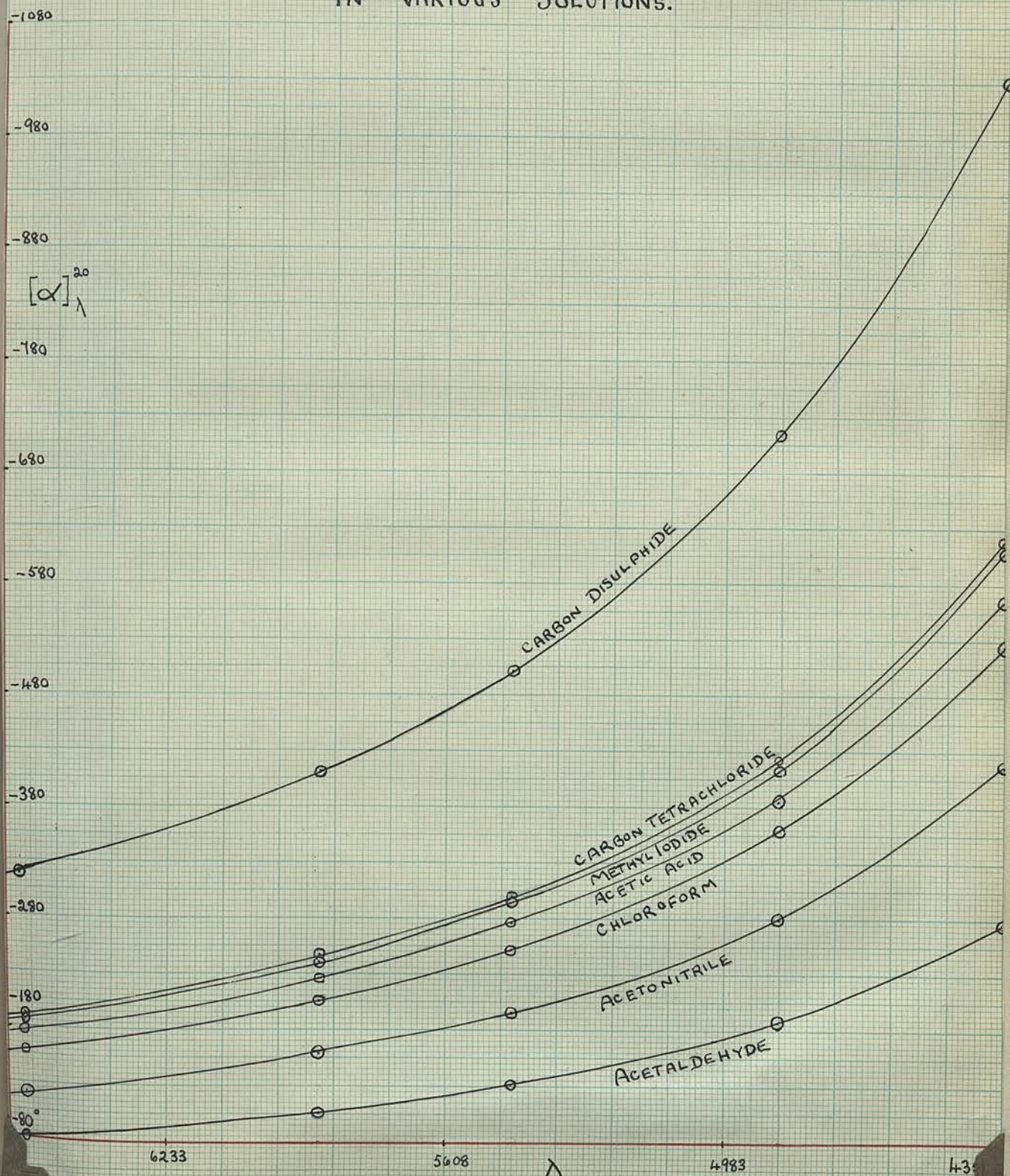
shows that 5- and 6- membered rings of this type are comparatively common. If such a structure does tend

to form, it may be expected to be favoured by low temperatures, when the molecular vibration is minimised. In this event *l*-Benzoin would probably exhibit certain peculiarities in optical behaviour as compared with the methyl ether, in which no chelation can occur.

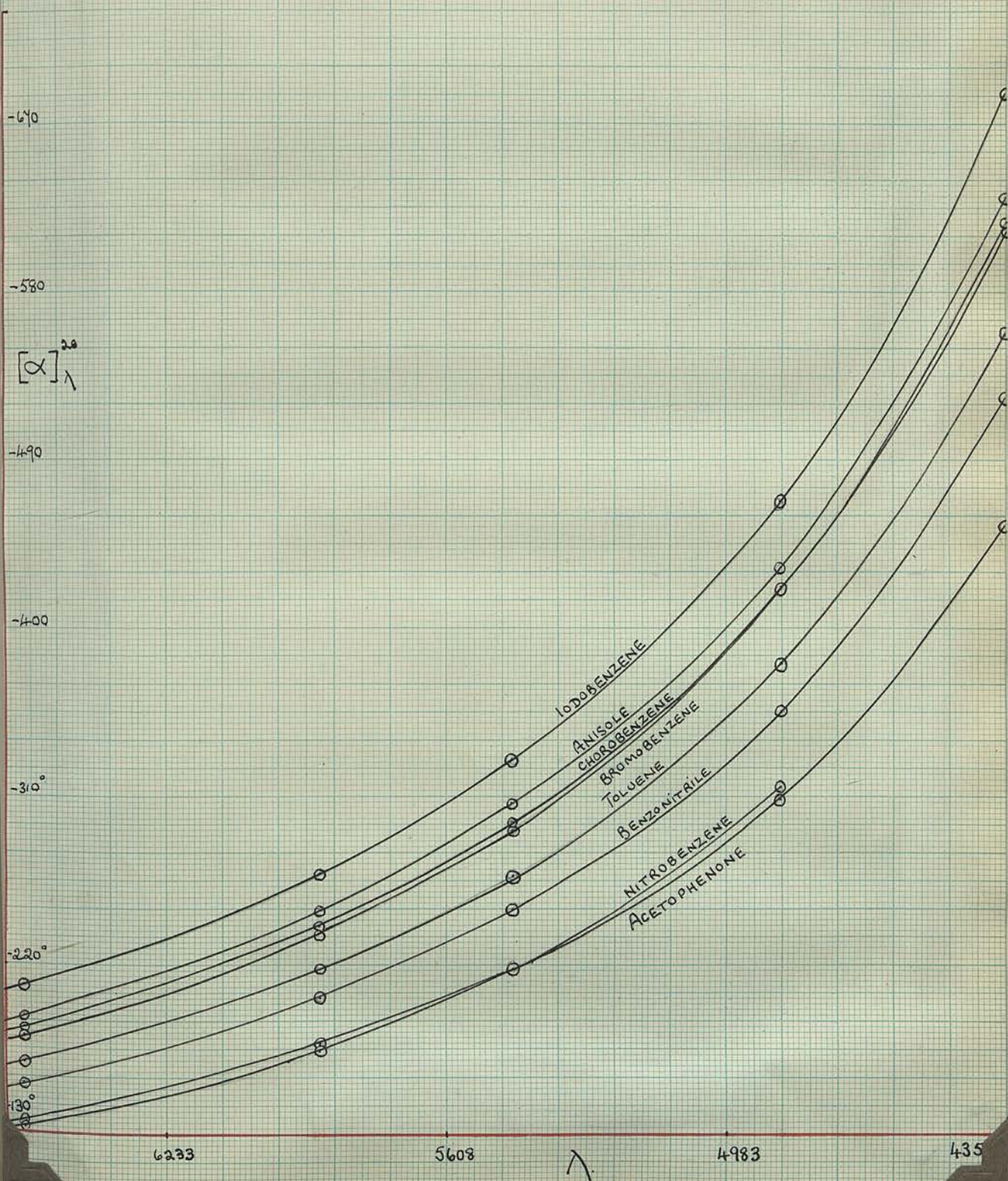
Setting aside the abnormally low rotatory powers observed for *l*-benzoin in hydrocarbon solvents, and which have been shown to be accompanied by self-association of the solute in these media, *l*-benzoin differs in two points from its methyl ether. In the first place the rotatory powers of the compounds in weakly polar media are opposite in sign, and secondly the optical displacements with change of solvent occur in opposite directions. It has already been pointed out that similar peculiarities are observed among aliphatic alcohols and their ethers, in which no chelate structure can be supposed to exist. A peculiar intersection has, however, been noted in the temperature-rotation curves for *l*-benzoin dissolved in benzene and toluene respectively (graph II.p.91) which has been discussed on p.92. It is possible that this inversion on passing from low to high temperatures is connected with the disruption of the co-ordinate link with rise of temperature. In polar solvents it is to be expected that the link would be broken even at low temperatures, since the electrostatic forces tending to aid its formation would be greatly weakened in the presence of a solvent of high dielectric constant.

