STUDIES IN SOLVENT ACTION:
POLAR SOLVENTS AND THE ROTATORY POWER OF 1-MENTHYL o-SUBSTITUTED BENZOATES.

THESIS for the DEGREE of
DOCTOR of PHILOSOPHY

by

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INTRODUCTION.

The present day worker, in the particular branch of chemistry about to be considered, has at his command a wealth of organised literature which might well be a source of envy to those engaged in one of the less studied sections of science. Nevertheless, there are numerous problems, for a solution of which the research worker in optical activity and its allied subjects is compelled to make excursions into the realms of qualified conjecture. This factor probably accounts for the great number of hypotheses which have been advanced, from time to time, in efforts to satisfy the experimental evidence so steadily accumulating. In the interests of clarity and economy of space, no attempt has been made in the present work to touch upon all these theories and it is realised that much work of a high standard has had to be passed over.

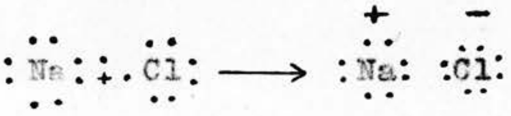
From 1924 onwards RULE and his co-workers have directed their efforts towards the elucidation of the problems of optical activity, as exhibited in a great variety of compounds, on the basis of an hypothesis that the rotatory power of a molecule is a function of the moments of the four groups attached to the asymmetric atom and that the influence of a substituent on the optical rotation would, therefore, depend in/

in sign and magnitude, upon the polarity of the substituent (J.C.S. 1924,1121) The experimental evidence obtained in the earlier part of the work was not conclusive, due largely, to the fact that the distinction between electropositive and electronegative dipoles was not clearly recognised. Later work however, based on the suggestions of DEBYE & J.J. THOMSON, has gone far towards putting the whole study of the problem on a more secure basis.

Before going on to describe the manner in which the degree of polarity of a group has been investigated, it is desirable that some indication be given of the way in which such polarity can be considered to exist in the generally accepted picture of the atom, due to RUTHERFORD, i.e. a planetary system consisting of a nucleus and having negatively charged electrons moving in orbits around it.

KOSSEL (Ann.d.Physik.,1916,49,229) postulated the polar bond , which was alternatively called an electrovalency by LANGMUIR. The essence of Kossel's postulation is that the two atoms undergoing the linkage should be dissimilar, one tending to lose, and the other to gain, electrons. There is no definite bond between the atoms, which are held together presumably by electrostatic attraction. They come apart readily in solution and form independently mobile ions. Compounds so united exhibit those properties/

properties which are connected with salts. Keeping in mind the rule of "ocets" one can represent the formation of the polar bonds typical in the case of sodium chloride by the equation:-



$$\mathrm{:\ddot{\underset{..}{Na}}:\,\dot{+}\,.\ddot{\underset{..}{Cl}}:} \longrightarrow \overset{+}{\mathrm{:\ddot{\underset{..}{Na}}:}}\ \ \overset{-}{\mathrm{:\ddot{\underset{..}{Cl}}:}}$$

Kossel himself recognized, that although his theory of electronic transference was quite satisfactory as an explanation of the ionized link between dissimilar atoms, it was entirely incapable of accounting for non-ionized links between similar atoms. LEWIS (J.A.C.S.,1916,38,762) explained this type of combination of atoms by suggesting that it was possible for an electron to be shared between two atoms so that, in some way, it could count towards the stability of both. Thus:-

$$\mathrm{:\ddot{\underset{..}{Cl}}^{\cdot} + .\ddot{\underset{..}{Cl}}:} \longrightarrow \mathrm{:\ddot{\underset{..}{Cl}}:\ \ddot{\underset{..}{Cl}}:}$$

The two chlorine atoms each with valency for one electron might satisfy themselves by sharing two electrons as above. The molecule in this case is a single structure and considerable forces are required to disrupt it. Valency bonds of this type are known as co-valencies. Thus, the theories of Kossel and Lewis provide an electronic mechanism for the two kinds of linkage, polar and non-polar, which chemical evidence requires. In the same paper, Lewis (loc.cit.) makes a further/

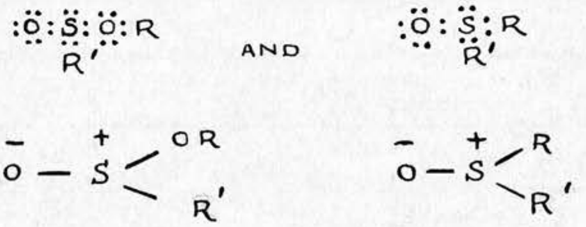
further suggestion, which has subsequently been shown to explain the co-ordination compounds of WERNER. He suggests that the two shared electrons, which constitute a co-valency, can arise in two ways: (1) as they normally do by each of the atoms concerned contributing one of them (as above) or (2) by one of the atoms contributing both. This new type of co-valency needs a name, and symbol. For this purpose the word co-ordinate link is used, and it may be expressed in formulae by an arrow pointing away from the atom which contributes the two electrons:-

$$A\!: + \; B \longrightarrow A : B \quad \text{or} \quad A \longrightarrow B$$

This linkage is the semi-polar link of LOWRY and others and may be written alternatively:-

$$\overset{+}{A} — \overset{-}{B} \quad \text{or} \quad A \Rightarrow B$$

Following on these theoretical considerations, a novel type of molecular asymmetry has been discovered which furnishes experimental confirmation of the existence of this semi-polar linkage. Asymmetric molecules, exhibiting optical activity, have been obtained with only three groups attached to the central atom. These are organic sulphinates and sulphoxides to which the following structural formulae have been assigned:-



It can be seen that the unshared electron pair takes the place of a separate group round the sulphur atom so that, virtually, there are four different groups present. If these are arranged tetrahedrally the molecule is asymmetric. PHILLIPS (J.C.S. 1925,2552) obtained compounds of the first type in an optically active state and HARRISON, KENYON & PHILLIPS (J.C.S., 1926,2079) resolved compounds of the second type, while CLARKE, KENYON & PHILLIPS (J.C.S., 1927, 188) resolved a sulphonylimine in which the semi-polar double bond is formed between a nitrogen atom and a sulphur atom. Further evidence of this semi-polar linkage is given by SUGDEN'S "Parachor" (Sugden, The Parachor & Valency,1930). A group containing a semi-polar bond might be compared to a small electro-magnet, the negative charge being associated with one of the two atoms so linked and the positive charge with the other. Such a group would be definitely and strongly polar. However, groups which contain only co-valencies also may exhibit polarity. In such cases we must suppose that although there is no actual transference of an electron from one atom to another, as is assumed in the case of a semi-polar double bond, yet the sharing of the electrons is not an equal one. The state of affairs might be represented somewhat as follows:-

Here/

Here two atoms A and B are linked by a co-valency, in which B has a greater share of the electrons than A; the electronic orbits consequently being disposed in favour of B. In effect then, B assumes a small negative charge, and A, a correspondingly small, positive charge. An important point as we shall see later is whether the group AB will be oriented towards the molecule into which it is about to be substituted as the doublet (— +) or as (+ —).

Partial polarities, of the type just dealt with, have been employed in modern theories of organic chemistry, and a good deal of information about them has been obtained by the aid of a theory of dielectric constants due primarily to DEBYE (Physikal Zeit., 1912,13,97). SIR J.J. THOMSON (Phil. Mag.,1923,46, 497) suggested a method, by which the relative polarity of groups of simple structure could be obtained by comparing the specific inductive capacities of compounds of the type RX for long wave lengths.

Utilising this conception, RULE (J.C.S.,1924, 1121) calculated the specific inductive capacities for a compound of the type C_6H_5X and after making allowance for molecular weight and density, found that the influence of the substituents, X, in affecting this factor was in the order $NO_2 > CN > COCH_3$ $CHO > Cl > Br > Et > Me > H$, which represents a progressively diminishing polar magnitude irrespective of sign.

Some/

Some years previously, FLURSCHEIM (J.C.S.,1909, 718) studied the influence of substituents on the dissociation constants of acids and bases and found that he could place them in a more or less well defined series which approximates to that given above. OLIVIER (Rec. Trav. Chim.,1914,244) carried out research on the influence of substituents on the chemical reactivity of atoms and groups. The criterion he made use of was the speed of formation of sulphones from p-bromo-benzenesulphonyl chloride and a substituted benzene. He found that the substituents affected the velocity coefficients in the order:-

$Me > H > Hals > NO_2$

An examination by the same author of the hydrolysis of substituted benzyl chlorides, the substituents again being in the p-position, (ibid.,1923,516,775) indicated a similar relative influence:-

$Me > H > Hals > COOH > NO_2$

BETTI (Summary in Gazz,chim. Ital.1923,53,424) correlated the influence of substituents on optical activity with their other properties. He condensed the optically active base, d-[illegible]-naphthol-benzylamine, with benzaldehyde and substituted benzaldehydes. The rotatory powers of the resulting compounds in benzene solution varied from $+2676^\circ$ to -991°, and when arranged/

arranged in order of magnitude, gave a series which agreed approximately with that representing the dissociation constants of the benzoic acids derived from the aldehydes employed. The following modified table indicates the results obtained.

TABLE I.

	$[M]_D^{20}$	Aldehyde Employed.	$k \times 10^5$ for derived acid.
p-Series	$+2676^\circ$	p-Dimethyl-amino-benzoic	1(?)
	$+1154^\circ$	Anisic	3·2
	$+1049^\circ$	p-Hydroxy-benzoic	2·9
	$+691^\circ$	p-Toluic	5·14
	$+373^\circ$	Benzoic	6·0
	$+282^\circ$	p-Chlorobenzoic	9·3
	$+207^\circ$	p-Nitrobenzoic	39·6
o-Series	$+894^\circ$	o-Methoxybenzoic	8·0
	$+373^\circ$	Benzoic	6·0
	-86°	Salicylic	102·0
	-128°	o-Chlorobenzoic	132·0
	-326°	o-Toluic	12·0
	-991°	o-Nitrobenzoic	616·0

From the Table it can be gathered that among the monosubstituted ortho-compounds the influence of substituents on rotatory power and on the dissociation constant/

constant respectively is

$[M]_D^{20°}$ $NO_2 < CH_3 < Cl < OH < H < OCH_3$

k $NO_2 > Cl > OH > CH_3 > OCH_3 > H$

and among the para-compounds

$[M]_D^{20°}$ $NO_2 < Cl < H < CH_3 < (OH, OCH_3) < N(CH_3)_2$

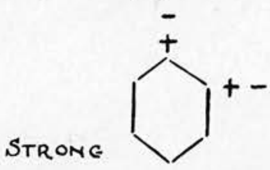
k $NO_2 > Cl > H > CH_3 > (OCH_3, OH) > N(CH_3)_2$

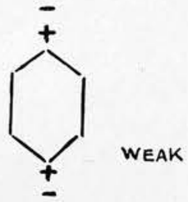
From considerations such as these it has been deduced that the similarity of substituent influence, in all these cases, is to be traced to a fundamental electrical change in the molecule due to the presence of the substituent group. This type of substituent effect has been referred to as the "general polar effect" (ROBINSON, Ann. Rep. Chem. Soc., 1922, 98). In the majority of cases the relative influence of a number of common substituents approximates to the following series:-

NO_2, COOH, Halogens, OCH_3, H, CH_3, $N(CH_3)_2$

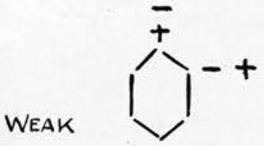
SIR J. J. THOMSON (loc. cit.) also advanced the hypothesis that the magnitude of the electrostatic doublet was a vector property, and that for di-substituted benzenes containing two substituents of similar type, the doublets will reinforce one another in the ortho-position and tend to neutralise one another in the para-position. In this case the di-electric constants should prove to be of the order/

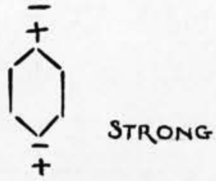
order, o > m > p





Where, however, the substituents are of opposite type they will reinforce one another in the para-position, and oppose one another in the ortho-position, the predicted order then being p > m > o





These suggestions have been largely confirmed by the experimental work of other workers although ESTERMANN (The Dipole Moment & Chemical Structure - DEBYE, page 27) points out some shortcomings of Thomson's theory in the quantitative application of this vector property, and J. J. Thomson himself remarks that there may be forces acting between the substituents which affect their relative positions and thus change the angles between the group moments.

The recent researches of C. P. SMYTH, J. W. WILLIAMS, K. HOJENDAHL, J. ERRERA, and others, based on the work of Debye and Thomson, have now established the fact that the presence of a polar group, such as NO_2 or CH_3, in a hydrocarbon molecule introduces an electrestatic doublet or dipole, and what is important, the seat of this dipole moment of the molecule is the group/

group in question. The definition of a dipole moment is given as follows. In general, the electrical centres of the nuclei and electrons, in a group or atom, do not coincide. The distance between the electrical centre of the electrons and that of the nuclei, multiplied by the charge at either of these poles, is termed the dipole moment. The values of the dipole moments for a great variety of compounds have now been calculated, and for monosubstituted hydrocarbons are found to be characteristic of the substituent groups and largely independent of the hydrocarbon radicals to which they are attached, Thus, nitro-paraffins and aromatic nitro-hydrocarbons have practically identical dipole moments, although the hydrocarbon radicals are very different. It was considerations such as these which led the investigators to consider that the electron displacement which constitutes the dipole, takes place within or in the immediate vicinity of the substituent group. From the researches mentioned above on o, m, and p di-substituted benzene, it has been concluded that substituents may be divided into two classes, identical with the older ideas of electronegative and electropositive radicals, namely:-

(1) Electronegative
NO_2, COOH, Cl, Br, I, OCH_3 and probably OH

and (2) Electropositive
CH_3, NH_2, $N(CH_3)_2$

From/

From the dipole moments found for different substituents it is possible to deduce series such as NO_2, CN, halogens, OCH_3, H, and H, CH_3, $N(CH_3)_2$, NH_2 representing a gradual transition from electronegative groups, through hydrogen, to those of increasingly electropositive character. The strong similarity of the above series to that representing the influence of substituents on the dissociation of carboxylic acids, chemical reactivity and the optical rotatory powers of the substituted series of compounds prepared by BETTI & RULE and co-workers will be at once apparent. As to the actual measurement of dipole moments one point must be stressed, namely, that in order to get a true measure of the contribution of the dipoles to the total polarization it is necessary to assess the dielectric constant under conditions which ensure that each molecule is well separated from its neighbours, so that no minimisation of the external field of the dipoles, due to association, or orientation of the molecules, can take place. This end can be achieved, either by taking measurements in the vaporous state, or in dilute solutions in an inert solvent. The latter method is the one most frequently employed. DEBYE (Polare Molekeln, Leipzig, 1929) gives a full description of the method employed in the calculation of these dipole moments

Following on the work of WILLIAMS, HOJENDAHLE, ERRERA & SMYTH, researches were carried out by RULE which/

which demonstrated a parallelism between the optical rotatory powers of a great variety of substituted compounds, the dipole moments of the respective substituents, and other properties of the compounds. The following table (Trans. Far. Soc., 1930, 325) typifies this work. (The values of the dipole moments quoted are due to J. W. WILLIAMS (J.A.C.S., 1928, 2350) and HOJENDAHL (Thesis, Copenhagen, 1928)).

TABLE II.

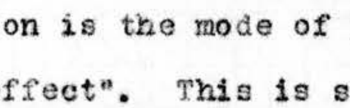
$[M]_D^{20°}$ for the HOMOGENEOUS ESTERS of MONOSUBSTITUTED ACETIC ACIDS, XCH_2COOH.

Substituents	D.M.	k of Acid	*l*-Menthyl Ester	*l*- Octyl Ester.
$N(CH_3)_2$	1·4 e.s.u.	1·3 x 10	-156·9°	-
H	-	1·8 x 10	157·3°	-11·8°
CH_3	0·4	1·4 "	160·2°	-13·0°
COOH	0·9	160 "	160·2°	-
OC_2H_5	-	23 "	160·6°	-
OCH_3	1·2	33 "	165°	-16·3°
OH	1·7	15 "	165° (at 94°C)	-
Br	1·5	138 "	169°	-28·8°
Cl	1·5	155 "	171°	-17·9°
CN	3·8	370 "	174°	-

The order of the molecular rotations corresponds closely with that of the dipole moments of the groups, and/

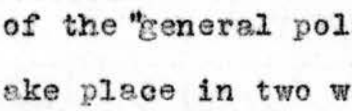
and, except for the carboxyl derivative, with the dissociation constants of the parent acids. It may be deduced also, that the stronger the electronegative character of the substituent present in the acid, the higher is the rotation of the ester. From these results, showing how the dipole nature of the substituent group is reflected in the degree of ionisation, reactivity and in a general manner in the optical activity of compounds, we cannot but be convinced of the fundamental character of such substituent influences.

The next point that suggests itself for discussion is the mode of propagation of the "general polar effect". This is supposed to take place in two ways namely, directly through space, and by means of a displacement of the valency electrons along the chain of atoms towards electronegative groups, or away from electropositive groups. In the majority of cases we are, as yet, unenlightened as to the orientation of an electronegative or an electropositive dipole with respect to the hydrocarbon chain; but general principles would indicate a mechanism like that below



$$\underset{\longleftarrow\qquad\qquad}{\overset{-\,+}{\mathrm{Cl\ CH_2}}\ \overset{\longleftarrow}{\mathrm{COO}\text{-----}\mathrm{H}}}$$

Electron shift facilitating ionization



$$\overset{+\ \ -}{\mathrm{H_3\ C}}\ \overset{\longleftarrow}{\underset{\longrightarrow}{\mathrm{COO}\text{------}\mathrm{H}}}$$

Electron shift repressing ionization

The above example illustrates the case of substituent influence on the ionization of hydrogen in carboxylic acids/

acids which is brought about by the loss of an electron.

If we now refer back to the properties of the ℓ-Menthyl and ℓ-octyl esters in TABLE II we can state in the light of the electron shift theory that the introduction of a substituent, which causes an electron shift away from the asymmetric complex, results generally, in an increase in the rotatory powers of these esters. A similar generalisation has been found to hold for a series of menthyl ethers of the type $C_{10}H_{19}OCH_2X$ (RULE, Trans.Farad. Soc.,1930 326). Conversely we might reasonably expect the negative rotations of these esters to be lowered by the presence of an electropositive amino or dimethylamino group in the acid radical, a change which has been shown to occur. (See TABLE II).

We can then see, from what has been given above, that the dipole nature of substituents and the consequent electron shift in the adjoining hydrocarbon chain can be made to account successfully for simple cases of ionization, and to predict, in a general way, the direction of the change in rotatory power following upon substitution in an optically active ester or ether of the type just dealt with.

All the compounds examined in the experimental part of this work were ℓ-menthyl o-substituted benzoates. The question then of substitution in benzoic esters should prove of particular interest. It/

It was found that the influence of groups in the meta and para positions of the benzene ring was in keeping with the general polar effect as exhibited in aliphatic esters; but it soon became evident that this was not the case when the substituents occupied the ortho-position to the optically active ester grouping. A comparison of the following Tables (III taken from RULE (Trans Far. Soc. 1930, 333) & IV taken from RULE, HAY, NUMBERS & PATERSON (J.C.S., 1928, 180)) will reveal some features peculiar to substitution in the ortho-position. A list of dipole moments is included in column 4 of the Table.

TABLE III

THE VALUES of $[M]_D$ for the o-SUBSTITUTED BENZOIC ESTERS (HOMOGENEOUS)

Ortho Substituent	*l*-Octyl	*l*-Menthyl	μ for substituent Groups.
NO_2	-122°	-381°	-3·9
COOH	- 91°	-332°	-1·0
SCH_3	-	-308°	-
$COOCH_3$	-	-268°	-2·1
CH_3CO	-	-261°	-3·0
OH	-78·2°	-279°	-1·7
H	-77·8°	-239°	-
CH_3	-68·1°	-231°	+ 0·4
I	-44·3°	-231°	-1·5
Br	-49·2°	-205°	-1·5
Cl	-47·1°	-195°	-1·5
OCH_3	-33·0°	-148°	-1·2
$N(CH_3)_2$	-28·1°	-200°	+1·4
NH_2	-23·0°	-261°	+1·5

TABLE IV

THE VALUES of $[M]_D^{20^\circ}$ of ℓ-OCTYL ESTERS of m & p-SUBSTITUTED BENZOIC ACIDS.

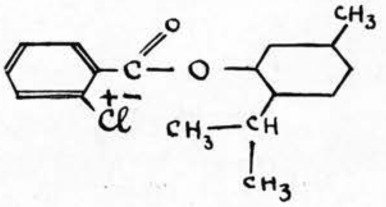
Substituent	m-Esters	p-Esters.
NO_2	-107·8°	-119·7°
COOH	-	-119·1°
OMe	- 93·7°	-113·3°
Cl	- 92·4°	-103·6°
Me	- 94·0°	-103·5°
H	- 77·8°	- 77·8°

In TABLE III it will be seen that H and CH_3 occupy unexpectedly high positions, so that the substituents, OMe, Cl, Br, and I, lower the rotation of the unsubstituted ester. In TABLE IV we see that OMe and Cl (Br and I act similarly) have exactly the opposite effect. Rule in discussing TABLE III pointed out that with few exceptions the substituents could be regarded as being of two types, namely those which are m-directive in benzene substitution, and raise the rotation, and those which are o,p-directive and lower it. Nevertheless, apart from the three groups, COOH, H and CH_3 the arrangement in the octyl derivatives corresponds roughly with that expected on the basis of a general polar effect as may be seen from the values of/

of μ in column 4. In the case of the menthyl series the anthranilate is also exceptional.