In conclusion it may be mentioned that Hassel and Naeshagen (Zeit. Phys. Chem., 1929, B.6., 152) have calculated the dipole moments of benzil and benzoin from the moments of the component groups and on the assumption of free rotation around single bonds. The resulting values agree comparatively well with those obtained experimentally, and therefore do not support the assumption of a chelate ring, which would involve the inhibition of free rotation around the single bonds. In this case the peculiar intersection of the TR - curves observed for ℓ -benzoin in benzene and toluene solutions with rise of temperature may be due to the dissociation of the benzoin aggregates, leading to a tendency for solutions in these solvents to give relatively higher rotations at higher temperatures. This would be in agreement with the abnormally low rotatory powers given in non-polar media at room temperatures, under which conditions a considerable degree of association occurs.

GRAPH VI

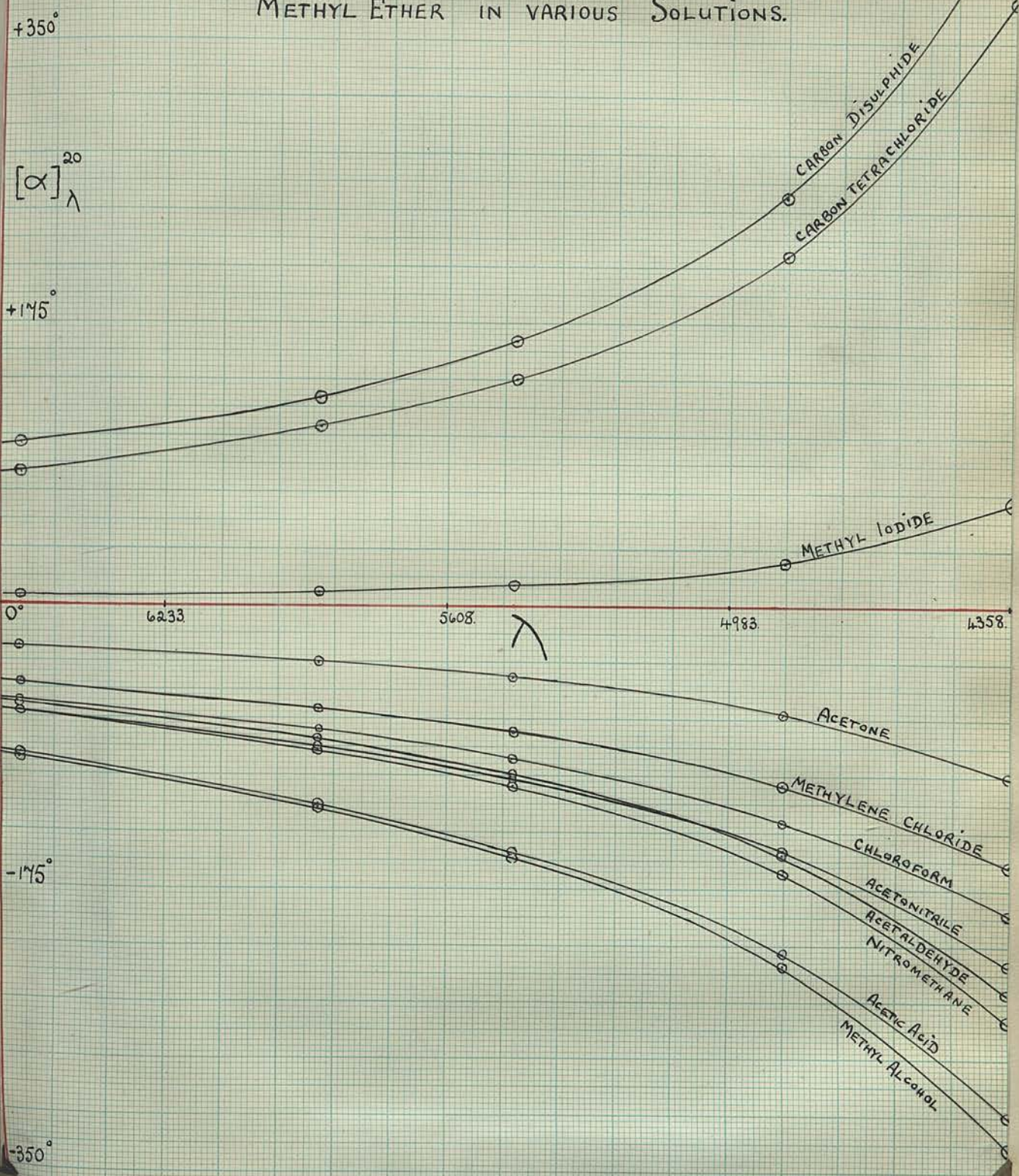
DISPERSION CURVES FOR *l*-BENZOIN
IN VARIOUS SOLUTIONS.

GRAPH VII
DISPERSION CURVES FOR *l*-BENZOIN
IN VARIOUS SOLUTIONS.



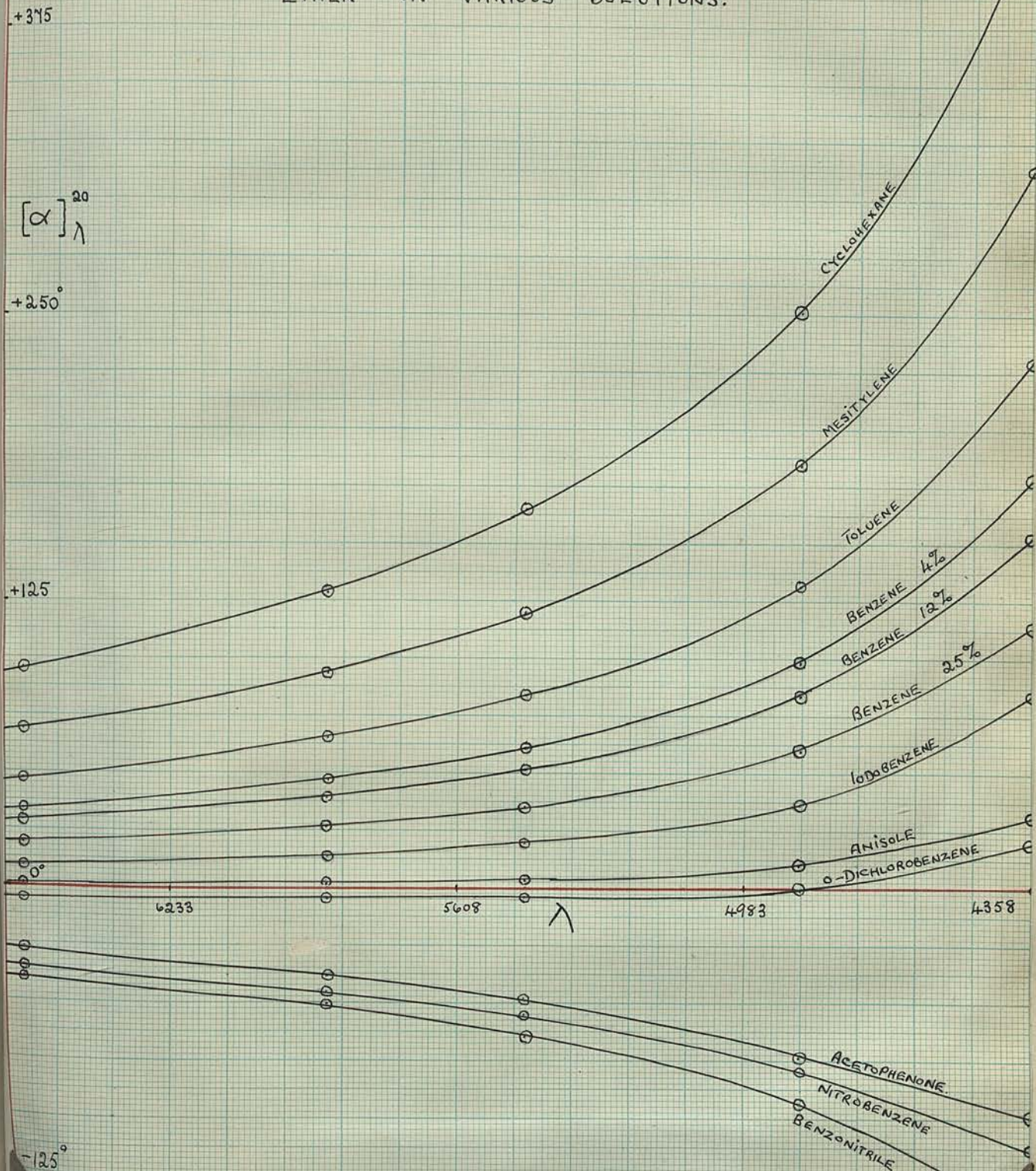
GRAPH VIII

DISPERSION CURVES FOR *l*-BENZOIN METHYL ETHER IN VARIOUS SOLUTIONS.



GRAPH IX

DISPERSION CURVES FOR l-BENZOIN METHYL
ETHER IN VARIOUS SOLUTIONS.



Types of Dispersion Shown by *l*-Benzoin and *l*-Benzoin Methyl Ether in the Various Solutions.

An extensive examination of the dispersion effects for *l*-benzoin and *l*-benzoin methyl ether in various solvents was not desired. Hence, only five wave-lengths ranging from the hydrogen red to the mercury violet were employed. These five lines were considered adequate for giving a general idea of the behaviour of the two substances in solution over the visible region of the spectrum. The preceding diagrams (graphs VI-IX pp. 109-112) not only illustrate the effect of non-polar and polar solvents on the rotatory power of the two solutes, but also show the dependence of the rotation upon the wave-length of the light employed.

In graph VI.p.109, are plotted the values observed for *l*-benzoin in aliphatic solvents, those for aromatic solvents being shown in graph VII.p.110. The corresponding values for *l*-benzoin methyl ether are given in graphs VIII & IX pp. 111 & 112.

On the whole it will be noted that the various curves represent a gradual transition from one extreme of solvent effect to the other. In some instances the (namely) dispersion curves fell so closely together that the scale of the graph was too small to show them separately. For this reason two or three of the solvents have been omitted, but in each of these cases the form of the

curve omitted was approximately parallel to the adjacent curves in the graph. From the various diagrams it is seen that the relative displacements due to change of solvent are practically independent of the wave length of the light employed in the visible region.

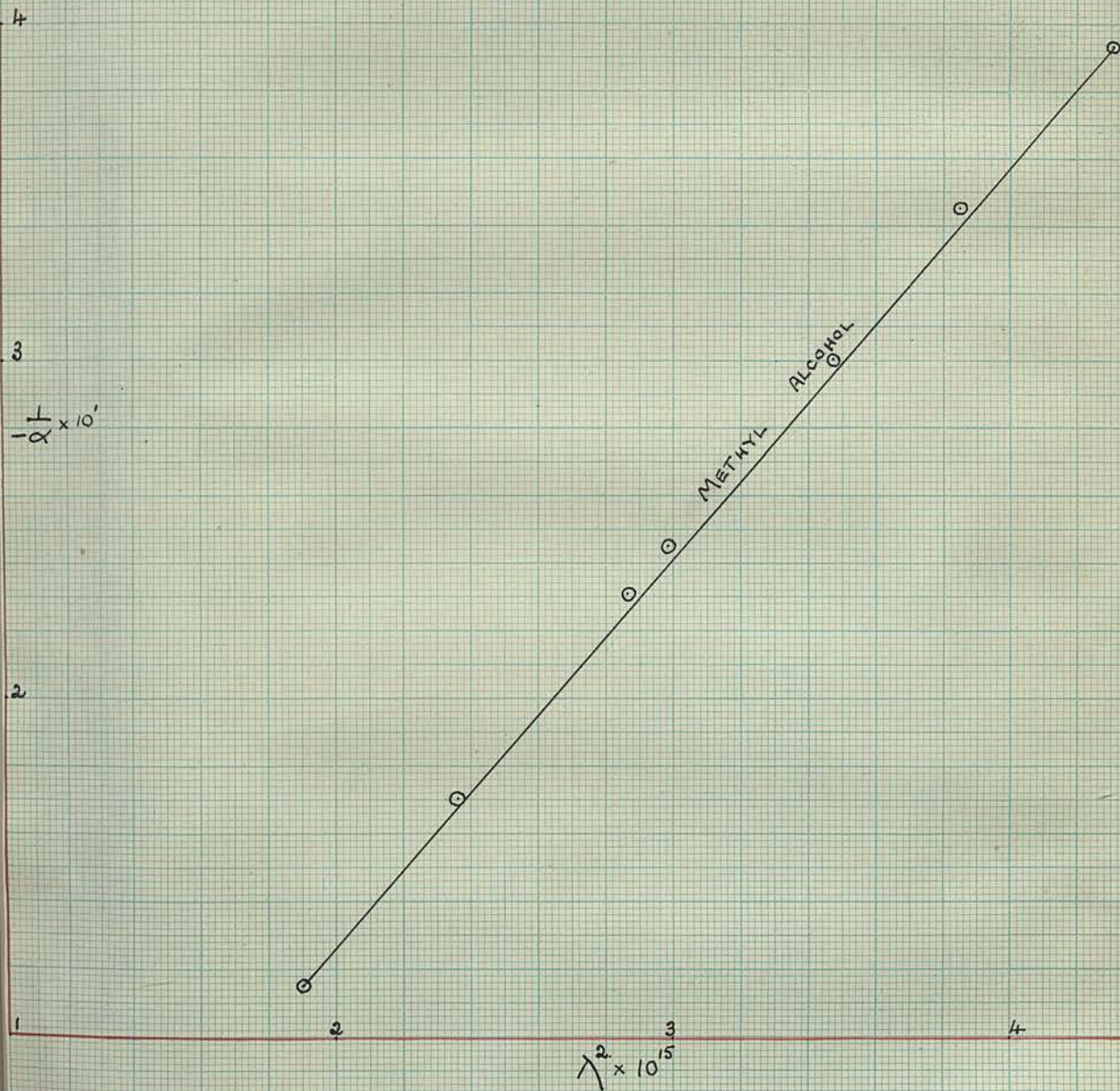
In the graph for *l*-benzoin in aromatic solvents (p. 110) two definite cases are found in which intersection of the curves occurs. The curve for nitrobenzene cuts that for acetophenone and the curves for bromobenzene and chlorobenzene also intersect. No special significance is to be attached to these deviations from the general trend of the diagram, however, because in these two cases the concentrations of the solute are not comparable, the value for nitrobenzene and bromobenzene being only half of that obtaining in the remaining polar solvents.

A similar intersection of the dispersion curves with change of concentration has been recorded for one and the same solvent by Freudenberg, using methyl *l*-mandelate in acetylene tetrachloride (Ber., 1925, 58, 1754).

Methyl *l*-Mandelate in Acetylene tetrachloride.

c.	λ 637	λ 578	λ 546	λ 434
1.08	-131.8	-172.0	-199.2	-351.9
5.46	-130.8	-170.0	-200	-365.8