It is well known, that although the electrical field in the immediate neighbourhood of a molecular charge may be very intense, it rapidly diminishes as the distance from the charge increases. In the case of p-substituted optically active benzoates we should thus expect that the substituent would be effective chiefly through the medium of the carbon chain separating it from the asymmetric centres; the same would be true to a great extent in the case of the m-substituted esters. An examination of o-substituted esters however should reveal the influence of the substituted dipole acting directly through space, as well as the effect propagated through the chain of atoms. We have just noted from TABLES III & IV that o-substituted octyl and menthyl-esters show an abnormal order of substituent influence, and RULE (loc. cit.) has suggested that the influence of certain substituents in the ortho-esters, as transmitted through the chain of atoms, is reversed by their influence propagated directly through space. He supposes that this reversal is associated with the peculiar orientation of the o-substituent with respect to the asymmetric complex, and to the fact that the spatial influence is here operating through a much shorter/

shorter distance. In the case of simple monatomic substituents such as Cl, I, and Br, this reversal is represented as follows:-



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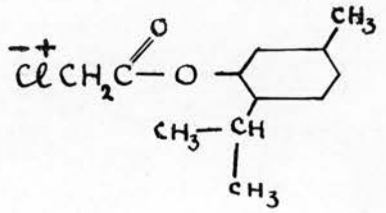


Investigations of a number of *l*-menthyl naphthoates indicates that the effects peculiar to o-derivatives in the benzene series are present to an even greater degree in the 1:8 or peri-compounds. McLEAN (J.C.S.,1931,686) considers that in *l*-menthyl hydrogen naphthalate the peri-substituents are in close proximity. He also shows that increase of temperature diminishes the high rotatory power of *l*-menthyl methyl naphthlate in dekalin solution, the value of $[M]_{5461}$ falling from -788° at 18° to -660° at 98°. This is interesting in view of the observation of L. EBERT (LeipzigerVortrage,1930,60) that increased molecular vibration leads to an increase in the mean distance between peri-groups. These facts, then, serve to support the opinion, that the effect of substituents in the ortho and peri-positions is chiefly a space effect.

THE ACTION OF SOLVENTS ON OPTICAL ROTATORY POWER.

A survey of the literature on the subject of solvent action in general reveals the fact that great use is made of the phenomenon of association to account for the features encountered. PICKARD & KENYON (J.C.S.,1914,830) examined a large number of esters of the general formula, $CH_3.CH.(O.CO.R)R'$, in solvents of various types and at varying temperatures, and made the important observation that in many cases the rotatory power of each ester was affected in a similar manner by a change of solvent. Now, the only atoms of marked polar character in the esters considered are the oxygen atoms contained in the carboxyl residue, and Pickard & Kenyon adopt the hypothesis that variations in solvent and temperature alter the degree of association of these esters, and consequently their rotatory power. Such association, however, they consider to be distinct from the ordinary process of polymerisation, probably involving no alteration in the mass of the optically active molecule, but rather a change in the valency of the oxygen atoms in the - COOR group. This rejection of association in its ordinary sense, as an explanation of the optical changes, is of interest in the light of more recent work by MISS E. B. SMITH (Thesis, Edinburgh, 1932) Here it is pointed out that ethers, like esters, are supposed/

supposed to undergo little or no association. Nevertheless, it was found that d - β - sec. - octyl methyl ether exhibited a higher rotation when dissolved in non-polar hydrocarbon solvents, than in the homogeneous state, a fact which the author attributes, in part at least, to the orientation of the ether molecules with respect to one another, and in such a manner as to cause a diminution of rotatory power, when the ether is in the homogeneous state. Here it would seem that the association that does exist escapes detection by the ordinary methods of molecular weight determination. The molecules may, in fact, be regarded as existing in a state of orientation which is not entirely fortuitous. Such orientation can, however, be traced by polarisation measurements.

An admirable illustration of the use to which association can be put in the elucidation of solvent action may be found in a thesis by MISS E. SMITH (loc.cit.) or in a paper by RULE, SMITH & HARROWER (J.C.S., at present in the press), from which the following table and discussion are taken.

TABLE/

TABLE

d - β - NITRO-OCTANE in SOLUTION ($c=4$. $t=20^\circ$. $l=2$.)

Solvent	C_6H_5OMe	C_6H_5Cl	C_6H_6	$C_6H_5NO_2$	C_6H_{14}	(None)
$[M]_{5461}$	$35{\cdot}5^\circ$	$31{\cdot}5^\circ$	$31{\cdot}1^\circ$	$27{\cdot}2^\circ$	$26{\cdot}9^\circ$	$(26{\cdot}7)$
$\mu \times 10^{18}$	1·25	1·52	0	3·90	0	-

"The rotatory powers of nitro-octane when dissolved in the above media seem at first sight to present few regularities; but they are readily interpreted in terms of the varying degrees of association of the active molecules with one another, or with the solvent. When nitro-octane is diluted with nitrobenzene, a medium very similar to it in polarity and molecular volume, it may be assumed that the electrical state of the active complex suffers little change, the nitro-octane complexes being merely converted into nitro-octane-nitrobenzene aggregates, to an extent dependent upon the degree of dilution. Hence there is only an insignificant change in rotatory power. An excess of a weakly polar solvent like anisole may be expected to dissociate the nitro-octane more or less completely at the concentrations employed, but it will not allow the rotation to rise to its maximum value owing to the/

the depressive influence of association between nitro and methoxyl groups. The addition of chlorobenzene operates in the same manner, but the solvent being relatively more polar than anisole, the depression in this case is greater, and the observed rotation lower, although not so low as that found in nitrobenzene. On this hypothesis, benzene, and to a still more noticeable extent, hexane, fails to effect any considerable disruption of the solute complexes at the concentration employed".

The effects in hydrocarbon solvents, traceable in the above table, are assumed to be due to the formation of definite association complexes. That such is probably the case may be shown by reference to molecular weight determinations. Nitro-ethane in cyclohexane ($c=3$) is stated by MASCARELLI & BENATI (Gazzeta,1909,39,2,652) to give a value for the molecular weight of 136, as against the theoretical value of 75; again AUWERS (Zeit.phys.,Chem.,1893,12,689) records a value of 94 for nitropropane (M.W.89) in benzene, at $c=4$, and 84, at $c=0{\cdot}3$.

Reference in the above discussion was made to molecular volume. This introduces another factor which may modify appreciably the interpretation of solvent effect in some cases. The influence of the size/

size of the solvent molecule is revealed by a comparison of the rotatory powers of ℓ-menthyl methyl naphthalate. (RULE & McLEAN, J.C.S., 1931, 678) in corresponding derivatives of four types of solvent.

Solvent	$[M]^{20^\circ}_{5461}$
CH_3I	-336°
C_2H_5I	-383°
C_6H_5I	-465°
$C_{10}H_7Br$	-553°

These four halides all have an electrical moment approximating to $1{\cdot}6 \times 10^{-18}$, and the observed variations in rotatory power are presumably due to the fact that the larger organic radical attached to a given dipole, the less frequently is the latter likely to come into the proximity of the polar groups in the optically active molecule. These same authors examined the above ester in the three isomeric butyl chlorides ($c = 4$). In this case there is no alteration in the molecular weight of the solvent molecules; the only change is that, owing to the structure of the compounds, the polar C.Cl group becomes increasingly screened as we pass from the normal, through the iso, to the tertiary chloride.

Solvent/

Solvent	$[M]_{5461}^{20^\circ}$
$CH_3CH_2CH_2CH_2Cl$	$-450{\cdot}1^\circ$
$(CH_3)_2CH\,CH_2Cl$	$-464{\cdot}0^\circ$
$(CH_3)_3C\,Cl$	$-511{\cdot}2^\circ$

In agreement with the above conclusions, the rotatory power was found to be lowest in the normal and highest in the tertiary isomeride, the behaviour of the latter being almost that of a non-polar liquid.

Not only may 'screening' be effected by the increasing bulk of the hydrocarbon radical, but also by variation in the volume of a substituent group in the solvent molecule. The parachor of the substituent group in question (cf. SUGDEN, The Parachor & Valency) supplies a means of estimating this volume.

RULE & MITCHELL (J.C.S.,1926,3202) prepared and examined the optically active d-β- octyl esters of methoxy-chloro-, bromo- and iodo-acetic acids in solvents C_6H_5X derived from the same parent hydrocarbon benzene. They found that the influence of substituents <u>in the ester group</u> in raising the rotatory power of d-octyl acetate fell into the order,

$I > Br > Cl > OMe > Me > H$

and this order was found to hold generally when the esters were examined in any one of the solvents employed. Passing from one solvent to another, they noticed/

noticed that the influence exerted by the various substituent groups in the solvent molecule upon the rotatory power of any single ester, gave the following sequence,

$Me > H > OEt > Cl > Br > I$

We see then, that the changes, produced by substitution in the optically active molecule, are almost the exact reverse of the changes resulting from identical substitution in the solvent molecule.

RULE & MITCHELL were of the opinion that efforts to determine the relationship between rotatory power and solvent influence would be attended by a greater measure of success if more use were made of solvent series, such as the above (C_6H_5X) in which the character of the molecule as a whole did not undergo any violent change from member to member.

Research was carried out along those lines and the advent of values for the dipole moments of various solvents, gave Rule a very definite method of testing his suggestion (J.C.S.,1927,58) that "polar groups, whether present in the asymmetric compound, or in the solvent, also exert an influence on neighbouring molecules, leading to corresponding changes in rotatory power".

The success that has attended the efforts of Rule and his co-workers in this direction is admirably shown/

shown by the following table extracted from a paper by RULE & McLEAN (J.C.S.,1931,674). The ester employed was ℓ-menthyl methyl naphthalate , which was selected on account of its extreme sensitivity to change of solvent.

TABLE

Solvent	$[M]^{20^\circ}_{5461}$	$\mu \times 10^{18}$ 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°	1·52
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
C_6H_{12}	-688°	0

Tables for solvents derived from Methane, Ethane and Naphthalene were also given and show the same type of regularity as the above. RULE & TOD (J.C.S.,1931, 1929) and MISS E. SMITH (Thesis, Edinburgh, 1932) showed/

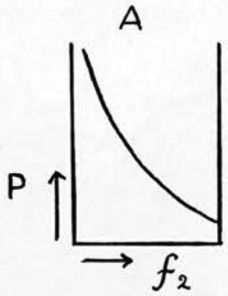
showed the same effect to obtain in ℓ-menthyl picryl ether and in several of the optically active compounds related to sec-β- octyl alcohol respectively, when examined in a series of related solvents .

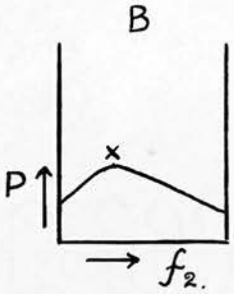
The most striking feature of the above series is the close relationship existing between polarity of solvent, as expressed by its dipole moment, and the rotatory power of the dissolved ester; the rotation being lowest in solvents of high dipole moments, and highest in those of zero dipole moment. Solvents of intermediate polarity fall, on the whole, into the order of their dipole values, but in this class, minor divergences from the aforementioned generalization are not infrequently encountered. Again, some optically active compounds (e.g. octyl bromide, and octyl chloride, RULE, SMITH & HARROWER, loc.cit.) show an alteration in rotatory power, with change of solvent, which is in the reverse sense to that encountered in the examination of ℓ-menthyl methyl naphthalate, i.e. the highest rotatory powers are exhibited in solvents of highest dipole moment, and vice versa.

RULE & McLEAN (J.C.S.,1931,686) advance the opinion that the observed effects are due to the influence of the solvent dipoles upon the internal field of the solute molecules acting either through deformation, or dipole association (see below)

DEBYE/

DEBYE (Polare Molekeln, p. 48) deduces characteristic polarisation-dissociation diagrams for an associated polar liquid on dilution with benzene or hexane. Thus nitrobenzene gave a curve of shape A, when progressively diluted with benzene, while ethyl alcohol exhibited a maximum in its polarisation curve, B





P = Polarisation

f_2 = Mole fraction of polar substance in hydrocarbon solvent.

In a compound, the polarisation curve of which assumes the form shown in A, we may suppose that the molecules in the homogeneous liquid undergo dipole association so as to neutralise each other's field thus, $\begin{pmatrix} + & - \\ - & + \end{pmatrix}$. Dilution of the solute under consideration leads to an increase in the proportion of molecules existing in the free state; the polarisation rising correspondingly. When we consider type B however, Debye assumes that with rising concentration, the alcohol molecules first orient themselves in the manner $(-\,+)(-\,+)$ which actually results in an increase in the polarisation; but that in still more concentrated solutions two, or more, molecules are arranged into aggregates of a different type possessing a lower polarisation. Hence a maximum value of the/

the polarisation will be obtained at some point X. By a simple calculation (a modification of which will be described in the discussion of this thesis) Debye, in the above diagrams, eliminates the contribution due to the non-polar liquid present, and is able to follow diagramatically, the change in the polarisation of the polar compound as it becomes progressively dissociated. In a similar manner the rotatory powers of *l* -menthyl methyl naphthalate, as determined in mixtures of polar and non-polar liquids, were corrected approximately for the rotation contributed by the non-polar component (RULE & McLEAN, J.C.S.,1931,681). For mixtures made up of a non-polar medium and nitrobenzene or ether, it was found that the rotation-dissociation diagrams thus deduced, (representing the change in rotation as the polar solvent became progressively dissociated) closely resembled those quoted by Debye for the corresponding variation in polarisation. Here also an increase in polarisation was accompanied by a fall in rotatory power, and the form of the polarisation curve proved to be the inverse of that obtained for the optical rotation. With ethyl alcoholic mixtures however, the agreement was less exact, and the result was regarded as inconclusive (RULE & McLEAN, loc,cit.)

Extending/

Extending this type of investigation to other alcohols, these same authors (J.C.S.,1932,1400) examined the various effects produced by n-propyl, n- and iso- butyl alcohols, and iso- and tert-amyl alcohols and give diagrams showing the polarisation curve of the alcohol in question, plotted on the same abscissae as the curve representing the rotatory power of ℓ-menthyl-methyl naphthalate in alcohol-benzene mixtures of varying composition. Here again it was found that changes in the polarisation curves are reflected in the variations in the rotatory power of the ester when dissolved in the corresponding benzene-alcohol mixture, and corrected for the rotation due to the benzene present: a maximum in the polarisation corresponding to a minimum in rotatory power. This agrees with the relationship already established in connection with mono-substituted hydrocarbon solvents, where an increase in polarity leads to a diminished rotation.

MISS SMITH (loc.cit.) records an interesting examination of octyl alcohol. Here any irregularities in its degree of polarisation brought about by dilution with a non-polar medium should be revealed directly in the polarimetric measurements carried out with a system of two components. Using n-hexane as the solvent and varying the concentration of the octyl alcohol/

alcohol, a graph was obtained which showed that the rotation varied irregularly with the concentrations.

Attacking the problem from another angle, it should be possible to correlate the direction of the optical change which occurs as increasingly polar solvents are employed, with that produced by a change in the concentration of the active solute in a given non-polar medium. If the rotatory power of the active compound is displaced in a certain direction by solution in a highly polar solvent, then, a displacement in the same sense should be observed when the compound is examined at rising concentrations in a non-polar solvent. In both of these cases, the change should lead to an increased degree of dipole association. In the one case we have a rise in the degree of association (or molecular orientation) due to an increase in the polarity of the solvent medium, and in the other case a similar rise due to the increased proximity of the polar solute molecules in the non-polar medium. Hence the optical changes should be in the same direction. An agreement of this kind was observed by Miss Smith for the octyl derivatives which she examined although the strongly polar nitro-octane was somewhat irregular. The last named compound has been mentioned on page 22

It/

It has been suggested (RULE & McLEAN, J.C.S.,1931 687) that the work of Rule might be correlated with that of KUHN (Trans. Far.Soc.,1930,293) through the medium of SCHEIBE'S researches (Ber.1926,59,2619) on ketones in the presence of different solvents. Scheibe observed a progressive displacement of the typical ketonic band towards the far ultra violet region, as the polarity of the solvent increased. If the rotation, for example, of an active ketonic derivative is governed by the position of the band, this change should lead to a progressive alteration in the rotatory power. Kuhn's original work upon the relationship of the rotatory power and the position, and circular dichroism of the absorption bands in the spectrum of the molecule, has been supplemented by later considerations,(KUHN, STEREOCHEMIE, FREUDENBERG 1932, p.417) which indicate that the change in rotation may in many cases, result from an alteration in the anisotropic properties of the band, without any appreciable change in its position.

With regard to the effect of temperature upon rotatory power of solutions of optically active compounds, there is but little in the literature which is of a sufficiently general character to warrant inclusion at this juncture. However, PATTERSON, DUNN, BUCHANAN & LOUDON (J.C.S.,1932,1715) are prompted, as/

as a result of their investigations, to generalise in the following manner. In solvents which confer a high rotational value, the rotatory power of an optically active compound should diminish, or else increase only slowly with rise of temperature; whereas in solvents of depressing influence, the rotation should increase fairly rapidly. Thus they show that for solutions of camphor in sulphuric acid, a solvent which has a marked effect in depressing the rotatory power of camphor, a rise of temperature results in an increase of rotation (in an absolute sense). PATTERSON & LOUDON (J.C.S.,1932,1731) find a similar effect, using α -chlorocamphor. In benzene, which has a depressing effect upon the rotatory power of this substance, it was found that an increase of temperature produced a pronounced rise in rotatory power. In ethylene bromide, however, which exhalts the rotation, increase of temperature resulted in a rise of only a few degrees in the rotatory power. Similar changes have been observed for ethyl tartrate by T. S. PATTERSON, (J.C.S.,1908,1843) and by PATTERSON & McDONALD (J.C.S.,1909,321).

With a view to obtaining confirmation and further information of the various hypotheses presented in this introduction, six *l* -menthyl esters of o-substituted benzoic acids were subjected to a detailed investigation/

investigation. These six esters were examined individually in series of solvents derived from methane and benzene. A further attempt to correlate rotatory power with the polarisation of an hydroxylic component was made in the case of *l*-menthyl salicylate in n-hexane. Rotation-dilution graphs were drawn for all the esters. Finally, an investigation was undertaken with a view to determining the effect that alteration of temperature had upon the rotatory powers of those esters in solution in polar and non-polar solvents.

Several of the *l*-menthyl o-substituted esters used in this work were first prepared by COHEN, who examined their activity in the homogeneous state for the sodium line only (cf. J.C.S.,1914,1892). Later, an investigation of some of these esters was made by KENYON & PICKARD (J.C.S.,1915,35). In that paper, values for the rotatory powers are recorded, not only in the homogeneous state, but in solution also; solvents of various types being employed. The effect on the rotatory power occasioned by an alteration of temperature, and by the utilisation of light of different wave-lengths, is also included in their results.

PREPARATION of ℓ-MENTHYL o-NITROBENZOATE.

A B.D.H. sample of 2-nitrobenzoyl chloride was available. Equal weights of this and ℓ-menthol were heated on an oil bath after the method of COHEN & ARMES (J.C.S.,1905,87,1190). The ester was purified by crystallisation from alcohol, after which it gave m.p. 62·5°C and $[M]^{20^{\circ}}_{5461} = -703{\cdot}1^{\circ}$ in benzene ($c = 4{\cdot}008$) COHEN & ARMES, (loc. cit.) quote m.p. 62 - 64°.

Another sample of the ester gave :-

$[M]^{20^{\circ}}_{5461} = -703{\cdot}4^{\circ}$ in benzene ($c = 4{\cdot}232$)

While KENYON & PICKARD, (J.C.S.,1915,107,56) quote:-

$[M]_{5461} = -702{\cdot}3^{\circ}$ in benzene (appx. 5% solution).

PREPARATION of l-MENTHYL HYDROGEN PHTHALATE.

A slight modification of the method of ARTH (Ann. Chim. Phys. 6, 7, 485) was here employed. Molecular proportions of phthalic anhydride and l-menthol were heated together, in a flask fitted with a ground-in glass condenser, on an oil bath maintained at 110°C, for 36 hours. When cold, the contents of the flask were taken up in ether and transferred to a separatory funnel. Water was added and then dilute NaOH until an alkaline reaction was shown after vigorous shaking. The ether fraction was separated off. More ether was then added and the contents of the separatory funnel thoroughly agitated again. The ether layer was allowed to separate out and the aqueous layer tapped off. This process was repeated two more times. The water layer now contained the Na salt of the l-menthyl hydrogen phthalate, which was then converted into the free acid, by the addition of excess dilute HCl. The free acid was extracted with ether until exhausted. The combined ethereal extracts were thoroughly washed with water, separated and evaporated down to dryness. The resulting solid was recrystallised twice from petroleum ether and dried in a vacuum desiccator. M.p. 111·5°C. Yield of purified ester was 62·5% of theoretical.

ARTH/

ARTH (loc. cit.) quotes m.p. 110°C, while COHEN WOODROFFE, and ANDERSON (J.C.S., 1916,109,232) record m.p. 111 - 112°C.

The rotation of the ester was found to be :- $[M]^{20^\circ}_{5461} = -345\cdot5^\circ$ in chloroform (4% concentration) KENYON & PICKARD (J.C.S.,1915, 107, 54) quote -342·8° in 5% chloroform solution.

In connection with this preparation it is interesting to note that PICKARD & LITTLEBURY (J.C.S.,1912, 101,118) who prepared their ester from l-menthol and the anhydride point out that when crystallised from acetic acid the ester has a melting point of about 110°C. If, however, it be kept for some days in contact with the mother liquor, large prismatic needles are formed, this stable variety melting at 122°C. Both varieties have $[\alpha]_D = -91\cdot43^\circ$ in 5% $CHCl_3$ solution.

PREPARATION of l -MENTHYL SALICYLATE.