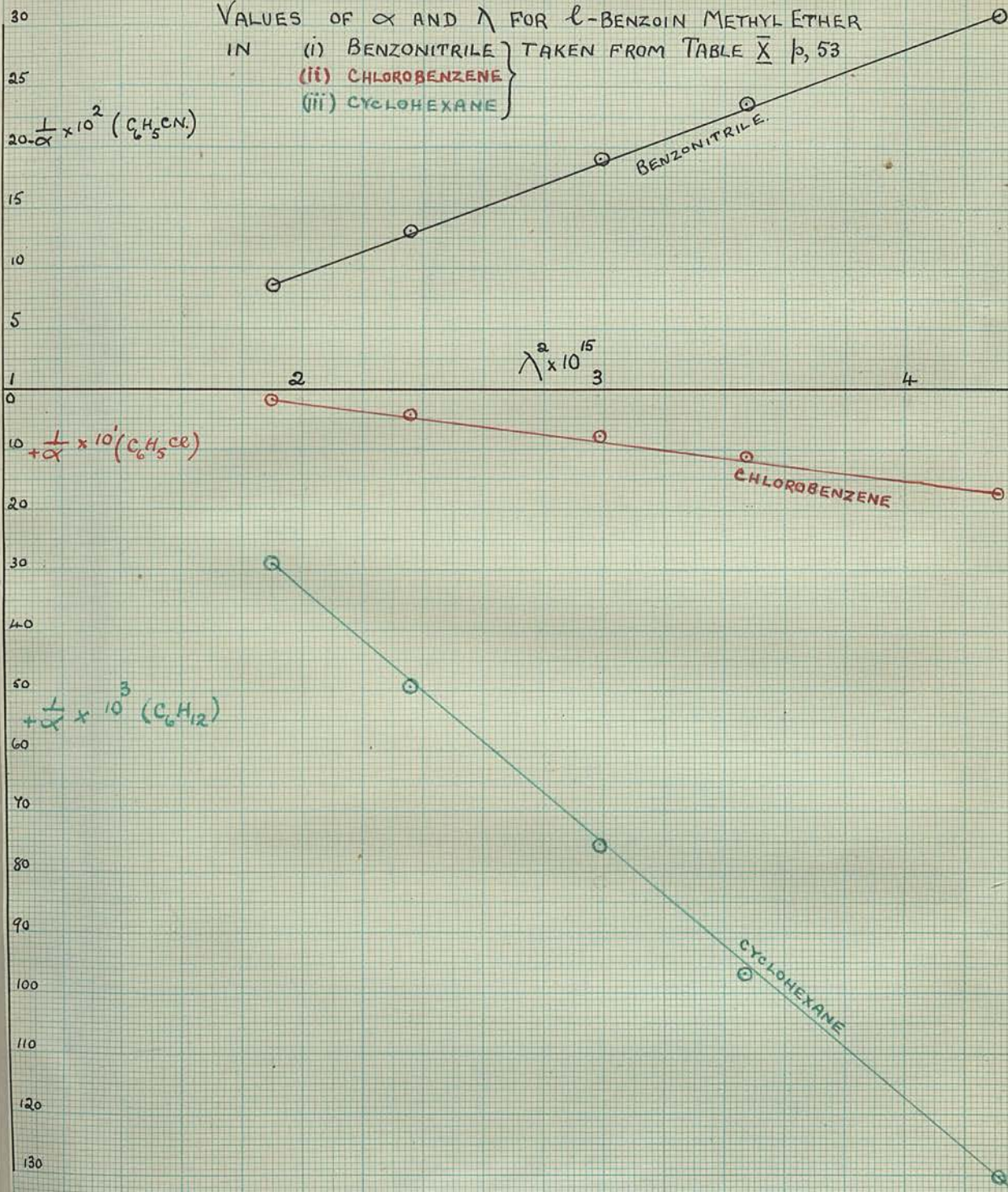
The type of dispersion for *l*-benzoin in all the solvents, whether aromatic or aliphatic, is similar to

GRAPH \bar{X} : $\frac{1}{\alpha}$ PLOTTED AGAINST λ^2 VALUES OF α AND λ FOR l-BENZOIN IN METHYL ALCOHOL
TAKEN FROM TABLE I p. 42

GRAPH XI

 $\frac{1}{\alpha}$ PLOTTED AGAINST λ^2

VALUES OF α AND λ FOR *l*-BENZOIN METHYL ETHER
 IN (i) BENZONITRILE } TAKEN FROM TABLE X p, 53
 (ii) CHLOROBENZENE }
 (iii) CYCLOHEXANE }

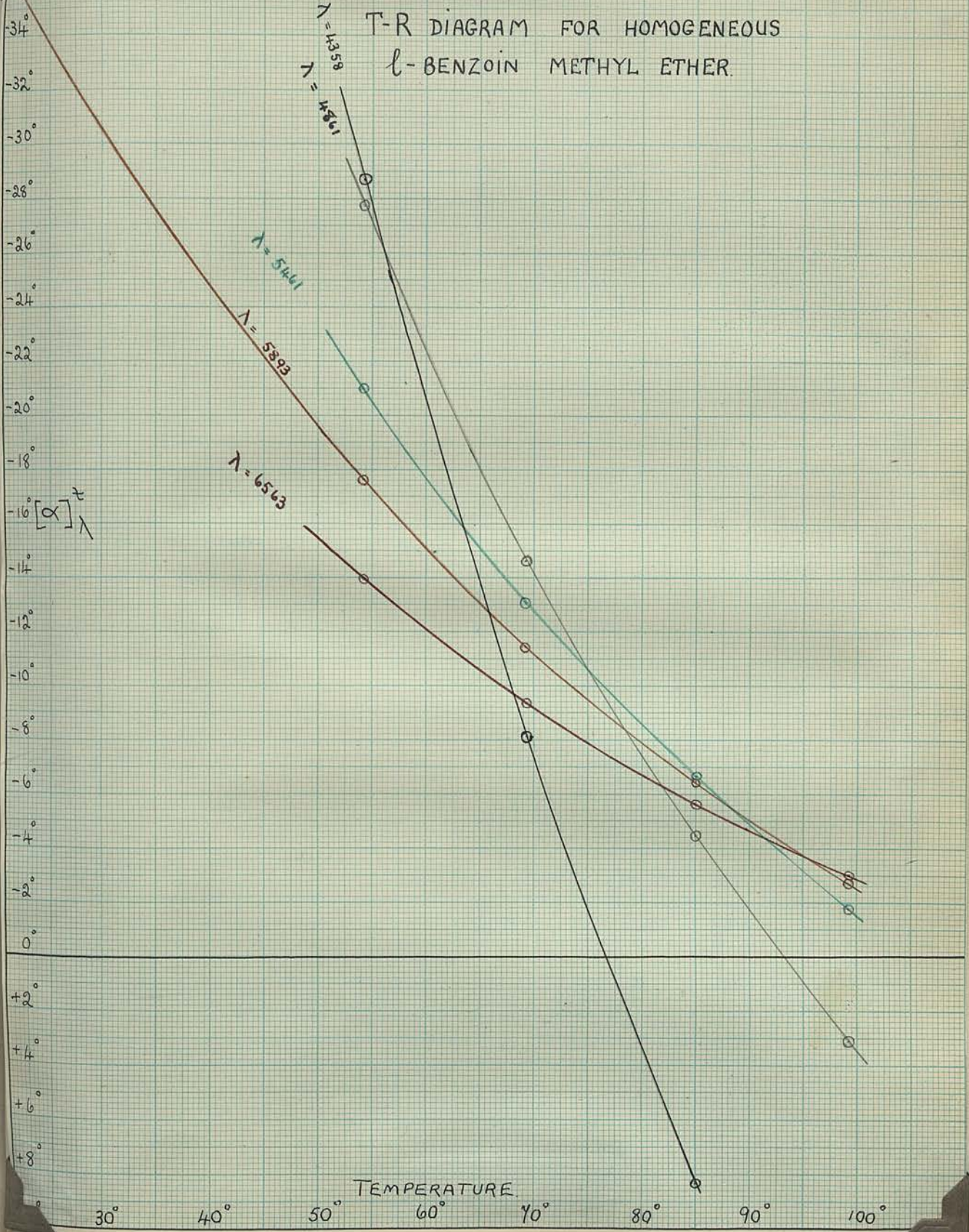


that found in methyl alcohol and illustrated in graph X. p. 115 in which $\frac{1}{\alpha}$ is plotted against λ^2 . The same type of dispersion, in which all intermediate points lie above the line joining the two extreme points, has been shown by Rogers to apply to mandelic acid and its esters (J.C.S., 1932, 2171). 9

The dispersions for the methyl ether in solution are very interesting. In solvents of the aromatic type, those which give high negative rotations, comprising nitrobenzene, benzaldehyde and benzonitrile, also those giving high positive values, consisting of benzene, toluene, mesitylene and cyclohexane, all show the same type of dispersion as *l*-benzoin. On the other hand, the solvents giving rise to lower negative rotations such as acetophenone, also those producing lower positive values such as anisole, bromobenzene, chlorobenzene and iodobenzene show dispersions of a different character. In these last named solvents the intermediate points all lie below the line joining the two extreme points as seen in graph XI. p. 116. This graph actually contains three diagrams representing the ether in benzonitrile, in chlorobenzene and in cyclohexane respectively, in which the two types of dispersions are evident. Further this type of dispersion for the solutions of low negative or positive values has been pointed out as peculiar to the lactate esters in comparison with those of mandelic acid (Rogers, loc. cit.). In the aliphatic series, all the solutions of the ether which are of high negative or