This ester was prepared by treating the acid chloride of salicylic acid with l -menthol. A number of references to salicylyl chloride are to be found in chemical literature. MEYER (Monatsh.,1901,22,430) failed to obtain any of the acid chloride by allowing salicylic acid to interact with thionyl chloride, although Mc MASTER & AHMANN (J.A.C.S., 1928,501,148.) record a small yield by this method. According to the CHEMISCHE FABRIK von HEYDEN (Cent.,1901,2,518.) salicylyl chloride may be prepared from sodium salicylate and benzene sulphonic chloride, a statement which was later contradicted, from this source and also by KOPETSCHNI & LADISLAUS (Ber.,1914,37,236). The last named workers, however give directions for the preparation of the acid chloride from sodium salicylate and thionyl chloride, and their method with slight modifications was employed here. The reagents used were sodium salicylate, powdered up finely and dried for eight hours at 120°C: purified pyridine (B.D.H.) was dried with stick KOH and fractionated: l -menthol (B.D.H. recryst.): and thionyl chloride(B.D.H. purified).

One molecular proportion of pyridine was added slowly at room temperature to excess thionyl chloride contained in a wide necked flask fitted with a cork and condenser. The reaction was vigorous at first and/

and all the sodium salicylate dissolved readily. The flask was next allowed to stand for half an hour at room temperature when an opalescent jelly with a bluish tint was obtained. The excess $SOCl_2$ was then removed by heating the flask on an oil bath at 60°C under diminished pressure. The contents of the flask were next thoroughly extracted with petroleum ether (b.p. 60 - 80°) and the ethereal solution immediately filtered from sodium chloride at the pump with as little loss of time as possible. The clear solution resulting was transferred to a distilling flask fitted with an air leak admitting dried air and the petroleum ether was removed by gently warming the flask under reduced pressure, when a faintly yellow liquid of characteristic odour was obtained. Yield, 88% of theoretical. KOPETSCHNI & LADISLAUS, (loc. cit.) quote a yield of 80 - 90% by this method. Mc MASTER & AHMANN quote a 36% yield using thionyl chloride and the sodium salt of salicylic acid and describe their product as being a white crystalline substance melting at 18°C to a colourless syrupy liquid which distils at 90°/11 mms. The salicylyl chloride obtained as described above was treated without further purification with a mixture of *l*-menthol (1 mol.) and pyridine (3 mols.) in a flask which was then heated over an oil bath. A precipitate of pyridine hydrochloride soon appeared and/

and the heating was continued for four and a half hours at 120°C. The reaction mixture once cold, was thoroughly washed with water to remove pyridine hydrochloride and then neutralised with $NaHCO_3$ solution and again washed with water. The excess menthol was removed by vigorous steam distillation and the ester was then extracted with petroleum ether (b.p. 60-80°) The extract was dried over freshly ignited sodium sulphate and finally fractionated, 50 grms of a pale yellow distillate being obtained from 80 grms. of sodium salicylate. RULE & Mac GILLIVRAY (J.C.S.,1929, 405) quote a 60% yield of pure ester. The ester at this stage showed a value of $\alpha^{20^\circ}_{5461} = -124{\cdot}2^\circ$ ($l = 1$). It was purified by dissolving it in warm methyl alcohol (cf. RULE & Mac GILLIVRAY, loc. cit.) and cooling to -18°C in a freezing mixture of ice and salt, when the ester layer which separated was removed, taken up in petroleum ether and washed with water. After drying over Na_2SO_4 it was refractionated into three portions. The middle fraction boiled at 175°/4 mms. and gave $\alpha^{20^\circ}_{5461} = -124{\cdot}8^\circ$ (1 dcm. tube). This was refractionated and the middle portion collected. After two more such treatments the rotation of the ester remained constant at $\alpha^{20^\circ}_{5461} = -125{\cdot}74^\circ$ ($l = 1$) whence $[M]^{20^\circ}_{5461} = -331{\cdot}6^\circ$ for the homogeneous liquid ($d^{20^\circ}_{4^\circ} = 1{\cdot}0467$.) It was a colourless, viscous, odourless/

odourless oil having a boiling point of $140^{\circ}/0{\cdot}05$ mms. RULE & Mac GILLIVRAY loc. cit. record $156^{\circ}/0{\cdot}5$ mms. and $[M]^{20^{\circ}}_{5461} = -333{\cdot}2^{\circ}$ in the homogeneous liquid. The ester so prepared was considered pure and was utilised for the examinations of rotatory powers in the various solvents.

With a view to improving the yield of the ester as prepared above three further experiments were carried out. The salicylyl chloride was treated with quantities of *l*-menthol ranging from 1½ to 3 mols. and the period of heating ranged from four to seven hours at temperatures of 100° to 140°. The longer period of heating and the higher temperature gave a crude product of somewhat lower rotational value ($\alpha^{20}_{5461} = -123{\cdot}5^{\circ}$ in a 1 dcm, tube) while the yield was not improved.

It was thought that an adaptation of the sodium menthoxide process (Cf. VERLEY, Bull. Soc. Chim. 1927 41,802) might yield the ester in more readily purifiable form and possibly in better quantity than the above method. The success that attended the efforts of RULE, MILES & Mac GILLIVRAY (J.C.S., 1929 2274) (cf. also RULE & Mac GILLIVRAY J.C.S. 1929, 407) in preparing *d* - sec.β-octyl salicylate by this method gave encouragement to the belief. Accordingly experiments, eight in number, were performed towards this end.

The/

The amounts of sodium used varied from 0·05 atomic proportions to 0·7 atomic proportions and of *l*-menthol from one to two moles. Temperatures ranging from 110° to 170° and periods of heating of from one half to forty hours were employed. Some of the experiments were performed in a current of nitrogen, others simply in a stream of dry air. Ordinary distilling flasks or Wittmar flasks and receivers were used.

The general procedure employed is given below. The freshly cut sodium was dissolved in the *l*-menthol at as low a temperature as possible. The methyl salicylate, previously dried was added to the flask containing the sodium menthoxide and a current of dry air or nitrogen passed through the solution. (In the experiments where nitrogen was used the dissolving of the Na in the menthol was conducted also in a current of N_2 in order to minimise possible oxidation of the Na metal). The passage of the air or nitrogen through the solution removes the methyl alcohol as it is formed and thus enables the reaction which is a balanced one, to be displaced as far as possible, in favour of the menthyl ester. The receiving flask was cooled in ice and the reaction allowed to proceed until the calculated volume of methyl alcohol had collected in the receiver. The reaction mixture was then neutralised with HCl, washed with water and then extracted/

extracted thoroughly with petroleum ether. This extract was dried over Na_2So_4 and the solvent taken off under reduced pressure, the residue was then distilled under reduced pressure. Excess menthol was first distilled off and the ester was collected in a separate receiving flask.

The best results were obtained using the following quantities :-

l-Menthol	65 grams.
Sodium	0·8 "
Methyl Salicylate	52 "

Here the heating was continued for twenty hours at 150°C in a current of N_2 and in a Wittmar flask. 63 grams of a faintly yellowish oil were obtained having $\alpha^{20^\circ}_{5461} = -119{\cdot}2^\circ$ (1 dcm. tube). The value is thus considerably lower than that of the crude product from the acid chloride preparation, which gave $\alpha^{20^\circ}_{5461} = -124{\cdot}2^\circ$. The above was fractionated into three portions, the middle portion having b.p. 180°/1·5 mms. and $\alpha^{20^\circ}_{5461} = -119{\cdot}9^\circ$ (1 dcm. tube). This fraction was purified by dissolving, as in the acid chloride method in methyl alcohol and refractionating. The middle fraction had b.p. = 175 - 178°/2 mms. and $\alpha^{20^\circ}_{5461} = -122{\cdot}4^\circ$ (1 dcm. tube). This on being treated again with methyl alcohol and refractionated boiled at 179°/3 mms. and gave a value of $-124{\cdot}2^\circ$ for $\alpha^{20^\circ}_{5461}$ in a 1 dcm. tube. By this time however, the yield was too small to justify further purification and the method was, for the time being, abandoned.

THE PREPARATION of l-MENTHYL BENZOATE.

This ester was prepared by heating together the calculated amounts of l-menthol and benzoic acid after the method of ARTH (Ann. Chim. Phys. 6. 7. 479), an ordinary round bottomed Pyrex flask however, being substituted for the sealed tube used by that worker. A fine crystalline colourless substance was finally obtained. M.p. 54°C, $[M]^{20°}_{5461} = -282.1°$ in benzene (c = 4·000).

Much of the work on this ester was done on a purified sample, very kindly supplied by Dr RULE, who utilised the acid chloride method in its preparation. His sample melted at 54°C and had $[M]^{20°}_{5461} = -280·5°$ in benzene, c = 5·032. (J.C.S. 1929, 403). KENYON & PICKARD (J.C.S., 1915,107,52) record $-276·5°$ for $[M]$gr. in benzene, 5% solution. COHEN & DUDLEY (J.C.S., 1910,97,1750) quote a melting point of 54°C for their ester prepared from benzoyl chloride, while PICKARD & LITTLEBURY (J.C.S.,1912,101,119) found that their ester melted at 55 - 56°C.

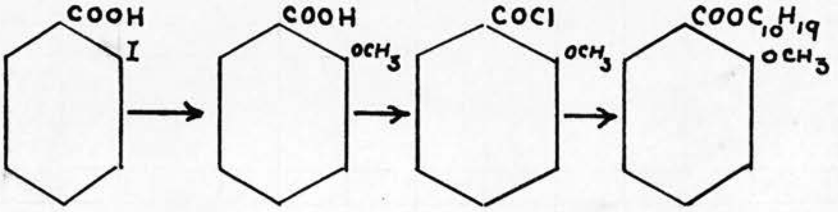
PREPARATION of *l*-MENTHYL o-CHLOROBENZOATE.

A pure sample of 2-chlorobenzoic acid prepared by Dr RULE was used as the starting point of this preparation. The acid was treated with excess thionyl chloride in a flask fitted with a ground-in condenser. The flask was gently warmed on an oil bath until the reaction began, after which the temperature was gradually raised to 75°C and then maintained at that temperature for an hour and a half. The excess $SOCl_2$ was removed under reduced pressure and an excess of *l*-menthol was added to the flask which was next heated on an oil bath at 130°C for two hours. The contents of the flask were neutralised with Na_2CO_3 solution and the excess menthol removed by steam distillation. The ester was isolated from a chloroform extract of the acidified residue, after dehydration over $CaCl_2$ and removal of the solvent under reduced pressure. The ester which is a colourless oil was next distilled under diminished pressure, a little of the solid acid passing over first (Compare COHEN & BRIGGS, J.C.S.,1903,83,1213). On redistilling, b.p. 218 - 220°/30 mms., the ester still showed signs of slight impurity and gave a value of -195° for its molecular rotation at 20°C, using the Na_D line and the compound in the homogeneous state. The ester was therefore taken up again in $CHCl_3$ and shaken thoroughly with/

with NaOH solution and then with water several times. It was then dried over $CaCl_2$ and filtered; the solvent was removed under diminished pressure and the residual liquid distilled in vacuo, when it came over quite steadily and without any separation of solid, b.p. 219°C/30 mms.
$[M]_D^{20°}$ = -198°. When redistilled it gave a boiling point of 204°C/10 mms. and $[M]_D^{20°}$ = -197·9°. Yield:- 68% of theoretical (calculated on o-chlorobenzoic acid)

PREPARATION of *l* -MENTHYL o-METHOXYBENZOATE.

Starting with o-iodobenzoic acid the course of the reaction may be represented as follows :-



a) Preparation of o-iodobenzoic acid.

A solution of sodium nitrite (50 grms. in 100 c.c. H_2O) was slowly added to a solution of anthranilic acid (80 grms.) in dilute H_2SO_4 with constant stirring; the temperature of the reaction mixture being kept down to 0°C by means of a freezing mixture of ice and salt. When excess of the nitrite, as indicated by starch iodide paper, had been added, a solution of 150 grms. KI in 250 c.c. H_2O was then slowly poured in, with constant stirring, and the whole then allowed to stand over-night: after which it was heated on a steam-bath until effervescence ceased, allowed to cool and filtered at the pump. The solid remaining was washed with warm sodium thiosulphate solution and then with water. The acid was next dried; firstly at the pump, and then on a porous plate, and finally recrystallised from boiling water, filtering whilst hot. M.p. 161°C. The yield was 90 grams. COHEN & RAPER (J.C.S.,85, 1272,1904) quote m.p. 162 - 163°C for their purified acid/

acid prepared by the above method and a weight of iodo acid about equal to the weight of anthranilic acid started with. BARNETT (Thesis, Edinburgh 1932) quotes a melting point of 161°C and a yield of 70% for the iodo acid prepared in the same manner.

b) Preparation of o-methoxybenzoic acid.

A method worked out by BARNETT, loc. cit., was used for this stage of the preparation. 90 grams of o-iodo benzoic acid were added to a solution obtained by dissolving 16·8 grams of sodium metal in 600 c.c. of methyl alcohol. Copper bronze was added to the mixture heated under a reflux condenser for eight and a half hours at 115°. The solution was then filtered at the water-pump, a deep amber coloured filtrate, strongly alkaline in reaction, being obtained. Some of the alcohol was next removed by heating on the steam-bath. To the well cooled solution an excess of HCl was added and the separated crystals were then removed by filtration. The crude acid, after drying, was recrystallised from ligroin from which solvent beautiful colourless fine needles were deposited. M.p. 101·4°C. Yield of o-methoxybenzoic acid was 91% of theoretical. BARNETT, loc. cit. quotes m.p. 99-100°, while COHEN & DUDLEY (J.C.S., 1910, 97, 1739) records 99 - 101° and BROMWELL (Amer. chem. jour. 1897, 19, 577) gives 98·5 - 99°.

c) Preparation of o-methoxy benzoyl chloride.

The o-methoxy benzoic acid and PCl_5 were heated in a flask under a reflux condenser for one hour at 125°. The $POCl_3$ produced was then removed as far as possible in a current of dry air and under diminished pressure. No attempt was made to distil the acid chloride which was converted directly into the -menthyl ester. Yield of undistilled acid chloride was 92% of theoretical.

d) Preparation of ℓ-menthyl o-methoxybenzoate.

The acid chloride above was heated with an equal weight of ℓ-menthol after the method of COHEN & DUDLEY loc.cit. The reaction began at about 60° and was completed by heating for two hours at 130°. The product was steam distilled to remove excess ℓ-menthol and then digested with a solution of Na_2CO_3 to remove free acid, after which it was extracted thoroughly with petroleum ether. The combined extracts were evaporated down and the ester recrystallised from alcohol. This was found to be the most suitable solvent, although the ester was much too soluble even in this medium for economical purification, and consequently the yield was poor. COHEN & DUDLEY, loc.cit. record difficulty in getting the ester to crystallise out from any solvent. No such difficulty/

difficulty was experienced in the present case, the ester crystallising out readily from a cooled alcoholic solution when seeded with a crystal of the ester. The ester was decolourised by dissolving it in warm alcohol and adding animal charcoal, the mixture being boiled gently on a water bath under a reflux condenser for twenty minutes. The solution was then filtered and the ester allowed to crystallise out. After three more crystallisations from alcohol, the value of $[M]^{20^\circ}_{5461}$ remained constant and the ester was then considered pure. M.p. 42°C. COHEN & DUDLEY, loc.cit. quote 42°C, and give a value of 1·045 for $d^{20^\circ}_{4^\circ}$ and $-148{\cdot}2^\circ$ for $[M]^{20^\circ}_{D}$ the ester being in the homogeneous state. In the present instance, the value found for $d^{20^\circ}_{4^\circ}$ was 1·039. Unfortunately at the time of this preparation no polarimeter for taking readings for the Na_D line was available, and so no direct comparison with COHEN & DUDLEY'S value could be made. A reading however, taken for the Hg yellow line gave a value for $[M]^{20}_{5780}$ of $-158{\cdot}5^\circ$ in the homogeneous state, while in benzene solution ($c = 4{\cdot}002$) a value of $-211{\cdot}6^\circ$ was obtained for $[M]^{20^\circ}_{5461}$

A second preparation of this same ester by the above method gave a product of m.p. 42°C and of $[M]^{20^\circ}_{5461}$ $-211{\cdot}0^\circ$ in benzene ($c = 4{\cdot}000$).

In some experiments thionyl chloride was tried as the reagent in the conversion of the o-methoxy benzoic acid into the acid chloride. An excess of $SOCl_2$/

$SOCl_2$(110 grams) was slowly added to 33 grams of o-methoxy benzoic acid contained in a flask fitted with ground-in condenser. The flask was warmed gently on an oil-bath and the reaction allowed to proceed gently for three hours. The excess $SOCl_2$ was then removed under reduced pressure and the crude acid chloride weighed. Yield 35 grams. Without attempting to purify this acid chloride further, 40 grams of *l*-menthol were added and the flask gently warmed on an oil-bath. The reaction set in about 42°C and HCl was evolved briskly. The heating was continued for two hours at 130°C. The excess menthol was removed by steam distillation and the solution neutralised with sodium carbonate solution. It was then thoroughly extracted with petroleum-ether and recrystallised as before from alcohol. A fine colourless crystalline compound m.p. 46·7°C was obtained. This gave a value of - 209° for $[M]^{20°}_{5461}$ in benzene (c = 5·000). The product was then distilled under reduced pressure, b.p. 200°C/11 mms. COHEN & DUDLEY loc.cit., quote 222 - 226°/12 mms. After distillation the compound melted at 48·8°C and gave a rotatory power, $[M]^{20°}_{5461}$ of - 209° as before in in benzene.

Qualitative analysis showed the presence of chlorine in this ester. Further, on hydrolysis with alcoholic KOH, an acid was obtained. This when crystallised twice from petroleum ether, melted over a range/

range of 83 - 89°. This acid was evidently contaminated with chloro-benzoic acid as qualitative analysis showed the presence of chlorine. The pure methoxy acid melts at 101°C. A second attempt to prepare the acid chloride using thionyl chloride was made, the heating of the acid and thionyl chloride being for two hours on an oil-bath maintained at 50 - 60°C. The acid chloride obtained was distilled after removal of the excess thionyl chloride. It boiled at 135 - 142°/15 mms. (FISCHER & SLIMMER, Ber., 1903 36. II, 2585., who also prepared their acid chloride by thionyl chloride quote a boiling point of 145°/17 mms.) As before the acid chloride was treated with *l*-menthol and the resulting ester recrystallised from alcohol. Qualitative tests again revealed the presence of chlorine in the final product. The reaction was therefore not further investigated.

PURIFICATION OF SOLVENTS.

1) METHYL ALCOHOL. This was purified by the method of BJERRUM & ZECHMEISTER (Ber. 1923, 56, 897) 1 litre of the alcohol was mixed with about 10 grms. of clean magnesium turnings (previously washed with ether and thoroughly dried) and allowed to stand in the 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 fraction being rejected. A middle fraction, b.p. 65°C was collected in receiver fitted with a $CaCl_2$ tube.

2) BENZONITRILE. The B.D.H. product was dried over freshly ignited Na SO - filtered and partially frozen out and the crystalline portion, (m.p. -12·9°C) was dried again and distilled under diminished pressure in a Wittmar flask. A middle portion of b.p. 68°C/10 mm. was collected as a colourless liquid.

3) TOLUENE. The B.D.H. product was dried with metallic sodium wire for three days. The liquid was then decanted off and fresh sodium wire put in and the whole refluxed for forty minutes,

after/

after which the liquid was directly fractionated over a twelve bulb column. A middle portion b.p. 110°C was collected.

4) METHYLENE DICHLORIDE. The B.D.H. product was washed with water and then dried over $CaCl_2$. It was then filtered and fractionated and a colourless middle fraction, b.p. 40·4 - 40·6°C. collected.

5) CARBON DISULPHIDE. Aytoun, Scott & Co's carbon disulphide was shaken with fresh Hg. until no further darkening of the metal took place. It was next separated, dried over $CaCl_2$, filtered and fractionated as a colourless liquid, b.p. 46 - 46·2°C.

6) BENZENE. B.D.H. benzene "Extra Pure" was dried over $CaCl_2$, filtered and partially frozen out the crystalline portion being re-dried and fractionated and a middle portion b.p. 80 - 80·1°C. was utilised.

7) HEPTANE. B.D.H. technical heptane was shaken successively with conc. H_2SO_4, alkali and finally water. Dried over $CaCl_2$ and fractionated over 6 bulb column. B.p. 98 - 98·5°C.

8) HEXANE. B.D.H. product ("free from aromatic hydrocarbons") was dried and fractionated, b.p. 68·5 - 68·9°C.

9) PENTANE. B.D.H. pentane was treated in similar manner to heptane. B.p. 35 - 37°C.

10/

10) **METHYL IODIDE.** Aytoun, Scott & Co.'s purified methyl iodide was shaken with dilute NaOH and then with water. It was dried over $CaCl_2$ and fractionated and a colourless fraction b.p. 42·7 - 43°C collected. Kept in a dark bottle over a small quantity of clean Hg.

11) **ACETIC ACID.** Kahlbaum's 100% acid was partially frozen out and the liquid fraction (about $^1/_3$) was discarded. The solid remaining (m.p. 16°) was then fractionated. B.p. 118° - 118·2°C.

12) **CHLOROFORM.** The product of Macfarlane & Co. was dried and fractionated. A middle portion b.p. 61 - 61·1°C was collected.

13) **CARBON TETRACHLORIDE.** A sample was obtainable which had already been purified. It was re-dried and fractionated. B.p. 77·6 - 77·8°C.

14) **BENZALDEHYDE.** The B.D.H. product was washed with Na_2CO_3 solution, dried over Na_2SO_4 and fractionated under reduced pressure rapidly, care being taken to avoid contamination with air as far as possible. This product was then freshly refractionated for each rotation in which it was employed. B.p. 179 - 179·2°C.

15) **ANILINE.** Kahlbaum's aniline "free from sulphate" was dried and fractionated. A colourless liquid - b.p. 182·9 - 183 was thus obtained.

16)/

16) ANISOLE. B. D. H. anisole was used. It was dried and fractionated. A middle fraction, b.p. 153·8° was colourless and gave no phenol reaction.

17) CHLOROBENZENE. The B. D. H. product was washed with alkali and then with water, dried over $CaCl_2$ and fractionated - b.p. 131·6 - 132°C.

18) BROMOBENZENE. The B. D. H. product was treated as the chlorobenzene. B.p. 154·8 - 155·2°C.

19) IODOBENZENE. B. D. H. iodobenzene treated in same manner as bromobenzene. B.p. 72·5 - 73°C./14 mm.

20) CYCLOHEXANE. The B. D. H. product was dried and partially frozen out. The solid fraction was re-dried and fractionated. M.p. 4°C. B.p. 80·1 - 80·3°C.

21) MESITYLENE. Merck's mesitylene was dried over $CaCl_2$ and fractionated, b.p. 164-165°C.

22) NITROMETHANE. B. D. H. nitromethane washed, dried and fractionated was used. A colourless liquid b.p. 100·8 - 101·1°C. was obtained.

23) ACETONITRILE. B. D. H. acetonitrile, dried and fractionated gave a colourless liquid, b.p. 80·7 - 81·4°C.

24) ACETALDEHYDE. Aytoun, Scott & Co's acetaldehyde was dried over $CaCl_2$, boiled over succinic acid to remove basic impurities and fractionated. B.p. 20·8°C.

25) NITROBENZENE. The B. D. H. product was fractionated and the portion of b.p. 190 - 190·4 was partially frozen out. The crystalline portion (f.p. 5·7) was melted, dried and fractionated under diminished pressure. B.p. 90 - 91°C/15mm.

26) m-DINITROBENZENE. Prepared in laboratory and purified by crystallisation from alcohol. Colourless crystals, m.p. 89·8°C.

27) p-DINITROBENZENE. The B. D. H. product was purified by repeated crystallisation from alcohol. Almost colourless solid of m.p. 172·5°C.

28) DEKALIN. (Decahydronaphthalene) The B. D. H. product was dried and fractionated, b.p. 191·6 - 192·4°C.

29) o-DICHLOROBENZENE. The B. D. H. product was cooled to -20°C. when a small amount of crystalline substance (possibly p-dichlorobenzene) deposited and was rapidly filtered off at the pump. The filtrate was dried over $CaCl_2$ and fractionated under reduced pressure, b.p. 60 - 61°C/11 mm.

30) p-DICHLOROBENZENE. B. D. H. p-dichlorobenzene was repeatedly re-crystallised from alcohol until the product had a constant sharp melting point. Colourless crystals, m.p. 54°C.

31)/

31) n-BUTYL ALCOHOL. The B.D.H. product was dried for several days over freshly ignited Na_2SO_4, refluxed for several hours with freshly cut calcium and then fractionated. B.p. 117·6 - 117·8°C.

THE DETERMINATION of ROTATORY POWER.

All the rotational values quoted in this research were determined on one of two polarimeters. One was a Hilger instrument used in conjunction with a Kelvin, Bottomley and Baird mercury vapour arc lamp, the other a Schmidt and Haensch instrument was used in the earlier part of the work to take readings for the Na_D and other lines. Later, this Schmidt and Haensch instrument was fitted with a "Doppel-Monochromator" which is briefly described elsewhere in the thesis. The mercury green line ($\lambda = 5461$ Å.U.) was used exclusively with the Hilger polarimeter and readings could then be repeated, under optimum conditions, with an accuracy of $0{\cdot}01^\circ$ in the observed α .

The length of the polarimeter tube used varied with the requirements of the various solutions to be examined, but the bulk of the values quoted were taken in one or two decimeter narrow bore tubes, which enabled the solution of ester to be made up in a 5 c.c. graduated flask. The larger tubes required an 8 or 10 c.c. flask. The polarimeter room was maintained by means of radiators and efficient ventilators, at a temperature of $20^\circ C$ within a range of $\pm 0{\cdot}5^\circ C$. In the examination of temperature effect, water-jacketed polarimeter tubes of Schmidt and Haensch were/

were employed , the bulb of a thermometer dipping into the solution under observation. Water driven by small rotary impellers from two thermostats was circulated through these jacketed tubes for a considerable period before the actual reading was taken. By altering the regulators of these thermostats, a range of temperature of approximately 20 - 60° could be obtained in the one and of 50 - 90° in the other. A layer of medicinal paraffin largely prevented evaporation of water from these vessels. The few readings taken below 20° were obtained by circulating water from the main water pipes through the jacketed tube.

Where it was desired to compare molecular rotations all taken at the same temperature the formula:- $[M]_{\lambda}^{t^\circ} = \frac{\alpha \times M}{l \times c}$ was used. Here α is the angle of rotation. M is the Molecular weight of the substance under consideration, l is the length of polarimeter tube used, c is the number of grams of substance contained in 100 c.c of the solution, t° is the temperature and λ is the wavelength of the light employed. Where however the temperatures at which the various determinations were made differed appreciably, as in the experiments showing temperature effect, then the more general formula :-

$[M]_{\lambda}^{t^\circ} = \frac{\alpha \times M}{l \times p \times d}$ is utilised. Here α, M, l, t, and λ represent the same as in the above first formula, while p represents the number of grams of substance in 100 grams of solution and d is the density of solution.

There/

There will be found under many of the tables quoted in this thesis, a range of experimental error which has been deduced on the assumption of an observational error of 0·03° in the determination of . These results must be considered as an indication of the limiting error rather than that in the average determination where repeated readings were obtained with closer agreement.

SOLVENT INFLUENCE.

From the point of view of the following discussion, the work undertaken in this thesis may be regarded as falling into three main sections, which may be classified as solvent effect, concentration, effect, and temperature effect. The esters, the preparation of which has just been described, will be discussed individually in each of these three sections, after which the whole of the experimental data will be reviewed, and any general relationships, where such appear to exist, established. A summary will finally be given.

TABLE I.

A scrutiny of Table I reveals the fact that there is an excellent agreement existing between the rotatory power of the ester and the dipole moment of the aromatic solvent employed; the value of the molecular rotation being greatest in those solvents of low and zero dipole moment, and lowest in those of high dipole moment. Aniline would appear to be the only real exception to this regularity. In this solvent, however, a distinct darkening in colour was noted when the ester went into solution. A probable explanation of the observed facts is that a molecular compound/

TABLE I.

ROTATORY POWERS of *l*-MENTHYL o-NITROBENZOATE in HOMOGENEOUS SOLVENTS of the BENZENE TYPE.

solvents are arranged in increasing values of $[M]^{20}_{5461}$

temperature 20°C.

solvent	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g./100 c.c.	l
$C_6H_5NO_2$	3·89	-436°	-11·47°	4·014	2
C_6H_5CN	3·85	468°	12·30°	4·008	2
o-$C_6H_4Cl_2$	2·24	498°	13·11°	4·018	2
C_6H_5CHO	2·75	501°	6·58°	4·005	1
C_6H_5Cl	1·52	570°	14·99°	4·012	2
C_6H_5Br	1·50	577°	15·15°	4·002	2
C_6H_5I	1·30	600°	15·76°	4·006	2
$C_6H_5OCH_3$	1·25	606°	15·97°	4·020	2
$C_6H_3(CH_3)_3$	0	660°	17·33°	4·006	2
$C_6H_5CH_3$	0·5	671°	17·65°	4·012	2
$C_6H_5NH_2$	1·60	680°	8·92°	4·000	1
C_6H_6	0	703°	9·76°	4·232	1

compound is formed between the aniline and the nitro ester. SIDGWICK (The Electronic Theory of Valency, p.138) has suggested that amines under certain conditions may exhibit strong donor properties, and BENNET & WILLIS (J.C.S., 1929. 258) have discussed formulae for co-ordination compounds formed by union of a nitro compound with an amine. It is of interest to note that the order, mesitylene, toluene and benzene, which obtains in the above Table, is the reverse of that found by RULE & McLEAN (J.C.S., 1931, 676) for l-menthyl methyl naphthalate. In view of a suggestion advanced by RULE, SMITH & HARROWER in reference to the strongly associated compound, nitro-octane, (see page 23) it is possible that this partial inversion is due to the fact that the nitro ester has a somewhat greater tendency to undergo association with itself in mesitylene than in benzene solution. Self-association would operate in the same sense as association with the solvent to bring about a lower rotatory power, and such a state of affairs would account for the observed order of values for the molecular rotations in these solvents. The halogen derivatives, although all of practically the same dipole moment, show a surprising difference in their effects upon the rotation of the solute. On page 24 there was shown the effect on the rotatory power of l-menthyl methyl naphthalate of passing from methyl iodide to ethyl/

ethyl iodide and finally to iodobenzene; the observed effect being attributed to the alteration in the size of the organic radical attached to the dipole in question. Here, it seems probable that the observed differences of rotatory power can be attributed, in large measure, to the considerable variation in the volumes of the Cl, Br, and I atoms respectively, some indication of which is given by a comparison of their parachors. SUGDEN (The Parachor & Valency, p.38) quotes the following values, Cl, 54.3, Br 68.0, I, 91.0. Iodine, then, has a very large parachor. We might well expect that the resulting "screening" would decrease the effective dipole moment of the iodobenzene by hindering the close approach of other polar molecules. Iodobenzene would thus behave as a less polar solvent than its dipole moment would indicate. In bromobenzene this effect should also be evident to a less marked degree, in comparison with chlorobenzene as standard. On these considerations the predicted order of molecular rotations of the nitro-ester dissolved in these solvents would be $C_6H_5Cl < C_6H_5Br < C_6H_5I$, which is the order existing in the above Table.

TABLE/

TABLE 2.

ROTATORY POWERS of l-MENTHYL o-NITROBENZOATE in HOMOGENEOUS SOLVENTS of the METHANE TYPE.

solvents are arranged in increasing values of $[M]^{20}_{5461}$

Temperature 20°C. l = 1 dcm.

solvents	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.
CH_3NO_2	3·78	-475°	-6·86°	4·402
CH_3CN	3·05	495°	7·56°	4·654
CH_3CHO	2·71	531°	8·63°	4·954
CH_3COOH	1·40 (0·75)	550°	8·65°	4·832
CH_2Cl_2	1·61	553°	8·35°	4·610
CH_3OH	1·64	557°	8·96°	4·870
CH_3I	1·66	584°	7·68°	4·008
C_7H_{16}	0	584°	8·42°	4·399
C_6H_{14}	0	585°	8·26°	4·304
$CHCl_3$	1·10	586°	8·40°	4·372
C_5H_{12}	0	587°	8·46°	4·393
C_6H_{12}	0	593°	8·45°	4·304
CCl_4	0	607°	9·88°	4·962
CS_2	0	625°	8·89°	4·338

TABLE 2

Turning to Table 2, the same agreement of molecular rotation and dipole moment of solvent as was noted in Table 1 is again manifested with aliphatic derivatives. The range of rotation values is here 150° indicating that the ester, although still sensitive to change of solvent, exhibits somewhat smaller variation in aliphatic than in aromatic solvents. In this respect it should be noted that heptane, hexane, pentane, and cyclo-hexane, although not simple derivatives of methane, have been included to show the effect of additional non-polar solvents. They have also been included in all the other tables of this type. The values of the molecular rotation in the homologous compounds heptane, hexane, and pentane differ only by three degrees. As has already been suggested, the molecules of the nitro-ester in mesitylene solution may tend to assume a definite orientation towards one another, i.e., to undergo dipole association through the medium of the strongly polar nitro group. If so, this tendency should be still more marked in the aliphatic hydrocarbon solvents which have an even lower dielectric constant and are known to promote association more than aromatic hydrocarbons. Such association would result in lowered/

lowered rotatory powers in the fatty hydrocarbons, and would explain not only the grouping of these solvents with chloroform in the Table, but also the fact that carbon disulphide and carbon tetrachloride yield more highly active solutions. The two last solvents are composed of a symmetrical arrangement of dipoles and are thus non-polar, in so far as their behaviour in a uniform field is concerned, but owing to their polar constituents they are more effective dissociating solvents than the hexane or heptane. (See also TURNER, Molecular Association, 1915, p.43.) The three chloro derivatives, carbon tetrachloride, chloroform, and methylene chloride, give progressively lower rotational values in keeping with their increasing dipole moments. KENYON & PICKARD (J.C.S., 1915, 48) quote $[M]^{20^{\circ}}_{5461} = -492^{\circ}$ for *l*-menthyl o-nitrobenzoate in the homogeneous state. The two extreme values quoted for $[M]^{20^{\circ}}_{5461}$ in highly polar and non-polar solvents in Tables 1 & 2 are -436° (in $C_6H_5NO_2$) and -703 (in C_6H_6). Hence the value for the homogeneous ester lies in between those two extremes. In the absence of other disturbing factors this relationship is to be expected, since hydrocarbons and nitro compounds represent the limiting types of non-polar and polar solvents respectively.

TABLES 3 & 4 /

TABLES 3 & 4.

ROTATORY POWERS of *l*-MENTHYL o-NITROBENZOATE in SOLVENT MIXTURES CONTAINING 0·580 MOLE FRACTION of BENZENE.

Temperature 20°C $\qquad$ *l* = 2 dcm.

Polar Solvent	$\mu \times 10^{-18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.
C_6H_5Cl	1·52	-637°	-16·72°	4·000
$p\text{-}C_6H_4Cl_2$	0	616°	16·15°	4·000
$o\text{-}C_6H_4Cl_2$	2·24	587°	15·41°	4·000

A preliminary experiment indicated that the maximum mole fraction of the solid $p\text{-}C_6H_4Cl_2$ which could be conveniently employed was 0·420. This value was then adopted for all the polar solvents in the table.

ROTATORY POWERS of *l*-MENTHYL o-NITROBENZOATE in SOLVENT MIXTURES CONTAINING 0·985 MOLE FRACTION of BENZENE.

Temperature 20°C. $\qquad$ *l* = 2 dcm.

Polar Solvent	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.
$p\text{-}C_6H_4(NO_2)_2$	0	-698°	-18·32°	4·000
$C_6H_5NO_2$	3·89	689°	18·08°	4·000
$m\text{-}C_6H_4(NO_2)_2$	3·81	685°	17·97°	4·000

Here the maximum mole fraction of the least soluble of the polar solvents - the $p\text{-}C_6H_4(NO_2)_2$ - was found to be 0·015 and this value was then adopted for the table.

TABLES 3 & 4

It was noted in Tables 1 & 2 that surprisingly large variations occurred in the rotatory powers of the nitro ester, as determined in non-polar hydrocarbon solvents. These variations in the particular solvents considered, may be possibly accounted for by variations in the degree of association of the solute molecules with each other. It seems unlikely, however, that such an explanation can account for the variations in rotatory power in certain solvents, the non-polarity of which is due to a symmetrical arrangement of substituent dipoles. Other factors would appear to come into operation. Consider the non-polar solvents, carbon disulphide and p-dichlorobenzene. The constitution of these would seem to permit of some degree of dipole association since they must exert a definite force on a point charge or dipole in their immediate vicinity, although, as we noted before in the case of CS_2 and CCl_4, with reference to a uniform external field they are non-polar. In carbon disulphide however the two oppositely oriented dipoles being separated only by one carbon atom, largely annul each other's influence. The polar properties of such a solvent will be extremely weak; if indeed they exist at all. In p-dichlorobenzene however, the case is different. Here the dipoles being/

being separated from each other by the full width of a benzene ring, will have an opportunity of exerting their polarity independently of each other, at least to some extent. On this assumption then, it might be expected that p-dichlorobenzene when used as a solvent for an optically active compound, would exhibit some features characteristic of polar solvents. These expectations were fully realized by an examination of the rotatory powers of ℓ-menthyl o-nitrobenzoate in the solvents tabulated in Tables 3 & 4. As some of these derivatives are solids, a comparison was effected by using them in equivalent proportions, mixed with benzene.

In Table 3 it is apparent that p-$C_6H_4Cl_2$ acts as a more polar solvent than the monosubstituted compound. The depression of the latter, as compared with pure benzene (-703°) is 66° while that caused by an equivalent molecular proportion of p-$C_6H_4Cl_2$ is 87°, a considerably greater decrease. In the case of o-$C_6H_4Cl_2$ the depression is 116°, almost double that due to the monosubstituted compound, which might be expected from a consideration of the fact that here the two CCl dipoles will reinforce each other's field. The depression caused by the p-$C_6H_4Cl_2$ is apparently the result of the increased frequency with which/

which the individual dipoles come into play, as compared with chlorobenzene.

In Table 4, for the corresponding nitro derivative, the range of values of the molecular rotation is only 13° owing to the fact that the polar component is present in small concentration because of the low solubility of p-dinitro benzene. We find that p-$C_6H_4(NO_2)_2$ causes a depression as compared with that for pure benzene of 5°, while the depression caused by m-$C_6H_4(NO_2)_2$ (18°) is 4° more than that due to the monosubstituted compound.

Similar experiments have been carried out by RULE & HILL (J.C.S., 1931. 2656) and RULE & McLEAN (J.C.S., 1931, 680) which in conjunction with the above results point conclusively to the fact that p-dichlorobenzene and p-dinitrobenzene act frequently as definitely polar substances, and that m-dinitrobenzene, although it has a dipole moment very similar to that of the monosubstituted nitro compound, is also capable of behaving in a more highly polar capacity; due to the fact that the dipoles are capable of acting, in some measure, independently towards neighbouring molecules. RULE & McLEAN'S figures for ℓ-menthyl methyl naphthalate are given below

TABLE 5.

THE ROTATORY POWERS of l-MENTHYL HYDROGEN PHTHALATE in HOMOGENEOUS SOLVENTS of the BENZENE TYPE.

Solvents are arranged in increasing values of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm.

SOLVENT	$\mu \times 10^{-18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.
x $C_6H_5NH_2$	1·60	-275°	-7·26°	4·008
$C_6H_5NO_2$	3·89	291°	7·68°	4·008
C_6H_5CN	3·85	296°	7·78°	4·000
C_6H_5CHO	2·75	306°	8·06°	4·008
o-$C_6H_4Cl_2$	2·24	314°	8·26°	4·004
C_6H_5Cl	1·52	344°	9·07°	4·004
C_6H_5Br	1·50	346°	9·13°	4·008
$C_6H_5OCH_3$	1·25	348°	9·17°	4·000
C_6H_5I	1·50	357°	9·41°	4·004
C_6H_6	0	402°	10·61°	4·008
$C_6H_5CH_3$	0·5	407°	10·73°	4·008
$C_6H_3(CH_3)_3$	0	431°	11·37°	4·006

x In this case the solution was strongly coloured and this would indicate some interaction of ester and aniline to form a salt.

$(f_2 = 0{\cdot}4)$	$[M]^{20}_{5461}$	Δ	$\mu \times 10^{18}$	$f_2 = 0{\cdot}015$	$[M]^{20^\circ}_{5461}$	Δ	$\mu \times 10^{18}$
C_6H_5Cl	-501°	42	1·52	$C_6H_5NO_2$	-527°	16	3·84
$o-C_6H_4Cl_2$	-470°	73	2·25	$m-C_6H_4(NO_2)_2$	-510°	33	3·80
$p-C_6H_4Cl_2$	-463°	80	0	$p-C_6H_4(NO_2)_2$	-508°	35	0

f_2 = Mol. fraction of polar solvent in benzene mixture.

Δ = Depression as compared with pure benzene.

TABLE 5

In Table 5, as in Tables 1 & 2, the agreement of the molecular rotatory power with the dipole moment of the solvent inwhich the ester is examined is the most outstanding feature. Here again a high value of molecular rotation goes hand in hand with a low or zero dipole moment, and vice versa. Aniline forms the only real exception to this regularity, but it has been already noted that in this solvent *ℓ*-menthyl hydrogen phthalate produced a strong colouration. The most probable interaction would be that of salt formation between the base, and the acidic ester. RULE (Trans. Faraday Soc. 1930, 331) points out that among the benzoic esters the ionization of such groups as COOH, NH_2, etc. in the ortho-substituted/

TABLE 6.

THE ROTATORY POWERS of l-MENTHYL HYDROGEN PHTHALATE in HOMOGENEOUS SOLVENTS of the METHANE TYPE.

Solvents are arranged in increasing order of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dem.

SOLVENT	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461}(obs.)	c. g/100 c.c.
CH_3CN	3·05	-300°	-7·92°	4·008
CH_3NO_2	3·78	301°	3·75°	1·896
CH_3CHO	2·71	323°	8·51°	4·000
CH_3OH	1·64	334°	8·81°	4·008
CH_3COOH	1·40(0·75)	334°	8·81°	4·004
$CHCl_3$	1·10	345°	9·10	4·004
CH_2Cl_2	1·61	353°	9·29°	4·000
CS_2	0	372°	9·80°	4·000
CH_3I	1·66	380°	10·00°	4·004
CCl_4	0	386°	10·17°	4·004
C_6H_{12}	0	393°	10·35°	4·002
C_7H_{16}	0	416°	2·76°	1·008
C_6H_{14}	0	419°	1·38°	0·500
C_5H_{12}	0	432°	1·32°	0·464

N.B. In those solvents in which the poor solubility of the ester prevented a 4% solution being made lower concentrations were employed. Even at the above low concentration in Pentane difficulty was experienced in preventing the ester from crystallising out on the stopper of the flask.

ortho-substituted compounds leads to a characteristic change of rotatory power. In the case of ℓ-menthyl hydrogen phthalate, salt formation results in a decreased rotation. Thus $[M]_{5461}$ for the acid ester in alcohol is -346°, while that of the corresponding sodium salt is -260°. Salt formation would then account for the low value found in aniline. The developement of a strong colour, however, would seem to be the outcome of some secondary reaction which doubtless also has an effect in prodicing the observed rotation.

The sequence, C_6H_6, $C_6H_5CH_3$, $C_6H_3(CH_3)_3$, which represents progressively increasing values of the rotatory power in this Table, is the reverse of that noted in Table 1. The above order coincides with that found by RULE & McLEAN (J.C.S., 1931, 676).