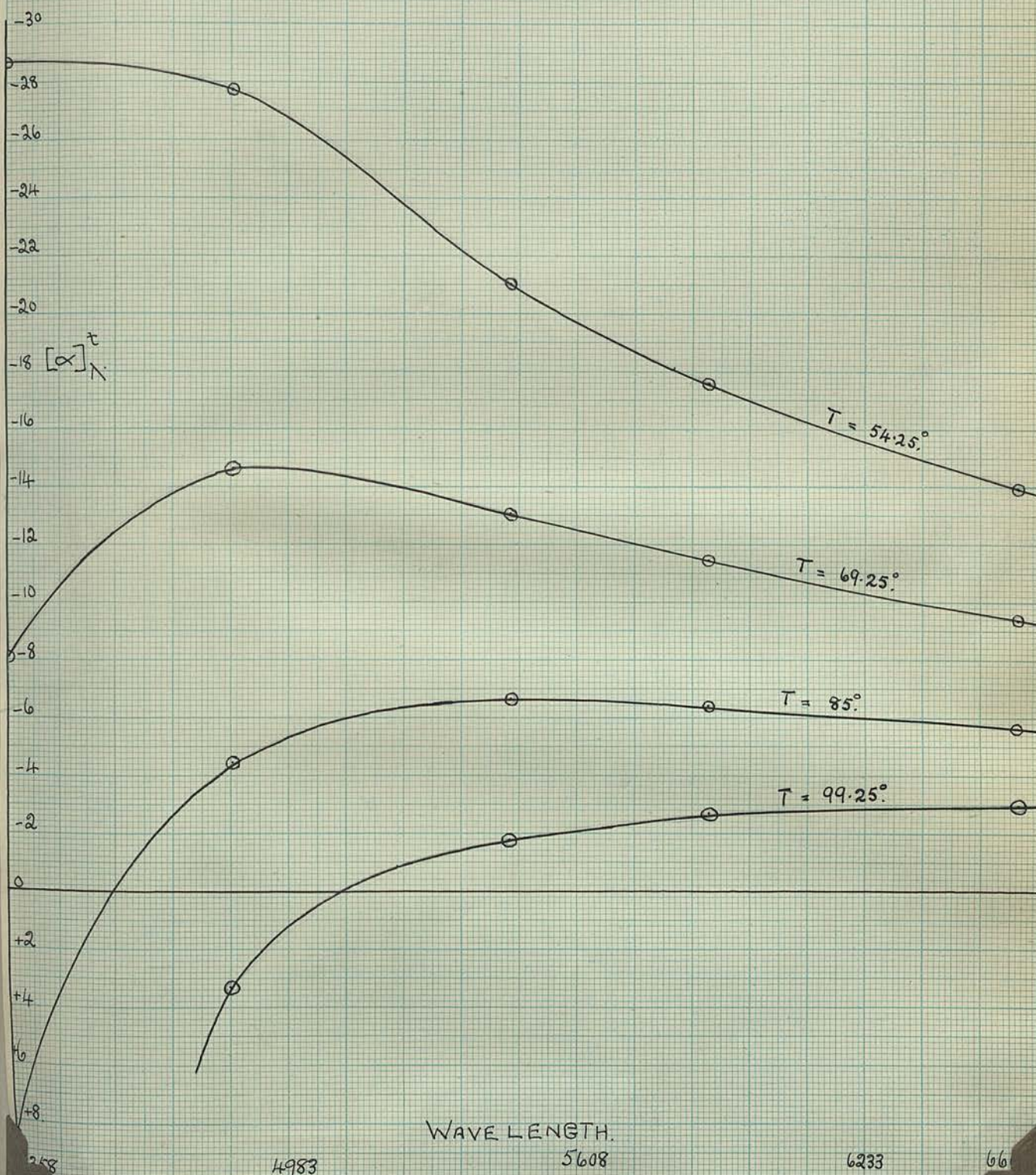
GRAPH XII

T-R DIAGRAM FOR HOMOGENEOUS
 l-BENZOIN METHYL ETHER.



GRAPH XIII

DISPERSION CURVES FOR HOMOGENEOUS
 L-BENZOIN METHYL ETHER AT DIFFERENT
 TEMPERATURES



positive rotations, with the sole exception of methyl iodide give the same type of dispersion as the mandelates. The exception, methyl iodide, of low positive rotation exhibits a dispersion similar to the lactates.

In the case of the ether there are two instances of anomalous dispersion. From graph IX, p. 112, it is seen that the dispersion curve for O-dichlorobenzene cuts the zero axis, passing from negative to positive values with decrease in wavelength. Also it is evident that the homogeneous ether exhibits a region of anomaly on the negative side of the axis over the temperature range 55° - 100° , c.f. graph XII, p. 118

By assuming that the infra-red absorption bands contribute somewhat to the rotation of an active substance, Wood & Nickolas (J.C.S., 1928, 1712.) postulated that the dispersion curves should cross the zero axis in a given manner for compounds of known configuration. According to these authors, if the positive values for the rotation are plotted on the top portion of the diagram, then the curve should cross the zero axis so that $\frac{d\alpha}{d\lambda}$ is positive for a compound of "d" configuration and vice versa. Lowry (J.C.S., 1929, 2858) (Proc. Roy. Soc., 1930, 127A, 271.), also Kuhn (Z.P.C., 1929, B4, 14) have, however, rejected Wood's basic conceptions. It is interesting to note that the dispersion curves for both the homogeneous methyl ether and the O-dichlorobenzene solution of the ether cross the zero axis so that $\frac{d\alpha}{d\lambda}$ is negative. According to Wood's theory, this means that the methyl ether has an "l" /h

configuration, and since the ether is related to *l*-mandelic acid, it must also have an "*l*" configuration. The work of Clough (J.C.S., 1918, 113, 526) and Freudenberg (B 1923, 56, 193; 1925, 58, 1753) has proved conclusively that *l*-mandelic acid is of the "d" configuration and unless there is a Walden inversion in converting *l*-benzoin into its ether by the silver oxide method, then Wood's theory is untenable.

The available evidence, however, indicates that no inversion occurs under the above conditions. From an extensive investigation on the conversion of mandelates to the corresponding ethers by Purdie's method, McKenzie (J.C.S., 1899, 75, 766) concluded that the reagent did not detach the oxygen atom from the carbon to which it is linked. The process is thus believed to involve the replacement of the hydrogen of the hydroxyl group by silver, which is subsequently exchanged by double decomposition for a methyl group. Again, Freudenberg, (Ann., 1933, 501, 199.) using Purdie's method has prepared a number of ether derivatives of *l*-mandelic acid, and though he finds that their optical behaviour differs in some respects from that of the parent hydroxy compound, he finds no evidence for the occurrence of an inversion of configuration during the methylation process.

A P P E N D I X.

Behaviour of Methyl *l*-Mandelate with Change of Solvent, Concentration and Temperature.

Methyl *l*-mandelate is a simple derivative of *l*-mandelic acid. It is therefore chemically related to the hydroxy derivative, *l*-benzoin, and probably shows an optical similarity to this last named compound as well. Hence it was decided to undertake a brief investigation of the optical behaviour of this ester, methyl *l*-mandelate, towards change of solvent, concentration and temperature. The rotations were observed in a dozen solvents typical of the methane and benzene series. Concentrations were determined for two solutions of $C = 5$ & $C = 25$ respectively, and temperature effects were observed in the three solvents previously used in such determinations, namely nitrobenzene, bromobenzene and mesitylene.

Preparation of Methyl *l*-Mandelate.

l-mandelic acid was prepared by the method of Wöhler (A.1848, 66, 238), which is fully described by Lewkowitsch (B, 1883, 16, 1565). Amygdalin, 50 gms., was treated at 100° with excess fuming hydrochloride acid for $3\frac{1}{2}$ - 4 hours.

The black mass was extracted at least six times with ether, the extracts being added together and the ether removed. Crude *l*-mandelic acid remained.

This was recrystallised once from benzene when slightly brown leaflets were obtained m.p., 131° - 132° , pure acid, m.p., 132.8° , Lewkowitsch loc. cit. yield, 7.7 gms. Lewkowitsch records 18 gms. of acid per 100 gms. of amygdalin.