The order of the rotational values in the halogen derivatives, $Cl < Br < I$, is the same as in Table 1, and the total range of molecular rotations, excluding that found in aniline, is 140°.

TABLE 6.

In Table 6 there again exists that relationship which was noted in Tables 5, 1 & 2, between polarity of solvent and the optical rotatory power of the solute. Furthermore, as in Table 2, methyl iodide is somewhat/

TABLE 7.

ROTATORY POWERS of l-MENTHYL SALICYLATE in VARIOUS HOMOGENEOUS SOLVENTS of the BENZENE TYPE.

Solvents are arranged in increasing values of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm. (except in case of Aniline where l = 1 dcm.)

SOLVENT	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c g/100 c.c.
C_6H_6	0	-323°	-9·37°	4·008
$C_6H_5CH_3$	0·5	327°	9·49°	4·008
$C_6H_5(OCH_3)$	1·25	328°	9·53°	4·004
$C_6H_5NH_2$	1·60	334°	4·85°	4·008
o-$C_6H_4Cl_2$	2·24	335°	9·71°	4·004
$C_6H_3(CH_3)_3$	0	335°	9·72°	4·000
$C_6H_5NO_2$	3·89	339°	9·83°	4·000
C_6H_5CHO	2·75	343°	9·96°	4·004
C_6H_5Cl	1·52	343°	9·97°	4·008
C_6H_5Br	1·50	346°	10·02°	4·000
C_6H_5I	1·50	352°	10·20°	4·002
C_6H_5CN	3·85	353°	10·25°	4·002

somewhat displaced, giving too high a value of the molecular rotation as compared to its position in the polar scale. The order of the non-polar solvents is that of their dielectric properties, and the ring compound cyclo-hexane gives a value somewhat lower than any of the aliphatic hydrocarbons. The total range of the molecular rotations is 132°.

TABLE 7.

l-Menthyl salicylate when examined in solvents, apparently presents a type of effect which is practically the reverse of that noted for *l*-menthyl o-nitrobenzoate and *l*-menthyl hydrogen phthalate. In Table 7 there is a tendency for the solvents of zero and low dipole moments to be related with the lower values of rotatory power. The relationship however is by no means a close one, and many irregularities are evident. Thus we find a rotational value of -339° in nitrobenzene, and a value of only 4° less in the non-polar solvent mesitylene. Again, iodobenzene gives a value only one degree lower than that found in the highly polar benzonitrile. That such discrepancies occur is not unexpected, since the total range of values is only 30°. Apparently then this ester is not particularly sensitive to change of solvent/

TABLE 8.

ROTATORY POWERS of *l*-MENTHYL SALICYLATE in VARIOUS HOMOGENEOUS SOLVENTS of the METHANE TYPE.

Solvents are arranged in increasing values $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm.

Solvent	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g./100 c.c.
CH_3I	1·66	-287°	-8·33°	4·000
CCl_4	0	292°	8·47°	4·000
C_6H_{12}	0	294°	8·52°	4·000
C_6H_{14}	0	299°	8·68°	4·008
CH_3OH	1·64	300°	8·71°	4·004
C_7H_{16}	0	304°	8·81°	4·004
C_5H_{12}	0	306°	8·87°	4·000
CH_3CN	3·05	308°	8·92°	4·000
CH_3CHO	2·71	309°	8·96°	4·000
CH_2Cl_2	1·61	310°	8·98°	4·000
CH_3NO_2	3·78	311°	9·04°	4·008
$CHCl_3$	1·10	315°	9·12°	4·000
CH_3COOH	1·40(0.75)	320°	9·27°	4·000
CS_2	0	337°*	9·77°	4·004

* checked & found O.K.

Note CH_3I & CS_2 of high refrac. index.

but C_6H_5I in previous table.

Aliph. give lower values than arom. Greater assoc. lower rotn. ?

solvent, and it is probable that experimental error will tend to mask some of the finer distinctions in the evaluation of the molecular rotation. The order of the solvents, chlorobenzene, bromobenzene, and iodobenzene, is however, the same as previously noted in Tables 1 & 5.

TABLE 8

The tendency of the l-menthyl salicylate to give an inverted series is more clearly illustrated in this Table than in Table 7. In this respect, it should be observed that the range of rotatory powers is greater in the former than in the latter series, being 50° in the case of Table 8. The two outstanding exceptions to this relationship are methyl iodide and carbon disulphide. The halogen derivative has been noted before as giving somewhat anomalous results. In this Table the lowest value quoted is that taken in methyl iodide, while that taken in iodobenzene is the highest but one in table 7. The value for the homogeneous ester is $[M]^{20^\circ}_{5461} = -332^\circ$, which lies between the two extreme values quoted in the Tables above, viz. -292° in carbon tetrachloride and -353° in benzonitrile.

TABLE 9/

TABLE 9.

ROTATORY POWERS of l-MENTHYL BENZOATE in HOMOGENEOUS SOLVENTS of the BENZENE TYPE.

Solvents are arranged in increasing values of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm.

SOLVENT	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs)	c. g/100 c.c.
$C_6H_5NO_2$	3·89	-279°	$-8{\cdot}59^\circ$	4·008
C_6H_6	0	280°	$8{\cdot}63^\circ$	4·008
o-$C_6H_4Cl_2$	2·24	282°	$8{\cdot}70^\circ$	4·004
$C_6H_5OCH_3$	1·25	282°	$8{\cdot}70^\circ$	4·004
$C_6H_5CH_3$	0.5	284°	$8{\cdot}75^\circ$	4·004
C_6H_5Cl	1·52	289°	$8{\cdot}89^\circ$	4·000
C_6H_5Br	1·50	293°	$9{\cdot}00^\circ$	4·004
C_6H_5CHO	2·75	294°	$9{\cdot}07^\circ$	4·006
C_6H_5CN	3·85	302°	$9{\cdot}30^\circ$	4·000
$C_6H_3(CH_3)_3$	0	302°	$9{\cdot}28^\circ$	4·000
$C_6H_5NH_2$	1·60	309°	$9{\cdot}52^\circ$	4·004
C_6H_5I	1·50	309°	$9{\cdot}52^\circ$	4·008

? Refrac. index effect

TABLE 10.

ROTATORY POWERS of l-MENTHYL BENZOATE in HOMOGENEOUS SOLVENTS of the METHANE TYPE.

solvents are arranged in increasing values of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm.

SOLVENT	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.
CCl_4	0	-243°	-7·50°	4·008
C_6H_{12}	0	246°	7·58°	4·002
CH_3I	1·66	250°	7·69°	4·004
C_7H_{16}	0	257°	7·92°	4·000
C_6H_{14}	0	261°	8·04°	4·006
$CHCl_3$	1·10	264°	8·15°	4·008
CH_3NO_2	3·78	264°	8·14°	4·004
C_5H_{12}	0	270°	8·31°	4·000
CH_2Cl_2	1·61	270°	8·32°	4·006
CH_3CN	3·05	273°	8·43°	4·008
CH_3CHO	2·71	276°	8·49°	4·004
CH_3OH	1·64	281°	8·66°	4·002
CH_3COOH	0·75(1·40)	293°	9·03°	4·006
CS_2	0	293°	9·01°	4·000

TABLE 9

The order of the rotatory powers relative to that of the dipole moments of solvents, would here seem to be quite haphazard, the values in nitrobenzene differing from that in benzene by only one degree, while in benzonitrile and in mesitylene the values are actually the same. The total range of rotation values is small, being only 30°, nevertheless the halogen derivatives maintain the order observed in the earlier Tables.

TABLE 10

In this Table, the order, although not very pronounced, would appear to be that of low rotatory and low dipole moment of solvent going hand in hand. Methyl iodide and carbon disulphide are once again displaced, the latter, as in the case of *l*-menthyl salicylate, being grouped with the non-polar solvents. The maximum range of values in the Table is 50°. For the molecular rotation of the homogeneous benzoate COHEN & DUDLEY have recorded $[M]^{20°}_{5893}$ = -239° (J.C.S. 1910, 1750). Utilising a conversion factor of 1·18 (cf. KENYON & PICKARD, J.C.S., 1915, 52) the value for the supercooled ester, $[M]^{20°}_{5461}$, should approximate to -282°, a value which is also indicated by a continuation of the concentration curve for this ester to/

TABLE 11.

THE ROTATORY POWERS of l-MENTHYL o-CHLOROBENZOATE in VARIOUS HOMOGENEOUS SOLVENTS of the BENZENE TYPE

Solvents are arranged in increasing value of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm. (except in case of aniline when l = 1 dcm.)

SOLVENT	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.
$C_6H_5NO_2$	3·89	-231°	-6·29°	4·002
o-$C_6H_4Cl_2$	2·24	232°	6·32°	4·000
C_6H_5CN	3·85	234°	6·38°	4·000
C_6H_5CHO	2·75	240°	6·54°	4·008
$C_6H_5OCH_3$	1·25	240°	6·53°	4·006
C_6H_5Cl	1·52	242°	6·59°	4·008
C_6H_5Br	1·50	242°	6·59°	4·000
C_6H_6	0	247°	6·72°	4·004
$C_6H_5CH_3$	0·5	248°	6·75°	4·008
$C_6H_3(CH_3)_3$	0	253°	6·90°	4·006
x C_6H_5I	1·50	254°	6·92°	4·000
$C_6H_5NH_2$	1·60	262°	3·56°	4·000

x Here the solution was tinged pink - due probably to liberation of Iodine.

TABLE. 12.

THE ROTATORY POWERS of *l*-MENTHYL o-CHLOROBENZOATE in HOMOGENEOUS SOLVENTS of the METHANE TYPE.

Solvents are arranged in order of increasing values of $[M]^{20}_{5461}$

Temperature 20°C. l = 2 dcm.

Solvent	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461}(obs.)	c g./100 c.c.
CH_3NO_2	3·78	-215°	-5·85°	4·004
CH_3CN	3·05	217°	5·91°	4·008
CCl_4	0	223°	6·08°	4·004
CH_3I	1·66	226°	6·16°	4·004
$CHCl_3$	1·10	227°	6·20°	4·008
CH_2Cl_2	1·61	228°	6·21°	4·000
CH_3CHO	2·71	230°	6·25°	4·000
CS_2	0	232°	6·31°	4·004
CH_3OH	1·64	234°	6·37°	4·000
C_6H_{12}	0	235°	6·39°	4·000
CH_3COOH	1·4(0·75)	237°	6·45°	4·008
C_7H_{16}	0	238°	6·48°	4·000
C_6H_{14}	0	239°	6·51°	4·008
C_5H_{12}	0	250°	6·82°	4·008

to a point where it intersects the ordinate corresponding to the homogeneous compound (See Figure p.) This value of -282° lies between the extreme values of -264° in nitromethane and -302° in mesitylene listed in the above Tables.

TABLE 11.

With the exception of aniline, and iodobenzene, both of which are in this case abnormal, the agreement of molecular rotatory power and dipole moment of solvent is good. The order moreover, is that noted for the nitro- and carboxy- esters, i.e., solvents of high dipole moment yield solutions of the lowest rotatory powers. In iodobenzene, the formation of a coloured solution possibly points to some chemical interaction which may vitiate the results. Benzene, toluene and mesitylene arrange themselves in the same order as was obtained by RULE & McLEAN (loc.cit.) for menthyl methyl naphthalate. The total range of values in this Table is only 31°, so that the general regularity found with this ester indicates that the irregular behaviour of ℓ-menthyl salicylate is not, per se, due to its relative insensitivity towards change of solvent.

TABLE 12/

TABLE 13.

THE ROTATORY POWERS of l-MENTHYL o-METHOXYBENZOATE in VARIOUS HOMOGENEOUS SOLVENTS of the BENZENE TYPE.

Solvents are arranged in increasing value of $[M]^{20}_{5461}$

Temperature 20°C.

SOLVENTS	$\mu \times 10^{18}$ e.s.u.	$[M]^{20}_{5461}$	α_{5461} (obs.)	c. g/100 c.c.	l
$C_6H_3(CH_3)_3$	0	-198°	$-5·47^\circ$	4·008	2
$C_6H_5CH_3$	0·5	199°	$5·50^\circ$	4·006	2
$C_6H_5OCH_3$	1·25	200°	$5·52^\circ$	4·002	2
o-$C_6H_4Cl_2$	2·24	201°	$5·54^\circ$	4·004	2
$C_6H_5NO_2$	3·89	205°	$5·66^\circ$	4·006	2
C_6H_6	0	212°	$5·84^\circ$	4·002	2
C_6H_5Cl	1·52	212°	$5·87^\circ$	4·008	2
C_6H_5Br	1·50	216°	$5·95^\circ$	4·002	2
C_6H_5CN	3·85	217°	$2·99^\circ$	4·000	1
C_6H_5CHO	2·75	218°	$6·03^\circ$	4·006	2
C_6H_5I	1·50	229°	$6·32^\circ$	4·004	2
$C_6H_5NH_2$	1·60	258°	$3·56^\circ$	4·008	1

TABLE 12.

In so far as the two most highly polar solvents give the lowest rotational values, and non-polar solvents the highest, some agreement with the relationship holding for the esters in the aromatic solvents may be claimed here. Carbon tetrachloride forms the biggest exception and it is significant that the rotatory powers in the chlorinated solvents are in the reverse order to that noted in the case of *l*-menthyl o-nitrobenzoate, while methyl iodide is displaced towards the polar end of the Table. The maximum range of values is 35° and the molecular rotation of the homogeneous ester at 20°, for the mercury green line, is -235°, which again lies between the extreme values of -215° in nitromethane and -253° in mesitylene quoted in Tables 11 & 12.

TABLE 13

Solvents influence the rotatory power of menthyl o-methoxybenzoate in a manner which is in many ways similar to that observed in the case of *l*-menthyl salicylate. This is not altogether surprising when the similarity of the two substituents, the methoxyl and hydroxyl groups, is recollected. Once again in this/

TABLE 14.

THE ROTATORY POWERS of *l*-MENTHYL o-METHOXYBENZOATE in VARIOUS HOMOGENEOUS SOLVENTS of the METHANE TYPE.

Solvents are arranged in increasing values of $[M]_{5461}^{20}$

Temperature 20°C. l = 2 dcm.

SOLVENT	$\mu \times 10^{-18}$ e.s.u.	$[M]_{5461}^{20}$	α_{5461} (obs.)	c. g/100 c.c.
C_6H_{12}	0	-151°	-4·18°	4·008
CH_3NO_2	3·78	154°	4·25°	4·008
C_7H_{16}	0	158°	4·36°	4·008
CH_3I	1·66	159°	4·39°	4·004
C_6H_{14}	0	164°	4·52°	4·004
CH_3CN	3·05	167°	4·62	4·004
CCl_4	0	168°	4·64°	4·008
CH_3CHO	2·71	171°	4·73°	4·008
CH_2Cl_2	1·61	171°	4·71°	4·002
$CHCl_3$	1·10	171°	4·74°	4·010
C_5H_{12}	0	171°	4·72°	4·004
CH_3OH	1·64	199°	5·51°	4·004
CS_2	0	203°	5·61°	4·004
CH_3COOH	1·40(0·75)	208°	5·73°	4·000

this Table the halogen derivatives fall into their previous order, Cl < Br < I. Nitrobenzene and o-dichlorobenzene give similar values, as they do in the case of the salicylate, and the position they occupy indicates that they are displaced towards the non-polar end of the Table, a fact which may be noted in Table 7, also, while iodobenzene is connected with a high rotation value in both Tables. The maximum range of molecular rotations, excluding the abnormally high value in aniline, is 31°

TABLE 14

No regularity of any kind is discernible for the aliphate solvents, which would seem to influence the rotation of the methoxy ester in an altogether haphazard manner. The maximum range of values is 57°. COHEN & DUDLEY (J.C.S., 1910, 1740) quote $[M]_D^{20} = -148{\cdot}2^\circ$ for *l*-menthyl o-methoxybenzoate in the homogeneous state whence $[M]_{5461}^{20^\circ}$ approximates to -175°, which lies between the extreme values of -154° in nitromethane, and 212° in benzene quoted in Tables 13 & 14.

The two extreme values exhibited by *l*-menthyl hydrogen phthalate in polar and non-polar solvents are -291° in nitrobenzene and -432° in pentane. No value of $[M]_{5461}^{20^\circ}$ for this ester in the homogeneous state/

TABLE 15.

MOLECULAR ROTATIONS of VARIOUS ESTERS in SOLVENTS of the BENZENE TYPE in a CONCENTRATION of APPROXIMATELY 4 PER CENT.

2 dm. tube employed. Temperature 20°C.

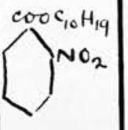
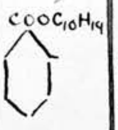
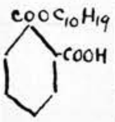
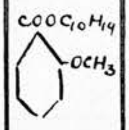
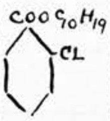
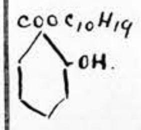
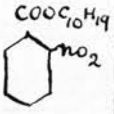
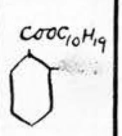
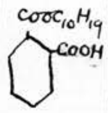
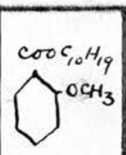
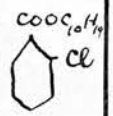
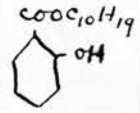
Solvents	$\mu \times 10^{18}$	$[M]^{20°}_{5461}$					
							
$C_6H_5NO_2$	3·89	-436°	-279°	-291°	-205°	-231°	-339°
C_6H_5CN	3·85	468°	302°	296°	217°	234°	353°
C_6H_5CHO	2·75	501°	294°	306°	218°	240°	343°
$O\text{-}C_6H_4Cl_2$	2·24	498°	282°	314°	201°	232°	335°
$C_6H_5NH_2$	1·60	680°	309°	275°	258°	262°	334°
C_6H_5Cl	1·52	570°	289°	344°	212°	242°	343°
C_6H_5Br	1·50	577°	293°	346°	216°	242°	346°
C_6H_5I	1·50	600°	309°	357°	229°	254°	352°
$C_6H_5OCH_3$	1·25	606°	282°	348°	200°	240°	328°
$C_6H_3(CH_3)_3$	0	660°	302°	431°	198°	253°	335°
$C_6H_5CH_3$	0	671°	284°	407°	199°	248°	327°
C_6H_6	0	703°	280°	402°	212°	247°	323°

TABLE 16.

l -MENTHYL o-SULSTITUED BENZOATES in VARIOUS SOLVENTS of the METHANE SERIES.

2 dm. tube employed. Temperature 20°C.

		$[M]^{20°}_{5461}$					
Solvents	$\mu \times 10^{18}$						
CH_3NO_2	3·78	-475°	-264°	-301°	-154°	-215°	-311°
CH_3CN	3·05	495°	273°	300°	167°	217°	308°
CH_3CHO	2·71	531°	276°	323°	171°	230°	309°
CH_3I	1·66	584°	250°	380°	159°	226°	287°
CH_3OH	1·64	557°	281°	334°	199°	234°	300°
CH_2Cl_2	1·61	553°	270°	353°	171°	228°	310°
CH_3COOH	(0·75) 1·40	550°	293°	334°	208°	237°	320°
$CHCl_3$	1·10	586°	264°	345°	171°	227°	315°
CS_2	0	625°	293°	372°	203°	232°	337°
CCl_4	0	607°	243°	386°	168°	223°	292°
C_6H_{12}	0	593°	246°	393°	151°	235°	294°
C_7H_{16}	0	584°	257°	416°	158°	238°	304°
C_6H_{14}	0	585°	261°	419°	164°	239°	299°
C_5H_{12}	0	587°	270°	432°	171°	250°	306°

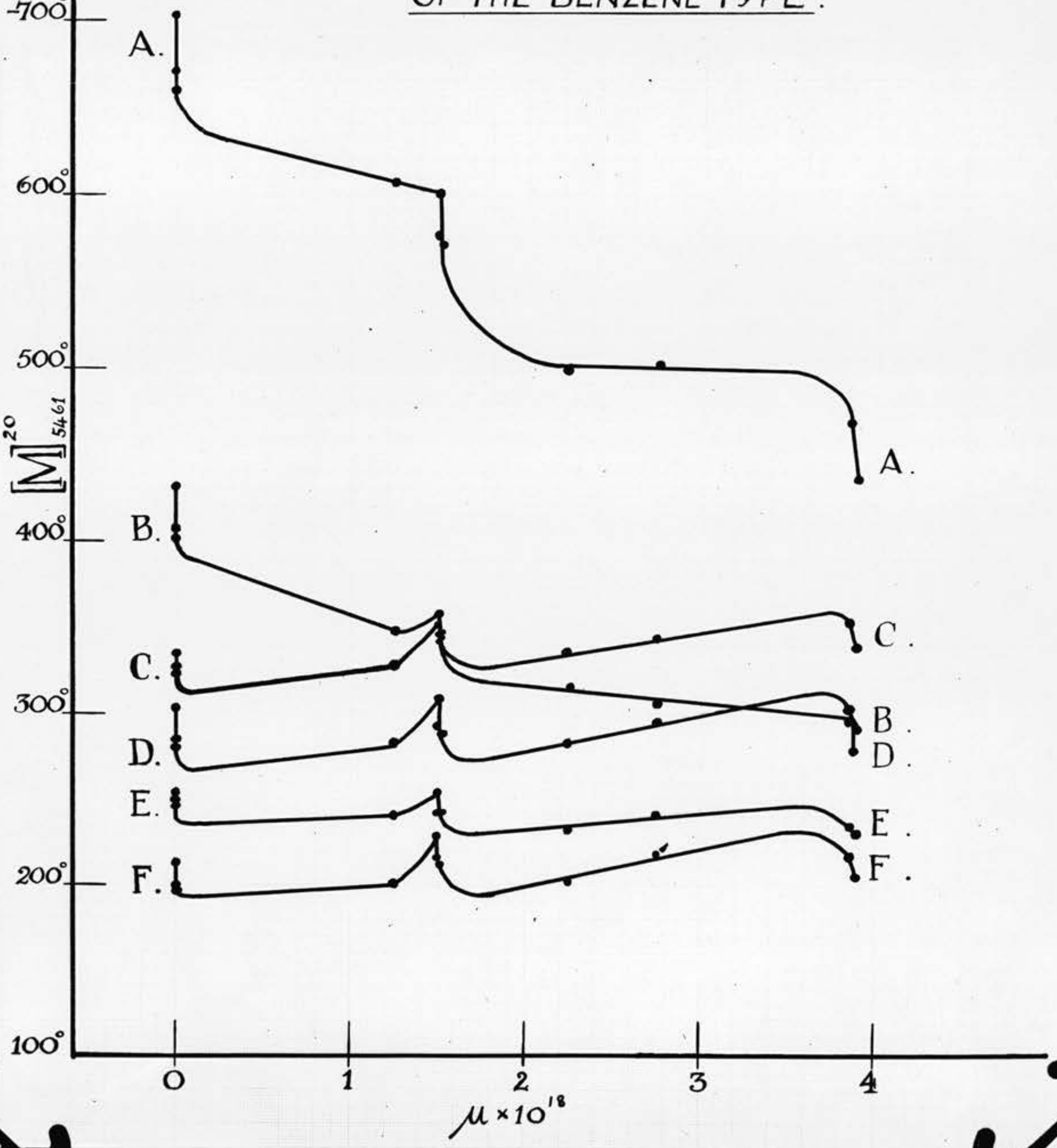
state could be found in the literature, but it may be deduced from the concentration curve B on page that this will probably lie well within the limiting values of -291° and -432°. This being so, it follows that for the six *l*-menthyl o-substituted esters considered above, the value of the rotatory power of the homogeneous ester in every case lies between the two extreme values for highly polar and non-polar solvents in the corresponding Tables. RULE, SMITH & HARROWER (J.C.S., in the press.) found a similar state of affairs to exist in various hydroxy, methoxy, halogen and nitro-derivatives which they investigated.