The acid was considered pure enough for conversion into the methyl ester. The esterification was carried out by the silver salt and alkyl halide method, which had previously been employed by Walker (J. Phys. Chem. 1909, 13, 580) for the preparation of this same ester.

The acid was dissolved in water and the requisite amount of caustic soda solution added for neutralisation. To this solution of the sodium salt, excess silver nitrate was added, the silver salt filtered off, washed with water and thoroughly dried in a dark vacuum desiccator.

The dry salt was finely powdered and put in a stout bottle with a well-fitting stopper. The bottle was then immersed in an ice bath and excess of methyl iodide added slowly. Thereafter the bottle was tightly stoppered and shaken for several hours. The methyl iodide solution of the ester was filtered off, both the filter paper and silver iodide being well washed with ether, and methyl iodide and ether subsequently removed in a vacuum desiccator. The crude ester soon solidified. The crude ester, 6.9 gms. represented an 82% conversion. The crude substance was recrystall-

ised twice from a mixture of benzene and cyclohexane giving white colourless crystals.

M.p., $54^{\circ} - 55^{\circ}$, McKenzie & Wren (J.C.S., 1908, 98, 312), quote $54^{\circ} - 55^{\circ}$.

The rotatory power in carbon disulphide solution for $c = 5.026$ was $\wedge_{5893}^{20} - 243.5^{\circ}$. Wren, (J.C.S., 1909, 95, 1576), for $c = 3.6335$ in carbon disulphide solution found $\wedge_{5893} - 236^{\circ}$.

Effect of Solvents on the Rotatory Power of
Methyl *l*-Mandelate.

TABLE I. Methyl *l*-Mandelate.

Methane Type of Solvent.

$l = 2$ dcm. for CS_2

$l = 1$ dcm. for all other solvents.

$t = 20^{\circ} + 1^{\circ}$.

Solvent	c .	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
CH_3CN	5.012	-5.27°	-6.69°	-8.02°	-10.80°	-14.59°
CH_3OH	5.034	5.89	7.40	8.94	11.96	16.09
CH_3CHO	5.026	6.39	8.12	9.72	13.07	17.54
CH_3COOH	5.088	6.70	8.53	10.25	13.74	18.42
CH_3I	5.022	7.23	9.25	11.14	15.04	20.41
CS_2	5.026	19.13	24.48	29.52	40.25	55.03

TABLE II. Methyl *l*-Mandelate.

Solvent.	$[\alpha]_{5563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{4861}^{20}$	$[\alpha]_{4358}^{20}$	$\mu \times 10^{18}$
CH_3CN	-105 ⁰	-133.5 ⁰	-160 ⁰	-215.5 ⁰	-291 ⁰	3.21
CH_3OH	117	147	178	238	320	1.68
CH_3CHO	127	161.5	193	260	349	2.70
CH_3COOH	132	168	201	270	362	1.73
CH_3I	144	184	222	299	406	1.35
CS_2	190	243.5	294	400	547	0

TABLE III. Methyl *l*-Mandelate.

Solvent.	c.	$[\text{M}]_{5461}^{20}$	$\mu \times 10^{18}$
CH_3CN	5.012	-266	3.21
CH_3OH	5.034	295	1.68
CH_3CHO	5.026	321	2.70
CH_3COOH	5.088	334	1.73
CH_3I	5.022	368	1.35
CS_2	5.026	487	0

TABLE IV. Methyl *l*-Mandelate.

Benzene Type of Solvent.

$$l = 1 \text{ dcm.}$$

$$t = 20^{\circ} + 1^{\circ}$$

Solvent.	c.	α 6563	α 5893	α 5461	α 4861	α 4358
$C_6H_5NO_2$	5.034	-6.98°	-8.84°	-10.65°	-14.39°	-
$S-C_6H_3(CH_3)_3$	5.106	7.06	8.96	10.78	14.59	19.79
$C_6H_5OCH_3$	5.030	7.21	9.16	11.02	14.87	20.12
C_6H_6	5.026	7.30	9.28	11.16	15.09	20.44
$C_6H_5Br.$	5.016	8.03	10.18	12.24	16.51	22.35

TABLE V. Methyl *l*-Mandelate.

Solvent.	$[\alpha]_{6563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5461}^{20}$	$[\alpha]_{4861}^{20}$	$[\alpha]_{4358}^{20}$	$\times 10^{18}$
$C_6H_5NO_2$	-138.7°	-175.6°	-211.5°	-285.9°	-	3.90
$S-C_6H_3(CH_3)_3$	138.2	175.5	211.2	285.8	387.5	0
$C_6H_5OCH_3$	143	182	219	296	400	1.20
C_6H_6	145	185	222	300	407	0
$C_6H_5Br.$	160	203	244	329	445.5	1.50

TABLE VI. Methyl *l*-Mandelate.

Solvent.	c.	$[M]_{5461}^{20}$	$\mu \times 10^{18}$
* $C_6H_5NO_2$	5.034	-348°	3.90
$S-C_6H_3(CH_3)_3$	5.106	350.5	0
$C_6H_5OCH_3$	5.030	363.5	1.20
C_6H_6	5.026	368.5	0
$C_6H_5Br.$	5.016	405	1.50

* Extrapolated from T-R diagram for $t = 20$.

Influence of Concentration on the RotatoryPower of Methyl *l*-Mandelate.TABLE VII. Methyl *l*-Mandelate.In Benzene Solution.

= 1 dcm.

$$t = 20^{\circ} + 1^{\circ}$$

Solvent.	c.	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
C_6H_6	5.026	-7.30°	-9.28°	-11.16°	-15.09°	-20.44°
C_6H_6	25.046	35.38	44.99	54.09	72.96	98.81

TABLE VIII. Methyl *l*-Mandelate.

Solvent	c.	$[\alpha]_{6563}^{20}$	$[\alpha]_{5893}^{20}$	$[\alpha]_{5461}$	$[\alpha]_{4861}$	$[\alpha]_{4358}$
C_6H_6	5.026	-145°	-185°	-222°	-300°	-407°
C_6H_6	25.046	141	180	216	291	394.5

Influence of Temperature on the RotatoryPower of Methyl *l*-Mandelate.TABLE VIII. Methyl *l*-Mandelate.In Nitrobenzene Solution.

= 1 dcm.

p = 4.185

t	26	42.8	61.6	79.8
$\frac{t}{D_4}$	1.196	1.180	1.161	1.144

t	D_4^t	α^{6563}_t	α^{5893}_t	α^{5461}_t	α^{4861}_t	α^{4358}_t
9.5	1.212	-	-	-10.95	-	-
18.25	1.203	-6.98	-8.84	-10.65	-14.39	-
52	1.1705	6.10	7.73	9.32	12.58	-
74.5	1.149	5.59	7.12	8.54	11.59	-
99.25	1.125	5.04	6.40	7.69	10.40	-

t	$[\alpha]^{20}_t^{6563}$	$[\alpha]^{20}_t^{5893}$	$[\alpha]^{20}_t^{5461}$	$[\alpha]^{20}_t^{4861}$	$[\alpha]^{20}_t^{4358}$
9.5	-	-	-216	-	-
18.25	-139	-176	-211.5	-286	-
52	124.5	158	190	257	-
74.5	116	148	178	241	-
99.25	107	136	163	221	-

TABLE IX. Methyl *l*-Mandelate.

In Bromobenzene Solution.

The tube of length, $l = 1$ dcm., was found to have a leakage in the outer jacket, hence the solution was transferred to a $\frac{1}{2}$ dcm. jacketted tube before proceeding to higher temperatures.

$$l = 1 \text{ dcm. } (10^\circ - 20^\circ)$$

$$\& \frac{1}{2} \text{ dcm. } (50^\circ - 100^\circ)$$

$$p = 3.391$$

t	22.6°	43.7°	68.1°	81.7°
D_4^t	1.477	1.450	1.418	1.401

t	D_4^t	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
9°	1.494	-9.41°	-10.64°	-12.79°	-17.30°	-23.43°
20.75	1.479	8.03	10.18	12.24	16.51	22.35
53.5	1.437	-	4.47	5.38	-	-
72.5	1.411	3.21	4.14	4.99	6.73	9.04
98.25	1.380	2.91	3.73	4.49	5.06	8.03

t	$[\alpha]_{6563}^t$	$[\alpha]_{5893}^t$	$[\alpha]_{5461}^t$	$[\alpha]_{4861}^t$	$[\alpha]_{4358}^t$
9°	-186°	-210°	-252°	-341°	-462°
20.75	160	203	244	329	445.5
53.5	-	183.4	221	-	-
72.5	134	173	208.5	281	378
98.25	124	159	192	216	343

TABLE X Methyl *l*-Mandelate.