With a view to obtaining additional information from the figures given in the foregoing Tables, the dipole moments of the various solvents were plotted against the corresponding molecular rotatory powers. In the resulting Graphs no values will be found for aniline which has been omitted on account of the abnormal results to which it gives rise.

For ease of reference the modified Tables 15 & 16 have been compiled. These show the data used in drawing the two GRAPHS I & II.

Any detailed examination must still be made by reference to the Tables because of the somewhat arbitrary manner of drawing the Graphs: this is due to the/

GRAPH I.



THE ROTATORY POWERS OF l-MENTHYL ESTERS PLOTTED AGAINST DIPOLE MOMENTS OF SOLVENTS OF THE BENZENE TYPE.

A .... l-Menthyl o-nitrobenzoate.
B .... l-Menthyl hydrogen phthalate.
C .... l-Menthyl salicylate.
D .... l-Menthyl benzoate.
E .... l-Menthyl o-chlorobenzoate.
F .... l-Menthyl o-methoxybenzoate.

the fact that in each curve, there are several rotation values which result from solution of the ester in solvents of the same, or very similar, dipole moment. For example, in GRAPH II there are six different values of $[M]^{20}_{5461}$ for each ester in non-polar solvents, and in GRAPH I three different rotations result from solution in the halogenated solvents, all of dipole moment, 1·5 approximately. However, the method of drawing adopted has been applied consistently in each case, so that the resulting curves are comparable.

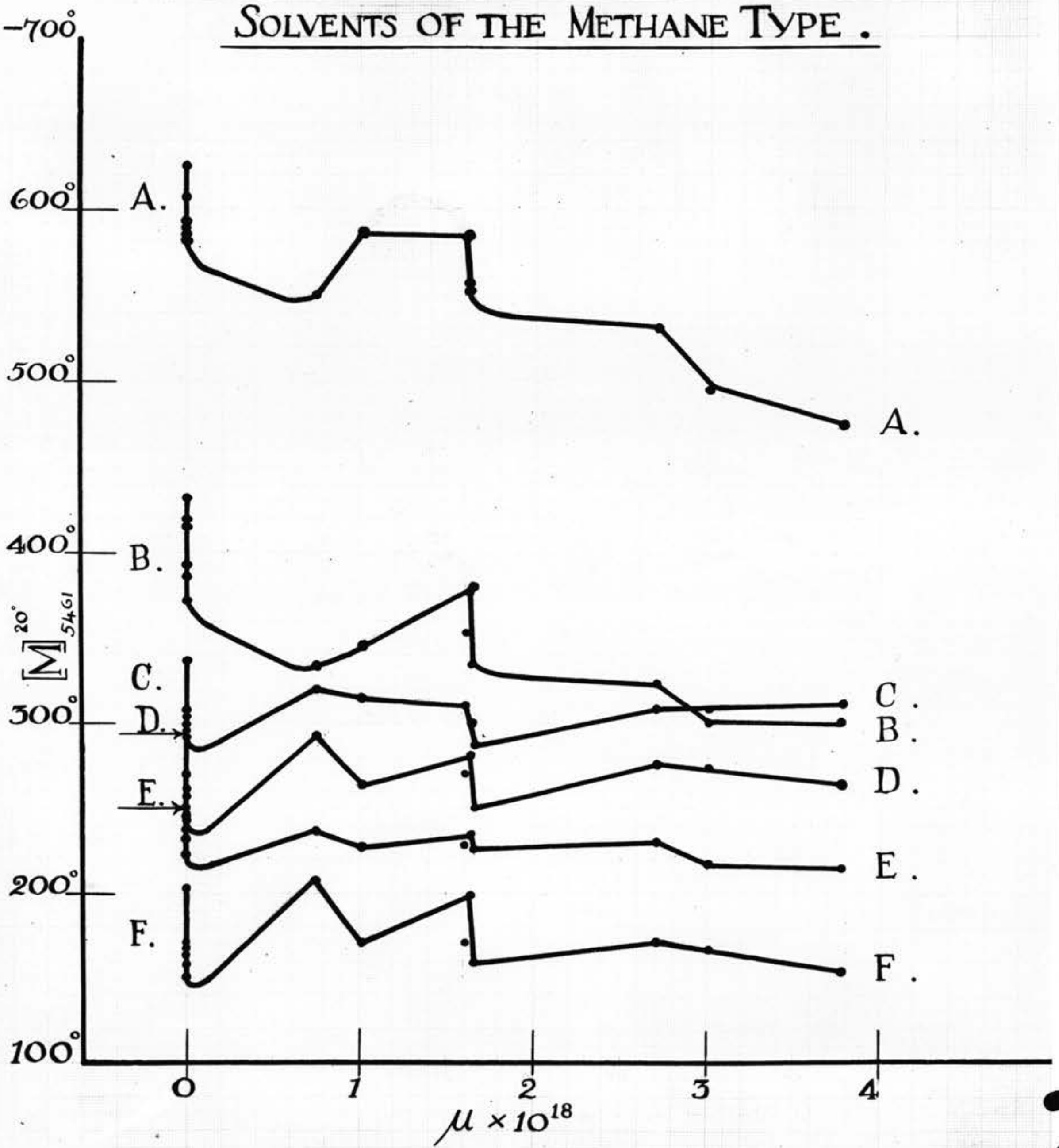
These curves illustrate, quite decidedly a feature that a scrutiny of the Tables would not reveal, viz., that there is a definite family relationship between the six sets of values, and indicate that no very specific solvent effects are brought about when the ortho hydrogen atom in menthyl benzoate is replaced by NO_2, COOH, OH, Cl, or OMe groups, despite the very large changes in the rotatory powers of the individual esters.

GRAPH I

A most striking feature of this diagram is that all the curves have similar shapes. The curious hump occurring in the middle of each at $\mu = 1·5$ is caused by the halogenated solvents which have practically/

GRAPH II

ROTATORY POWERS OF *l*-MENTHYL ESTERS PLOTTED AGAINST DIPOLE MOMENTS OF SOLVENTS OF THE METHANE TYPE.



A .... *l*-Menthyl o-nitrobenzoate.
B .... *l*-Menthyl hydrogen phthalate.
C .... *l*-Menthyl salicylate.
D .... *l*-Menthyl benzoate.
E .... *l*-Menthyl o-chlorobenzoate.
F .... *l*-Menthyl o-methoxybenzoate.

practically the same dipole moment, and which, in the case of each ester examined, caused depressions of rotatory power in the order Cl > Br > I. A second interesting feature is the slope of the curves. The nitro ester (A), in which the o-substituent produces the maximum effect in raising the rotatory power, has the steepest slope. The carboxy ester (B) of relatively high rotation has also a comparatively steep slope. For these two highly active compounds, therefore, a rise in the polarity of the solvent results in a considerable diminution in rotatory power, as has already been deduced from the Tables. The changes observed in the remaining four esters are much less marked.

GRAPH II

Here the similarity of the shape of the curves is not so pronounced as in GRAPH I . In other words the effect of aliphatic solvents of varying polarity upon the rotatory powers of the esters is not so regular as that obtained with solvents derived from the parent hydrocarbon benzene. The divergent properties of the two series of solvents has already been commented upon by other workers on the subject (cf. RULE & HILL, J.C.S., 1931. 2655). It seems not unlikely/

unlikely that the greater bulk and rigidity of the benzene ring in the aromatic solvents tends to minimise differences arising from the variable structure of the attached substituent groups. The sudden drop occurring about the middle of these curves for aliphatic liquids, is caused by the solvents, methyl iodide, methyl alcohol and methylene chloride, all of which have dipole moments of approximately 1·65 e.s.u. The vertical fall at the left-hand end of the curves is due to the various non-polar solvents, the order of which, among themselves, may vary from case to case. But for a difference in the relative positions of the chloroform point ($\mu \times 10^{18} = 1{\cdot}0$) the curves A & B would be almost identical in shape. Once again it may be seen as in GRAPH I that the nitro ester and the carboxy ester suffer a pronounced diminution of rotatory power when examined in solvents of increasing polarity. The remaining four esters give curves less definite in their slope, but it would appear that curve C has a general upward trend not discernible in the others, indicating that *l*-menthyl salicylate should possibly be classified separately. However, the extent of this divergence is slight and further evidence for such an action must be sought before a definite pronouncement can be made. Such additional evidence is forthcoming from an examination of the concentration/

concentration changes which is described in the following section. RULE (cf. RULE, SMITH & HARROWER, J.C.S., in the press) has suggested that if the change in rotatory power consequent upon dissolving a given optically active solute in solvents of increasing polarity, is caused by an increase in the degree of association between solute and solvent, then an optical change in the same direction may be anticipated when the solute is examined at increasing concentrations in a non-polar solvent; because such a procedure leads to a greater degree of association between the solute molecules themselves (cf. page 32.)

From an examination of the solvent Tables, in conjunction with the above Graphs, it may be concluded, therefore, that four of the esters under examination show definite variations in rotatory power, in relation to the polarity of the solvent. For three of these, the nitro, carboxy and chloro derivatives, the rotations diminish as the polarity increases, whilst for the salicylic ester the change apparently occurs in the opposite direction.

If the suggestion quoted above holds, it should be found that increasing the concentration of the nitro- carboxy and chloro- esters in a non-polar solvent will result in a progressively decreasing value of the rotatory power, while *l*-menthyl salicylate under similar conditions will give an increasing value.

Reference/

TABLE 17.

THE ROTATORY POWERS of l-MENTHYL o-NITROBENZOATE at VARYING CONCENTRATIONS in BENZENE.

Temperature 20°C.

c. g./100 c.c.	α_{5461}(obs)	$[M]^{20}_{5461}$	l.
2·002	- 9·33°	- 711°	2
2·060	9·58°	709°	2
4·008	18·48°	703°	2
9·976	22·36°	684°	1
25·428	107·97°	647·5°	2
26·552	55·77°	644·4°	1
37·200	75·67°	620·4°	1

The range of experimental error is from $[M]^{20}_{5461} = \pm 2·3^{\circ}$ when c = 2·002 g/100 c.c. to $[M]^{20}_{5461} = \pm 0·25^{\circ}$ when c = 37·200 g/100 c.c.

Assuming observational error in reading α_{5461} of ± 0·03°

TABLE 18.

THE ROTATORY POWERS of l-MENTHYL HYDROGEN PHTHALATE at VARYING CONCENTRATIONS in BENZENE.

Temperature 20°C.

c. g./100 c.c.	α_{5461} (obs.)	$[M]^{20}_{5461}$	l
3·038	- 4·00°	-400°	1
4·004	10·55°	400°	2
6·044	15·87°	399°	2
13·976	18·23°	397°	1
14·180	18·48°	396°	1
20·094	25·94°	392·4°	1
21·684	27·88°	391°	1
26·264	33·62°	389·1°	1
43·034	54·04°	381·7°	1

Above a concentration of 43·034 g./100 c.c. satisfactory readings could not be obtained.

Experimental error in the graph ranges from $[M]^{20}_{5461} = \pm 3{\cdot}0^{\circ}$ at a concentration of 3·038 g/100 c.c to $[M]^{20}_{5461} = \pm 0{\cdot}21^{\circ}$ at C = 43·034 g./100 c.c. assuming an error of ± 0·03° in observing α_{5461}

TABLE 19.

THE ROTATORY POWERS of l-MENTHYL SALICYLATE in VARYING CONCENTRATIONS in n-HEXANE.

Temperature 20°C.

c. g./100 c.c.	α_{5463}(obs)	$[M]^{20}_{5463}$	l
4·008	- 8·63°	-297°	2
9·016	19·57°	300°	2
16·838	37·54°	306·0°	2
27·308	61·37°	310·1°	2
34·268	38·90°	313·3°	1
36·088	41·41°	316·7°	1
42·110	48·68°	319·1°	1
45·492	52·78°	320·2°	1
52·256	60·83°	321·3°	1
60·132	70·08°	321·7°	1
69·288	81·25°	323·6°	1
75·230	88·83°	325·9°	1
82 ·876	98·40°	327·7°	1
Homogeneous	125·74°	331·6°	1

Assuming an observational error of ±0·03° in the reading of the observed α_{5463}; the experimental error in the resulting graph ranges from $[M]^{20}_{5463}$ = ±1·03° at a concentration of 4·008 g/100 c.c. to $[M]^{20}_{5463}$ = ±0·08° in the homogeneous liquid.

In the above concentration graph and in all those that follow any point lying out of the general direction of the graph was checked by taking another point at approximately the same concentration.

The above Rotatory Powers were determined in a Schmidt & Haensch polarimeter fitted with a "Doppel-Monochromator" in which the incident light is passed through two sets of dispersion prisms.

The value of the Hg. green line here is λ = 5463 Å.U.

TABLE 20.

THE ROTATORY POWERS of *l*-MENTHYL BENZOATE at VARYING CONCENTRATIONS in BENZENE.

Temperature 20°C.

c. g/100 c.c.	α_{5461}	$[M]^{20}_{5461}$	l
1·998	- 4·35°	- 283°	2
3·064	6·68°	283°	2
4·000	8·68°	282°	2
10·002	21·70°	282°	2
15·114	32·75°	281·7°	2
25·908	27·11°	281·9°	1
38·584	41·88°	282·2°	1
45·072	48·94°	282·3°	1

The experimental error ranges from $[M]^{20}_{5461} = \pm 1·9°$ at $c = 1·998$ g/100 c.c to $[M]^{20}_{5461} = \pm 0·17°$ at $c = 45·072$ g/100 c.c. on the assumption that the observational error in reading α_{5461} is $\pm 0·03°$

TABLE 21.

THE ROTATORY POWERS of *l*-MENTHYL o-CHLOROBENZOATE at VARYING CONCENTRATIONS in BENZENE.

Temperature 20°C. *l* = 2 dcm.

c. g./100 c.c.	α_{5461} (obs.)	$[M]^{20}_{5461}$
2·164	- 3·62°	-246°
4·004	6·72°	247°
4·252	7·15°	247°
5·480	9·23°	248°
10·164	17·07°	246·9°
13·822	23·29°	247·7°
23·136	38·82°	246·7°
42·196	70·06°	244·1
62·928	103·46°	242°
77·012	125·80°	240°
Homogeneous (108·70)	173·47°	234·6°

Assuming an error of ± 0·03° in the observation of α_{5461} then the experimental error in the graph ranges from ± 1·02° at 2·164 g/100 c.c. to ± 0·04° in the homogeneous state.

Lack of clarity at the higher concentrations viz. 62·928 g/100 c.c. and 77·012 g/100 c.c. made accurate readings difficult.

TABLE 22.

THE ROTATORY POWERS of [illegible]-MENTHYL o-METHOXYBENZOATE at VARYING CONCENTRATIONS in BENZENE.

Temperature 20°C

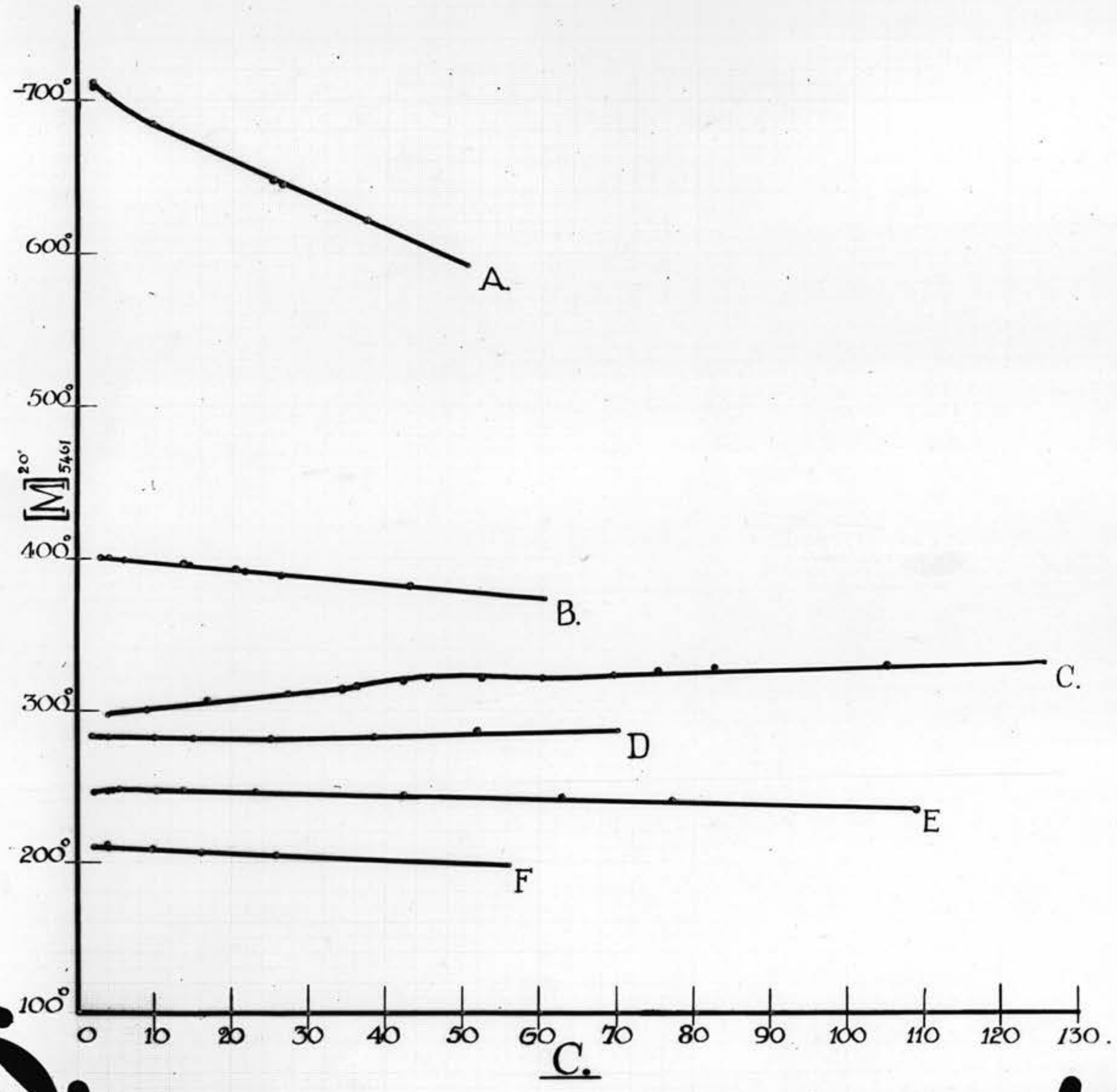
c. g./100 c.c.	α obs (5461)	$[M]^{20}_{5461}$	l
2·026	$-1{\cdot}47^{\circ}$	-210°	1
4·000	$2{\cdot}91^{\circ}$	211°	1
4·008	$5{\cdot}81^{\circ}$	210°	2
9·986	$7{\cdot}18^{\circ}$	209°	1
16·020	$2{\cdot}85^{\circ}$	206°	¼
25·976	$4{\cdot}59^{\circ}$	205°	¼

The range of experimental error is from $[M]^{20}_{5461} = \pm 4{\cdot}3^{\circ}$ at c = 2·026 g/100 c.c to $[M]^{20}_{5461} = \pm 1{\cdot}3^{\circ}$ at c = 25·976 g/100 c.c. assuming an observational error of $\pm 0{\cdot}03^{\circ}$ in the reading of α_{5461}

Readings could not be obtained beyond a concentration of 25·976 g/100 c.c. on account of the opacity of the solution in the polarimeter tube.

GRAPH III.

ROTATORY POWERS OF l-MENTHYL ESTERS PLOTTED AGAINST CONCENTRATIONS IN NON POLAR SOLVENTS.



A .... l-Menthyl o-nitrobenzoate.
B .... l-Menthyl hydrogen phthalate.
C. .... l-Menthyl salicylate.
D .... l-Menthyl benzoate.
E .... l-Menthyl o-chlorobenzoate.
F .... l-Menthyl o-methoxybenzoate.