In Mesitylene Solution.

= 1 dcm.

p = 5.769

t	25.4°	45°	59.5°	81°
D_4^t	.8720	.8557	.8441	.8260

t	D_4^t	α_{6563}	α_{5893}	α_{5461}	α_{4861}	α_{4358}
9.5°	.8852	-	-9.37°	-11.28°	-	-
21	.8756	-7.06	-8.96	-10.78	-14.59	-19.79
53.5	.8488	6.21	7.84	9.43	12.73	17.26
71	.8344	-	7.34	8.82	-	-
99	.8112	5.20	6.58	7.92	10.73	14.41

t	$[\alpha]_{5893}^{20+t}$	$[\alpha]_{5461}^{20+t}$	$[\alpha]_{4861}^{20+t}$	$[\alpha]_{4358}^{20+t}$
9.5	-	-183.5 ⁰	-221 ⁰	-
21	-140	-177	-213	-392
53.5	127	160	193	352.5
71	-	152.5	183	-
99	111	141	169	308

Influence of Temperature on the Rotatory Power
of Methyl ℓ -Mandelate in Solution.

In $C_6H_5NO_2$ p = 4.185			In $C_6H_5Br.$ p = 3.391			In $S-C_6H_3(CH_3)_3$ p = 5.769		
t	$[M]_{5893}^t$	$[M]_{5461}^t$	t	$[M]_{5893}^{20+t}$	$[M]_{5461}^t$	t	$[M]_{5893}^{20+t}$	$[M]_{5461}^{20+t}$
9.5 ⁰	-	-359 ⁰	9	-348.5	-418 ⁰	9.5 ⁰	-305 ⁰	-367 ⁰
18.25	-292	351	20.75	337	405	21	294	354
52	262	315	53.5	304.5	367	53.5	266	320
74.5	246	295	72.5	287	346	71	253	304
99.25	226	271	98.25	264	319	99	234	281

DISCUSSION.

A glance at the following table reveals a general agreement with the rotation and the polarity of the solvent medium. As in the case of *l*-benzoin, the more polar solvents give solutions of low negative rotations, and the non-polar or weakly polar solvents give solutions of higher negative rotations. Also it is evident that the methane solvents exhibit a better defined agreement than the benzene derivatives, a fact which is also noticeable in considering the solvent influences on the activity of *l*-benzoin.

Solvent.	c.	$[M]_{5461}^{20}$	$\mu \times 10^{18}$
CH_3CN	5.012	-266 ⁰	3.21
CH_3OH	5.034	295	1.68
CH_3CHO	5.026	321	2.70
CH_3COOH	5.088	334	1.73
CH_3I	5.022	368	1.35
CS_2	5.026	487	0
$\text{C}_6\text{H}_5\text{NO}_2$	5.034	348	3.90
$\text{S-C}_6\text{H}_3(\text{CH}_3)_3$	5.106	350.5	0
$\text{C}_6\text{H}_5\text{OCH}_3$	5.030	363.5	1.20
C_6H_6	5.026	368.5	0
$\text{C}_6\text{H}_5\text{Br}$	5.016	405	1.50

From T-R diagram for $t = 20^{\circ}$.

The displacement towards the polar end of the table with mesitylene and to a slight extent with benzene was also discussed very fully when considering *l*-benzoin. The reason previously given for these relatively low rotations in non-polar aromatic solvents was an extensive degree of self-association of the active solute. There is no doubt that association is also operative in the case of the solutions of the methyl ester in non-polar solvents, with a resulting lower rotation. This is supported by the very considerable degree of association reported in Turner's "Molecular Association" for hydroxy esters in non-polar media, e.g. methyl lactate M.W. 104 gives values of 99 - 162 for $C = 0.7 - 9.3$ in benzene, (no values for methyl mandelate are quoted).

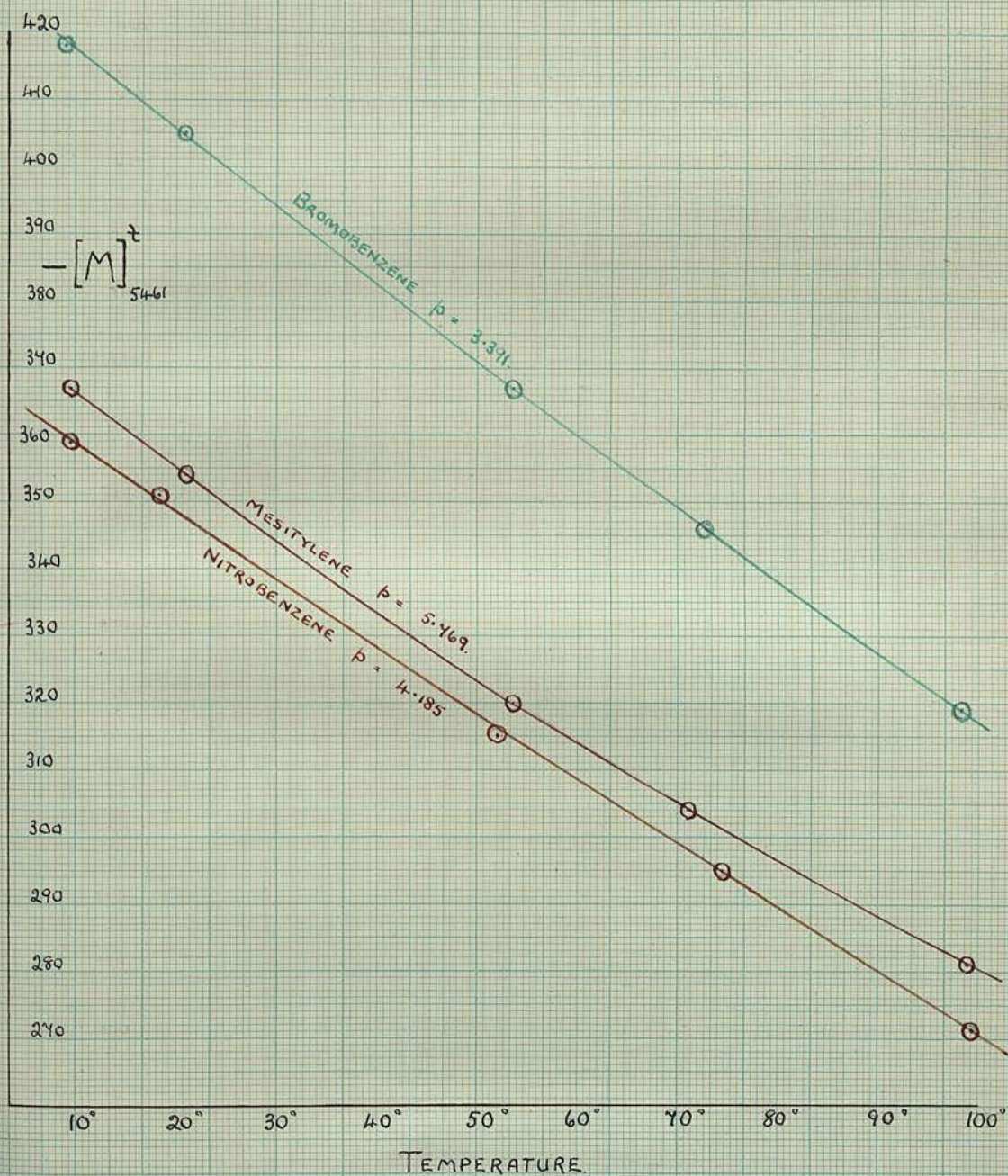
The direction of the change in rotatory power to be expected with an increase in the degree of association is shown by the following determinations in benzene solution.