Reference to GRAPH III, which is drawn from the data recorded in Tables 17 to 22, indicates that these expectations are realized. The curves A & B & E representing the nitro- carboxy and chloro esters respectively, have a decided downward slope, indicating that increasing concentration in the non-polar solvent benzene, results, as predicted, in a decreasing rotatory power. Curve C, representing *l*-menthyl salicylate in n-hexane,(1) has a distinct and decided upward trend, which indicates that in this solvent, increase of concentration gives rise to an increase of rotation; again as predicted. Furthermore, the slope of Curve A is steeper than that of B or E, in keeping with the greater range of values noted for the more polar nitro-ester with change of solvent (See GRAPHS I & II.) With regard to the remaining Curves D, and F, it may be stated that the somewhat indeterminate results obtained for the esters, *l*-menthyl benzoate, and *l*-menthyl o-methoxybenzoate in the solvent Tables and Graphs, is here reflected in the comparative flatness of the corresponding concentrations curves, although, as reference to Tables 20 & 22 will indicate, there is no tendency in either of these Curves towards an upward trend. In this respect these two esters fall into line with the/

---

(1) Hexane was selected in this case in the hope of detecting the presence of a maximum or minimum in the Curve, which would be expected to show more definitely in hexane than in benzene (cf. RULE & McLEAN, J.C.S., 1932, 1405)

the nitro- and carboxy- esters. In general, therefore, these results confirm the conclusions drawn by RULE HARROWER & SMITH (loc. cit.) from a study of d-octyl and d-amyl derivatives (cf. p. 32.)

Considering the results just discussed relating to the optical changes produced by varying the solvent and concentration, it would appear that in the case of the nitro, carboxy and hydroxy esters, the phenomenon of association supplies a ready means of explaining the observed data. The normal effect of the nitro and the carboxy group in the ortho position, is to raise the rotation of the unsubstituted *l*-menthyl benzoate. In the homogeneous esters it would appear that the full effect of the exaltation is masked by a certain degree of association between the ester molecules themselves. Dissolving the ester in non-polar solvents results in the more or less complete breakdown of the association aggregates and the free ester molecules may then exhibit the full effect of their substituent groups, the rotation of the ester consequently rising. On the other hand, dissolving the esters in highly polar solvents, such as nitro-benzene, leads to the formation of solute-solvent aggregates, which further diminishes the field exerted by the substituent grouping, causing a fall/

fall in rotation, below that of the homogeneous ester. Solvents of intermediate polarity act in a similar manner, the formation of solute-solvent complexes bringing about a more partial neutralisation of the dipole fields in the ester, and yielding solutions of intermediate rotatory powers. A similar explanation may be applied to the salicylic ester (which will be dealt with in greater detail later) although in this case all the optical changes are reversed in direction, possibly owing to some structural peculiarity of the hydroxy compound, such as the co-ordination between the hydroxy and ketonic groups in the ortho positions. It is probably significant that the three esters which give definite variations, are those containing the three most polar ortho substituents.

When we consider the remaining three esters, it is clear that factors other than that of dipole association are coming into play. The normal effect of the chloro and methoxy groups is to lower the rotation of the unsubstituted ℓ-menthyl benzoate. By analogy with the arguments applied to the carboxy and the nitro ester, it might have been expected that dissolving the esters in non-polar media would result/

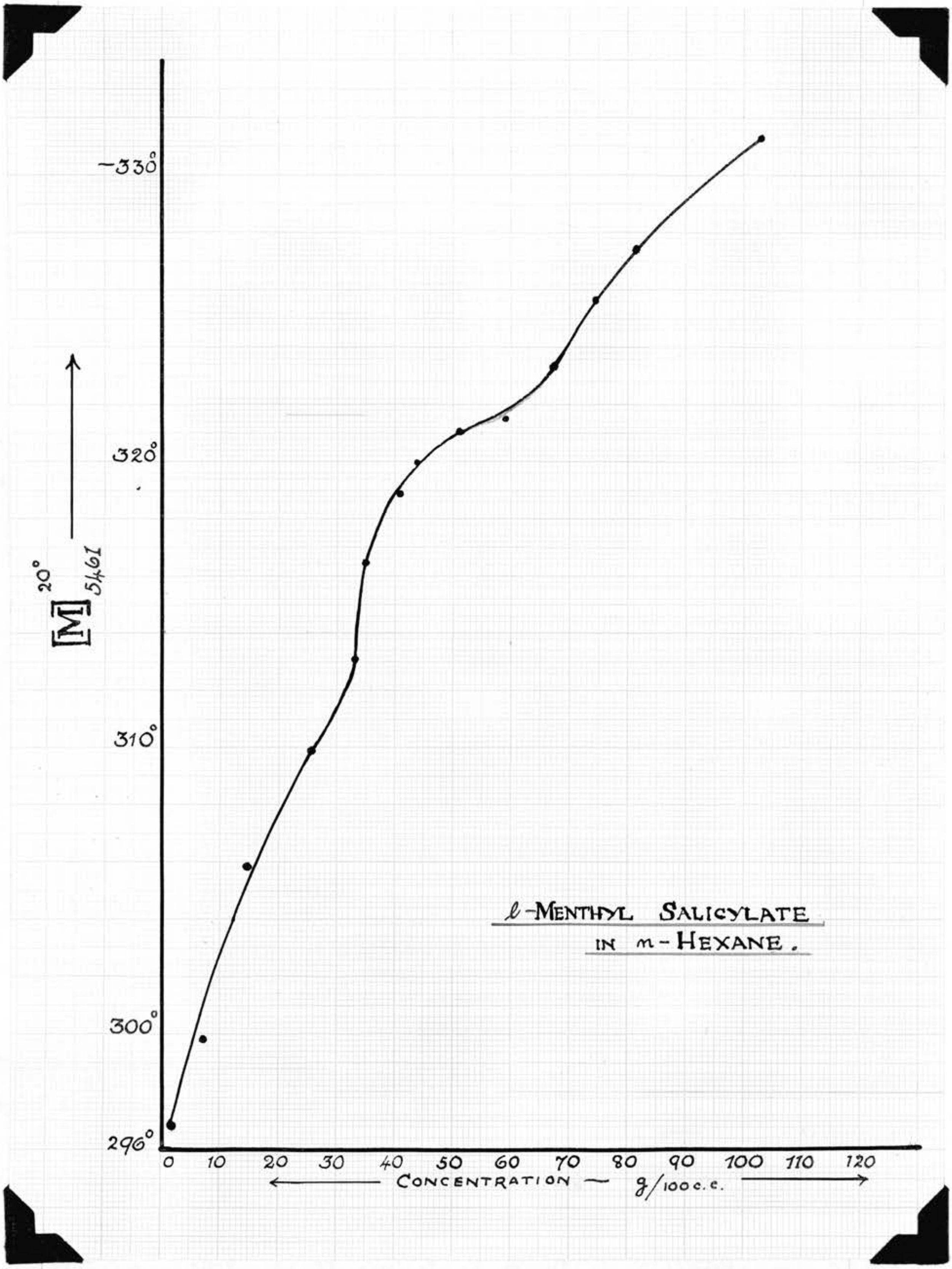
result in a lowering of the rotation, while solution in the highly polar solvents should raise the value. The solvent effect Curves show the limited extent to which such expectations are realized, and moreover, that the unsubstituted ester behaves in much the same manner. Again, on this hypothesis, increasing the concentration of the methoxy- or chloro- esters in non-polar media might have been expected to result in a rise of rotation, due to the masking of the characteristic effect of the ester dipoles by the formation of solute-solute complexes, or at least by some specific orientation of the solute molecules with respect to each other. No such effect is, however, found, as may be seen from GRAPH III. It is probable that one of the factors responsible for the small influence of solvent or concentration, is that of "screening". A comparison with the solvent effects recorded in the literature for ℓ-menthyl acetate and ℓ-octyl o-methoxy benzoate supports such a view. ℓ-Menthyl acetate (RULE & RITCHIE, J.C.S., 1932, 2335) when examined in solvents of varying polarity, showed definite changes in rotatory power, which were in good agreement with the dipole moment of the solvent. In this ester the dipoles situated in the carboxy group may be regarded as being screened by the/

the bulky menthyl residue on one side, but relatively accessible from the opposite direction. In -octyl o-methoxy-benzoate (cf. MISS SMITH, Thesis Edinburgh, 1932, or RULE, SMITH & HARROWER, J.C.S., in the press.) the dipoles of the carboxy- and methoxy-groups are again strongly screened on one side only, this time by the phenyl group. The open chain octyl residue on the other side, apparently does not seriously hinder the approach of other polar molecules, since this ester, when examined in various solvents, showed the same type of regularity as was noted in the case of ℓ-menthyl acetate. ℓ-Menthyl o-methoxybenzoate, on the other hand, showed but little regularity when examined in solvents, which may partly be attributed to the fact that here the dipoles of the carboxy and methoxy groups are screened on both sides - on one side by the phenyl and on the other by the menthyl residues, thus preventing any free approach of the solvent molecules. Such a state of affairs would also seem to apply to ℓ-menthyl o-chlorobenzoate and ℓ-menthyl benzoate. It appears, however, that the more powerful dipoles of the nitro- & carboxy groups, and to a lesser extent of the hydroxy group, when considered in relation to their molecular volumes, are sufficientyl strong to over-ride such screening/

screening effects.

In *l*-menthyl salicylate we have a compound which has abnormal properties, and it is clear that the arguments applied to the o-nitrobenzoate and hydrogen phthalate, which like the hydroxy ester have higher rotations than the unsubstituted compound, cannot hold without modification in this case. RULE & MACGILLIVRAY (J.C.S., 1929, 404) state that the menthyl esters of salicylic and anthranilic acids are the only compounds in which the presence of an o,p-directive substituent in the ortho position is known to raise the rotatory power of *l*-menthyl benzoate. These authors consider that the effects are possibly a result of the compounds existing in an internally co-ordinated state (cf. SIDGWICK, J.C.S., 1920, 402; SIDGWICK & EWBANK, J.C.S., 1921, 979), and quote in support of this view the low boiling points of the ortho isomerides as compared with those of the m- and p-compounds, and also the relatively low solubility of the salicylate in hydroxylic solvents (cf. SIDGWICK, loc.cit.). In this connection, it may be noted that TURNER (Molecular Association, p.134) records that methyl salicylate (M.W. 152) gives molecular weight values in naphthalene at C = 1·7 to C = 23 ranging from 151 to 171. This suggests that in this solvent, some/

GRAPH IV


-330°
320°
310°
300°
296°
$[M]^{20°}_{5461}$
0
10
20
30
40
50
60
70
80
90
100
110
120
CONCENTRATION ~ g/100 c.c.
l-MENTHYL SALICYLATE IN n-HEXANE.

some at least of the ester molecules are in the uncoordinated state and consequently free to participate in ordinary molecular association. It is evident, however, that if ordinary association does occur with the menthyl ester, it must lead to a rise in the rotatory power, a change which also follows when the ester is dissolved in highly polar solvents.

In addition, the optical changes which take place when the salicylate is diluted with hexane, are irregular in character, as becomes more obvious when the values of the rotatory power are plotted on a larger scale in GRAPH IV. It will be seen that a maximum is superimposed on the normal trend of the curve between the concentrations $c = 35$ and $c = 60$. This irregularity resembles that found for the rotatory power of octyl alcohol in hexane by MISS SMITH (Thesis, Edinburgh, 1932) and the maxima in the polarisations of various alcohols in non-polar solvents as observed by LANGE. Probably the explanation advanced for the polarisation phenomena by DEBYE, viz. association of the hydroxylic dipoles in the form $(-\,+)(-\,+)$ instead of the more usual $\begin{matrix}(+\,-)\\(-\,+)\end{matrix}$, also accounts for the abnormal optical properties.

Before leaving the subject of hydroxylic compounds, it was decided to investigate the optical variations/

TABLE 23.

THE ROTATORY POWERS of *l*-MENTHYL o-NITROBENZOATE in MIXTURES of BENZENE and CARBON DISULPHIDE.

Temperature 20°C.

f_2	c g/100 c.c.	α_{5461} (obs)	$[M_{1,2}]_{5461}$	$[M_2]_{5461}$	l
1·000	4·338	- 8·89°	-625°	-625°	1
0·910	5·000	41·38°	631°	622°	4
0·602	5·000	42·93°	655°	618°	4
0·318	5·000	44·22°	674°	616°	4
0·233	5·000	44·76°	683°	613°	4
0·152	5·000	45·28°	690°	600°	4
0·117	5·000	22·74°	694°	600°	4
0·035	5·000	22·93°	699°	571°	2
0·000	4·232	9·76°	703°	——	1

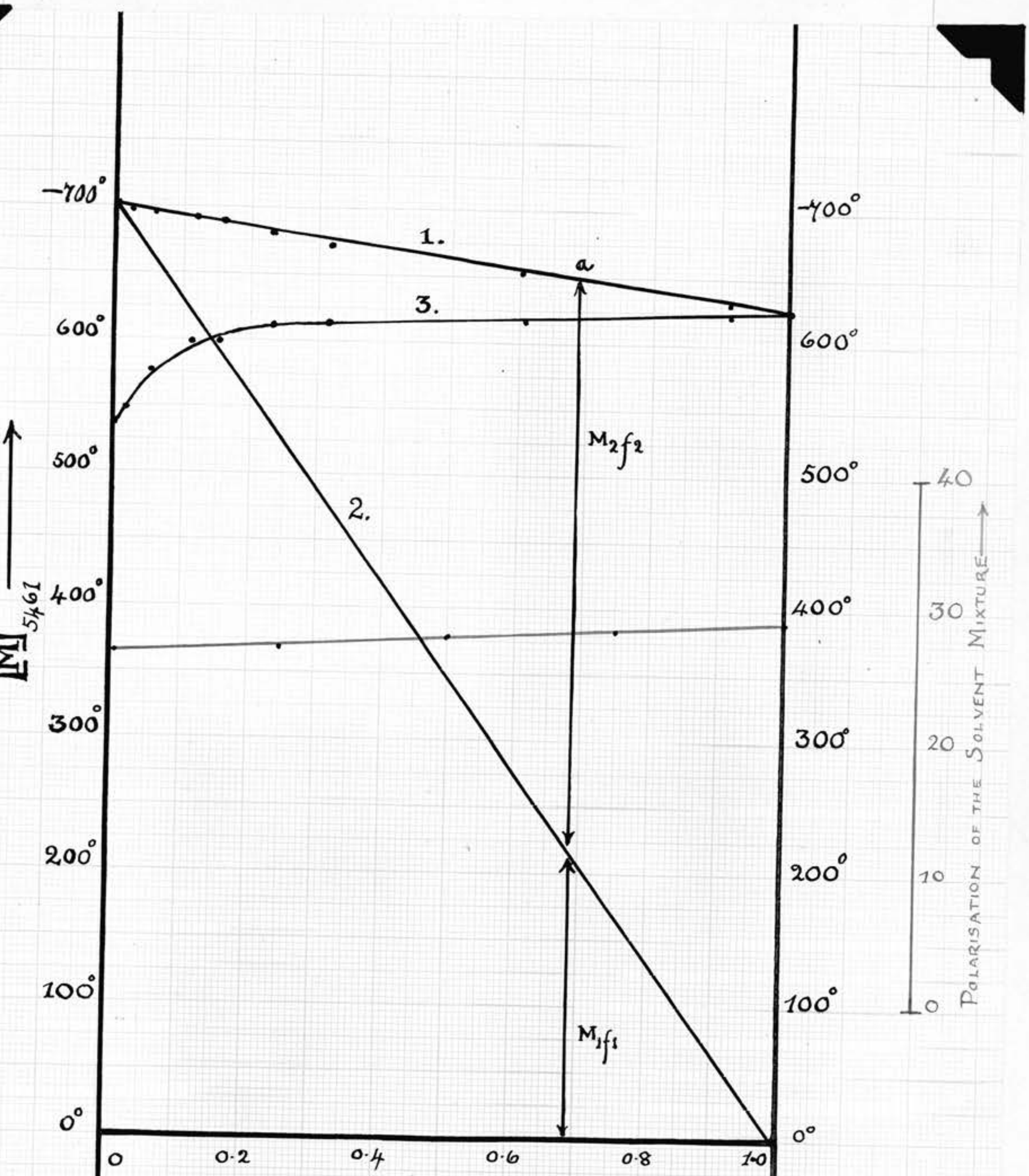
Where :-

f_2 = Mole fraction of CS_2

$[M_{1,2}]$ = Molecular rotation of ester in the C_6H_6 -CS_2 mixture.

$[M_2]$ = Calculated value of the molecular rotation used in plotting the deduced curve, indicating the rotation in the CS_2 component of the mixture.

GRAPH V



l·MENTHYL o-NITROBENZOATE
IN MIXTURES OF
BENZENE AND CARBON DISULPHIDE.

TABLE 24.

THE ROTATORY POWERS of l-MENTHYL o-NITROBENZOATE in MIXTURES of BENZENE and CARBON TETRACHLORIDE.

Temperature 20°C.

f_2	c. g/100 c.c.	α_{5461} (obs)	$[M]_{1,2(5461)}$	$[M]_{2(5461)}$	l
1·000	4·962	- 9·88°	-607°	-607°	1
0·955	5·000	40·01°	610°	606°	4
0·863	5·000	40·43°	617°	604°	4
0·631	5·000	41·89°	639°	599°	4
0·385	5·000	43·47°	663°	587°	4
0·282	5·000	44·08°	672°	582°	4
0·150	5·000	44·98°	686°	573°	4
0·060	5·000	45·62°	696°	533°	4
0·000	4·232	9·76°	703°	—	1

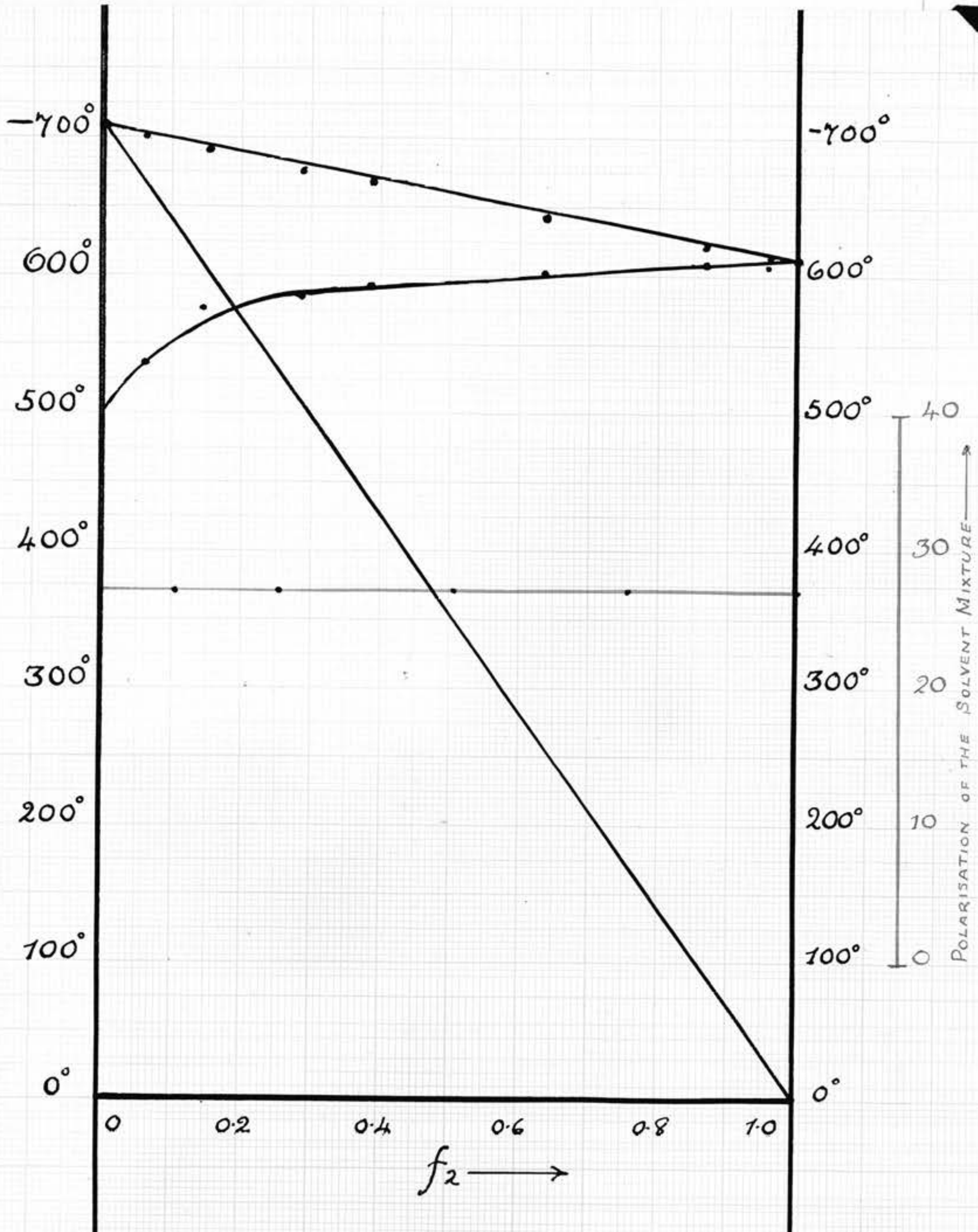
Where :-

f_2 = Mole fraction of CCl_4

$[M]_{1,2(5461)}$ = Molecular rotation of ester in C_6H_6-CCl_4 mixture.

$[M]_{2.(5461)}$ = Calculated value of the molecular rotation used in plotting the deduced curve, indicating the rotation in the CCl_4 component of the mixture.

GRAPH VI



l-MENTHYL o-NITROBENZOATE
IN MIXTURES OF
BENZENE AND CARBON TETRACHLORIDE.

TABLE 25.