In Benzene Solution.

c.	$[M]^{20}$
5.026	5461 -368.5°
25.046	- 358.5°

The direction of the optical change observed for methyl mandelate with increased concentration thus agrees with that which would be predicted on the dipole theory from the above table illustrating solvent influences. The more polar solvents, owing apparently to their greater power of entering into association with the active solute,

GRAPH XIV

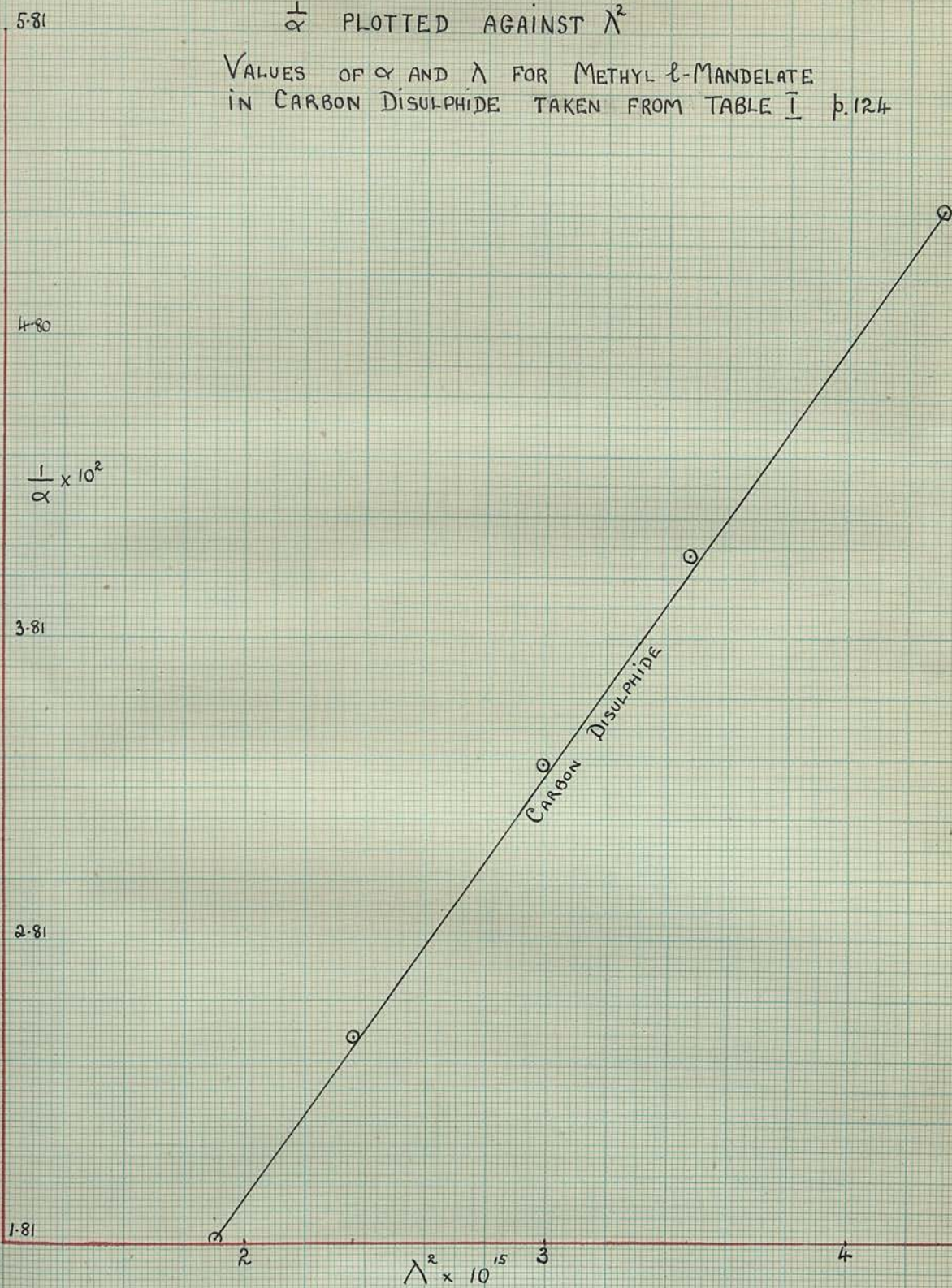
T-R DIAGRAMS FOR METHYL *l*-MANDELATE
IN SOLUTION

yield solutions of low negative rotations. An increase in the concentration of the ester in benzene solution has a similar effect, because of the resulting rise in the degree of association of the ester molecules with one another.

In considering the temperature effects, graph XIV. p. 133, the position of the three curves is akin to those found for *l*-benzoin, mesitylene lying in an intermediate position to nitrobenzene and bromobenzene. The curves for the nitrobenzene and bromobenzene solutions of the ester converge at higher temperatures, this being in agreement with the dipole hypothesis discussed previously. It is noteworthy, however, that in the case of the mesitylene solution, the curve is convex with respect to the temperature axis. This may be due to the dissociation of the solute aggregates at higher temperatures causing the mesitylene curve to exhibit a tendency to assume its true position, which if the solute were not associated, would be above that of bromobenzene. The dissociation of the solute aggregates in non-polar media with rise of temperature has already been discussed on p. 92, where it was suggested that this might be the reason for the intersection of the T-R diagrams for benzene and toluene solutions of *l*-benzoin at different concentrations.

Little need be said concerning the type of dispersion shown by the ester in solution. In all the above solvents the dispersion is similar to that of

GRAPH XV

 $\frac{1}{\alpha}$ PLOTTED AGAINST λ^2 VALUES OF α AND λ FOR METHYL *l*-MANDELATE
IN CARBON DISULPHIDE TAKEN FROM TABLE I p.124

l-benzoin, and is also of the same type as for ethyl
l-mandelate (Rogers, loc. cit.). The accompanying
diagram for the ester in carbon disulphide in which
 $\frac{1}{\alpha}$ is plotted against λ^2 is typical of all the
solvents, (graph xv. p.135).

7

S U M M A R Y.

The optical behaviour of *l*-benzoin, *l*-benzoin methyl ether and methyl *l*-mandelate, with change of solvent, concentration, and temperature has been examined for a range of wavelengths over the visible region of the spectrum. The results may be summarised as follows.

(a) On the whole the negative rotation of *l*-benzoin varies with the polarity of the solvent in such a manner that solvents of high polarity depress the negative rotatory power. This depression is attributed to the greater degree of association existing between the active solute and solvents of higher polarity.

(b) In agreement with (a), an increase in the concentration of *l*-benzoin in a non-polar solvent also lowers the negative rotation, owing to a rise in the degree of association of the solute molecules with one another.

(c) Among non-polar solvents the solutions with cyclohexane, mesitylene, toluene and benzene gave abnormally low negative rotations as compared with their non-polar character. These displacements were assumed to be due to the association of *l*-benzoin in such media, and this view is supported by molecular weight measurements.

(d) On rise of temperature the T-R curves for

l-benzoin in bromobenzene and nitrobenzene respectively (typical of weakly and strongly polar solvents) tend to converge. This is in agreement with the dipole theory.

(e) For *l*-benzoin methyl ether, molecular weight determinations now show that very little association at low concentrations occurs even in non-polar solvents. In agreement with this difference, the rotatory powers of the ether are in much closer agreement with the polarity of the solvents than was found for *l*-benzoin. Cyclohexane, mesitylene, and other non-polar solvents fall into position at one end of the series to give dextro-rotatory solutions. Strongly polar solvents on the other hand yield laevo-rotatory solutions.

The typical effect of polar and non-polar solvents corresponds to the remarkable variation in rotatory power of *l*-benzoin ~~with~~ methyl ether with change of concentration in benzene solution. With increase in concentration, the dextro-rotation changes into a laevo-rotation.

With rise of temperature the T-R curves for mesitylene, bromobenzene and nitrobenzene converge strongly. These solvents were selected as being typical of non-polar, weakly polar and strongly polar media respectively.

(f) Methyl *l*-mandelate, as was expected, resembles *l*-benzoin in many of its optical properties. The laevo-rotation tends to fall with increase in the dipole moment of the solvent, although certain non-

polar media yield abnormally low values. The latter may be explained by the fact that the ester exists in these solvents in the associated state. The changes with rise of concentration and temperature are also in agreement with the predictions of the theory of dipoles.

(g) The dispersions of *l*-benzoin and methyl *l*-mandelate are in every case normal and complex. When $\frac{1}{\alpha}$ is plotted against λ^2 , the deviation of the graph from the line joining the extreme points is in the same direction.

This statement also holds for *l*-benzoin methyl ether in non-polar and strongly polar solvents respectively. In solvents of medium polarity, or in the homogeneous state the deviation of the graph may be in the opposite direction to the above, or anomalous dispersion may be exhibited.

In conclusion, the author desires to record his deep appreciation and gratitude for the friendly criticism and advice so freely bestowed by Dr. H. G. Rule throughout this investigation.