THE ROTATORY POWERS of l-MENTHYL o-NITROBENZOATE in MIXTURES of n-BUTYL ALCOHOL and n-HEXANE.

Temperature 20°C.

f_2	c. g/100 c.c.	α_{5461}	$[M_{1,2}]_{5461}$	$[M_2]_{5461}$	l
1·000	5·000	-19·16°	-584°	-584°	2
0·936	"	19·16°	584°	584°	"
0·843	"	19·15°	584°	584°	"
0·787	"	19·13°	583°	586°	"
0·717	"	19·12°	583°	587°	"
0·699	"	19·14°	584°	585°	"
0·625	"	19·13°	583°	586°	"
0·601	"	19·15°	584°	586°	"
0·491	"	19·10°	583°	584°	"
0·381	"	19·04°	581°	579°	"
0·328	"	19·14°	584°	591°	"
0·266	"	19·20°	586°	604°	"
0·262	"	19·18°	585°	601°	"
0·203	"	19·15°	584°	599°	"
0·106	"	19·03°	580°	593°	"
0·000	"	18·98°	579°	-	"

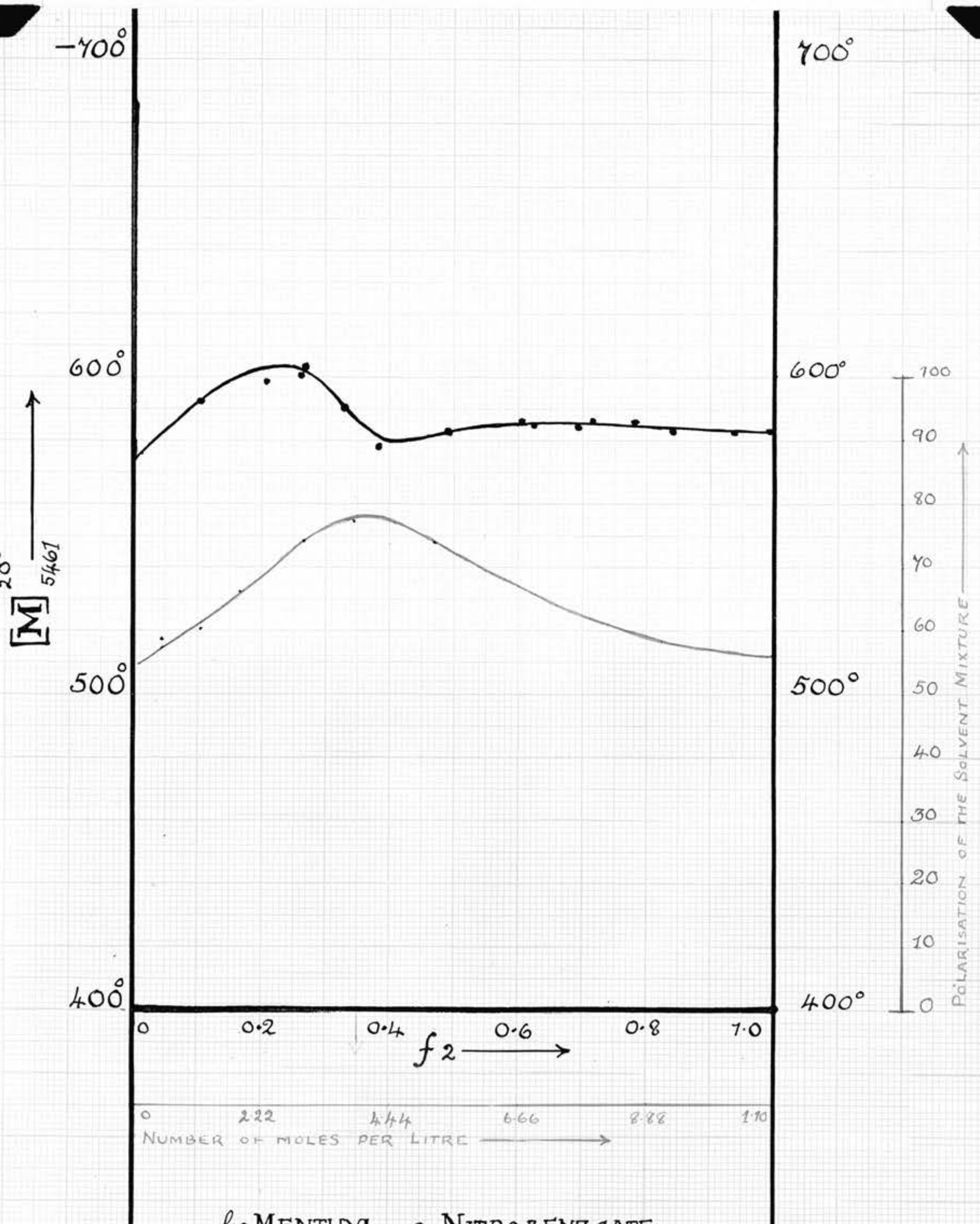
Where:-

f_2 = Mole fraction of the n-Butyl Alcohol.

$[M_{1,2}]_{5461}$ = Molecular rotation of the ester in the alcohol-hexane mixture.

$[M_2]_{5461}$ = The calculated value of the molecular rotation used in plotting the deduced curve.

GRAPH VII



l-MENTHYL o-NITROBENZOATE
IN MIXTURES OF
n-HEXANE AND n-BUTYL ALCOHOL

variations undergone by one of the benzoic esters in solvent mixtures composed of an alcohol and a non-polar medium. *l*-Menthyl o-nitrobenzoate was selected as the active solute on account of its high rotation, and n-butyl alcohol as the hydroxylic solvent because of the definite effects it has been found to give with *l*-menthyl methyl naphthalate (cf. RULE & McLEAN, J.C.S., 1932, 1400) The observed readings are given in Table 25 and the Curve deduced from these data is drawn on GRAPH VII.

As butyl alcohol exhibits a maximum value of polarisation at moderate concentrations in benzene, it was expected that this effective increase in the polarity of the benzene-alcohol mixture might be revealed in a minimum rotation power of the nitro-ester in solution. Such a depression, if it did occur, would only become fully evident when a correction had been applied for the presence of the non-polar diluent. On the other hand, if the binary mixture consisted of two non-polar solvents, such as benzene and carbon tetrachloride, or benzene and carbon disulphide,, we would expect the Graph representing change of rotation with varying composition of the solvent mixture, to be a straight line. (cf. RULE & McLEAN, J.C.S., 1932, 1401, also the introduction to this Thesis, p.31)

The/

The method of drawing the necessary deduced Curves is adopted from that due to DEBYE ("Polare Molekeln"). Reference to GRAPH V will indicate the procedure. Molecular rotations are plotted as ordinates, and mole fractions of polar solvent (f_2) as abscissae. ($f_2 = \frac{n_2}{n_1 + n_2}$, where n_1 is the number of molecules of non-polar solvent and n_2 the number of molecules of polar solvent)$^{(1)}$ In all these diagrams, the left-hand axis of ordinates represents solution in pure benzene or hexane ($f_1 = 1$) and the right-hand axis solution in pure butyl alcohol, CS_2 or CCl_4 ($f_2 = 1$). By plotting the observed molecular rotations $\left[M_{1,2}\right]^{20^\circ}_{5461}$ against the corresponding mole fractions f_2 of polar solvent, we obtain Curve 1. If we assume that the rotation due to the benzene alone is proportional to the mole fraction of this compound present in the solvent mixture, then the contribution of this component to the rotatory power is represented by a straight line, 2, joining the point representing the rotation in pure benzene to the right-hand origin. This amounts to the assumption that the benzene remains completely normal even in presence of strongly polar substances, which, as several workers have pointed out, is not necessarily the case. Nevertheless, the success that has already attended the use of such diagrams in giving/

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(1) For this purpose, CS_2 and CCl_4 are classed as potentially polar compounds.

giving results in a predicted direction would seem to indicate that the error involved is not very considerable. If from any point a on the experimental Curve, a perpendicular be dropped to the horizontal axis, then:-

$$[M_{1,2}] = [M_1] f_1 + [M_2] f_2$$

$[M_{1,2}]$, corresponding to point a, is obtained directly from Curve 1 and $[M_1] f_1$ is given by the point where the perpendicular cuts the above straight line. Hence by difference we have the value of $[M_2] f_2$ which, when divided by f_2, gives $[M_2]$, enabling us to plot a point on the curve showing the effect of the polar solvent alone on the rotation. A succession of such points (cf. Table 23) defines the Curve 3, which indicates the effect of the progressive dilution of the polar liquid on the rotatory power.

The above argument is based on the assumption that each component in the ternary system examined is at all times evenly distributed throughout the entire system. According to DEBYE & HUCKELS' theory of solutions, however, polar molecules tend to cluster around other polar molecules. When a polar solute such as ℓ-menthyl o-nitrobenzoate, is present in a mixture of polar and non-polar solvents, we might therefore expect the concentration of the polar solvent/

solvent molecules to be greater in the neighbourhood of the solute molecules than in the body of the liquid. Actually it is found that this only appears to take place to any great extent when the polar solvent is present in small concentration. In the deduced Curves 3, in GRAPHS V & VI, this influence is observable as an increased depression of the left-hand end. The depression is particularly marked below concentrations of 0·2 mole fraction in GRAPHS V & VI. (cf. RULE & McLEAN, J.C.S., 1931. 684) where the deduced Curves dip downwards towards more positive values.

The polarisation Curves of carbon disulphide in benzene (WILLIAMS & OGG, J.A.C.S, 1928, 50.1.,94) and of carbon tetrachloride in benzene (WILLIAMS & KRCHMA, J.A.C.S. 1927. 49.2., 2408) are drawn in red on GRAPHS V & VI respectively for the purpose of comparison. It may be noted that in both of these Graphs the deduced Curves, 3, are, for the major part straight lines in agreement with what might be anticipated from the corresponding polarisation Curves of carbon disulphide and carbon tetrachloride. In GRAPH VII it should be noted that the polarisation Curve (in red) of n-butyl alcohol shown is that determined by LANGE (Z. Physik, 1925, 33, 174) in benzene/

benzene solution, no data being given for n-hexane. The comparison therefore between this Curve and the deduced Curve for *l*-menthyl o-nitrobenzoate, which alone is here shown, can only be made in an approximate sense. Even so, it is evident that the maximum in the polarisation of the alcohol-benzene mixtures corresponds to a minimum in the rotatory power of the menthyl o-nitrobenzoate dissolved in the mixtures. This fluctuation realises the anticipations outlined above, and is also in agreement with the results of RULE & McLEAN (loc. cit.) for menthyl methyl naphthalate. At lower values of f_2 the rotation Curve falls in the same manner as in the CS_2 and CCl_4 diagrams.

It may therefore be concluded that the presence of a hydroxy group either in the molecule of the solvent or in that of the optically active solute, gives rise to anomalies in the rotation, such irregularities in general having a counterpart in the abnormal polarisation of the hydroxy compounds.

TABLES 34 & 26.

l-MENTHYL o-NITROBENZOATE.

a) IN NITROBENZENE.

Temperature	20°	25°	38°	59°	77°
$d_{4^\circ}^{t^\circ}$	1·200	1·195	1·182	1.163	1·147

c = 4·000 l = 1 dm.

Temperature	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
12·5°	1·207	- 5·82°	- 441°
20·0°	1·200	5·75°	439°
44·5°	1·177	5·55°	432°
46·5°	1·175	5·54°	431°
71·8°	1·151	5·38°	428°
95·8°	1·128	5·28°	429°

l-MENTHYL o-NITROBENZOATE.

b) IN DEKALIN

Temperature.	19°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	0·893	0·878	0·864	0·849

c = 4·000 l = 1 dm.

Temperature.	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
13·0°	0·898	- 7·64°	- 581°
16·0°	0·896	7·55°	576°
21·8°	0·891	7·44°	570°
34·0°	0·885	7·20°	556°
49·0°	0·871	6·96°	546°
69·2°	0·856	6·69°	533°
96·0°	0·836	6·35	519°

TABLES 35 & 27.

ℓ-MENTHYL HYDROGEN PHTHALATE.

a) IN NITROBENZENE.

Temperature	20°	40°	60°	80°
$d^{t^\circ}_{4^\circ}$	1·199	1·180	1·161	1·143

c = 4·000 ℓ = 1 dm.

Temperature	$d^{t^\circ}_{4^\circ}$	α_{5461}	$[M]^{t^\circ}_{5461}$
10·5°	1·209	- 3·91°	- 295°
20·0°	1·200	3·89°	296°
34·5°	1·186	3·82°	294°
50·0°	1·171	3·72°	290°
81·0°	1·142	3·62°	289°
98·5°	1·125	3·58°	290°

ℓ-MENTHYL HYDROGEN PHTHALATE.

b) IN DEKALIN.

Temperature.	20°	40°	60°	80°
$d^{t^\circ}_{4^\circ}$	0·8930	0·8784	0·8636	0·8496

c = 4·000 ℓ = 1 dm.

Temperature.	$d^{t^\circ}_{4^\circ}$	α_{5461}	$[M]^{t^\circ}_{5461}$
10·8°	0·899	- 5·32°	- 402°
17·0°	0·895	5·33°	404°
35·5°	0·882	5·22°	402°
47·5°	0·873	5·10°	397°
76·0°	0·853	4·97°	396°
94·5°	0·839	4·82°	390°

TABLES 36 & 28.

l - MENTHYL SALICYLATE.

a) IN NITROBENZENE.

Temperature.	20°	42°	60°	80°
$d_{4^\circ}^{t^\circ}$	1·197	1·176	1·159	1·140

c = 4·000 l = 1 dm.

Temperature.	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
13·2°	1·203	- 4·98°	- 341°
22·0°	1·195	4·91°	339°
34·0°	1·184	4·82°	336°
48·2°	1·170	4·72°	333°
74·5°	1·145	4·61°	332°
97·0°	1·123	4·45°	327°

l - MENTHYL SALICYLATE

b) IN DEKALIN.

Temperature.	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	0·891	0·876	0·862	0·847

c = 4·000 l = 1 dm.

Temperature.	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
13·4°	0·896	- 4·92°	- 337°
22·3°	0·890	4·88°	337°
36·0°	0·879	4·85°	338°
47·0°	0·871	4·82°	339°
[illegible]	0·851	4·75°	343°
	0·834	4·68	344°

TABLES 37 & 29.

l-MENTHYL BENZOATE.

a) IN NITROBENZENE.

Temperature.	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	1·195	1·176	1·157	1·139

c = 4·000 l = 1 dm.

Temperature.	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
14·5°	1·201	- 4·38°	- 283°
21·6°	1·194	4·32°	281°
35·5°	1·181	4·25°	280°
47·2°	1·170	4·17°	277°
73·0°	1·145	4·07°	276°
97·7°	1·122	3·96°	274°

l-MENTHYL BENZOATE.

b) IN DEKALIN.

Temperature.	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	0·890	0·875	0·861	0·846

c = 4·000 l = 1 dm.

Temperature.	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
15·2°	0·893	- 4·19°	- 272°
21·5°	0·888	4·17°	272°
34·5°	0·879	4·15°	274°
48·2°	0·869	4·12°	275°
67·0°	0·855	4·09°	277°
96·8°	0·834	4·08°	284°

TABLES 38 & 30.

l-MENTHYL o-CHLOROBENZOATE

a) IN NITROBENZENE.

Temperature	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	1·119	1·180	1·160	1·141

c = 4·000 l = 1 dm.

Temperature	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
12·5°	1·206	- 3·19°	- 233°
21·2°	1·198	3·15°	232°
36·0°	1·186	3·06°	227°
46·2°	1·174	3·02°	227°
72·0°	1·149	2·99°	229°
96·0°	1·126	2·91°	228°

l-MENTHYL o-CHLOROBENZOATE

b) IN DEKALIN.

Temperature	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	0·893	0·878	0·863	0·849

c = 4·000 l = 1 dm.

Temperature	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
10·5°	0·900	-3·57°	-260°
19·5°	0·893	3·55°	260°
35·0°	0·882	3·52°	262°
50·0°	0·870	3·50°	264°
72·0°	0·854	3·50°	268°
98·0°	0·835	3·52°	276°

TABLES 39 & 31.

l-MENTHYL o-METHOXYBENZOATE

a) IN NITROBENZENE.

Temperature	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	1·197	1·178	1·159	1·140

c = 4·000 l = 1 dm.

Temperature	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
12·0°	1·204	− 2·81°	− 202°
21·0°	1·196	2·74°	199°
36·0°	1·182	2·65°	194°
45·0°	1·173	2·59°	191°
77·0°	1·149	2·51°	189°
98·0°	1·123	2·48°	192°

l-MENTHHYL o-METHOXYBENZOATE

b) IN DEKALIN.

Temperature	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	0·891	0·876	0·861	0·847

c = 4·000 l = 1 dm.

Temperature	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
12·5°	0·896	−2·29°	− 165°
20·0°	0·891	2·38°	172°
35·5°	0·879	2·51°	184°
48·5°	0·869	2·52°	187°
74·0°	0·851	2·64°	200°
98·5°	0·833	2·72°	211°

TABLES 32 & 33.

l- MENTHYL o-NITROBENZOATE.

c) IN BROMOBENZENE.

Temperature.	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	1·483	1·457	1·431	1·405

c = 4·000 l = 1 dm.

Temperature	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
13·2°	1·492	- 7·81°	- 591°
20·0°	1·483	7·60°	579°
48·0°	1·447	7·05°	550°
66·0°	1·423	6·80°	540°
98·5°	1·381	6·35°	519°

l -MENTHYL o-NITROBENZOATE.

b) IN BENZONITRILE.

Temperature.	9°	20°	40°	60°	80°
$d_{4^\circ}^{t^\circ}$	1·019	1·008	0·9919	0·9752	0·9581

c = 4·000 l = 1 dm.

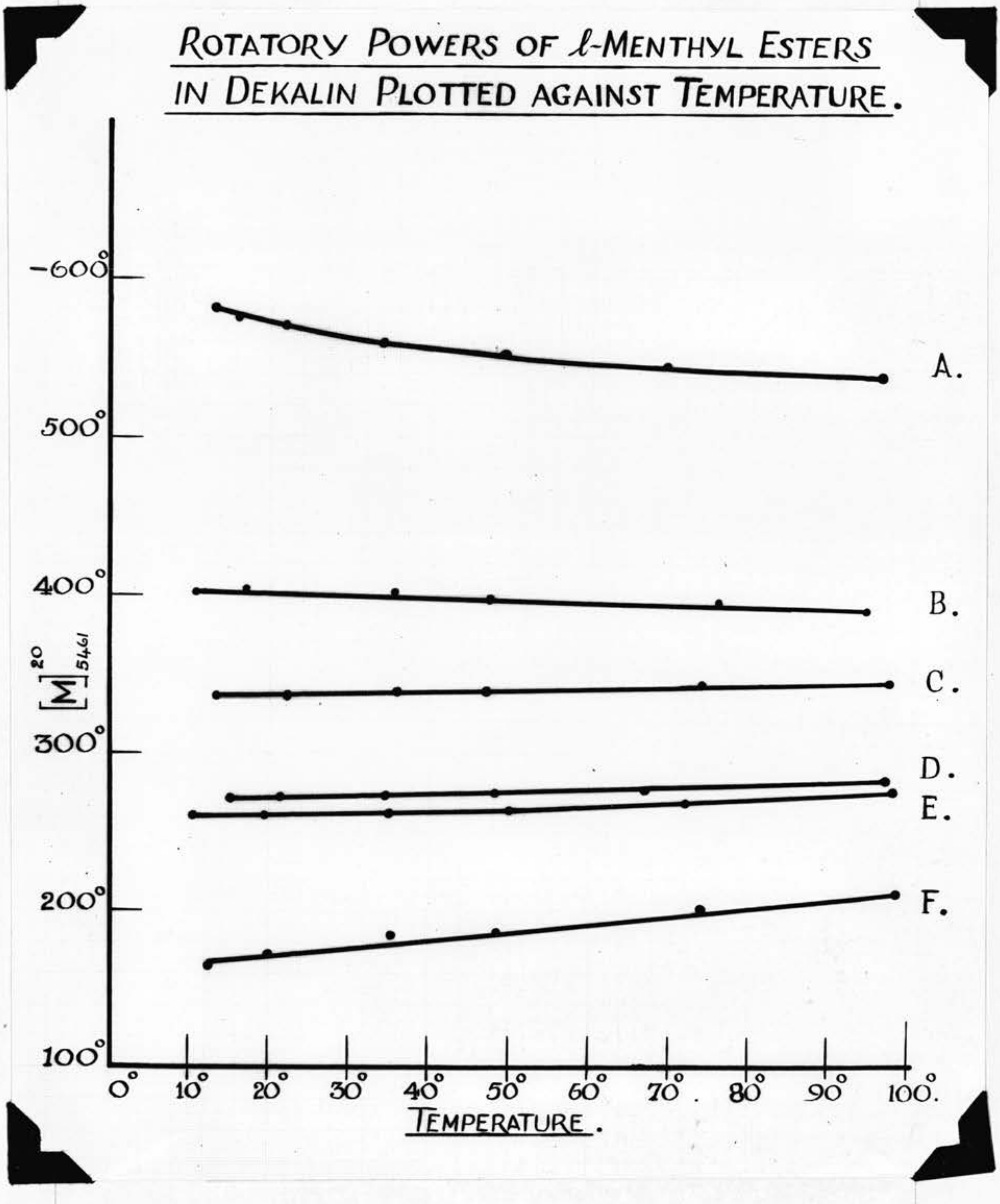
Temperature.	$d_{4^\circ}^{t^\circ}$	α_{5461}	$[M]_{5461}^{t^\circ}$
11·0°	1·017	- 6·27°	- 476°
21·0°	1·005	6·13°	471°
36·0°	0·994	5·92°	459°
49·8°	0·983	5·79°	454°
78·0°	0·960	5·55°	446°
96·8°	0·944	5·39°	441°

INFLUENCE OF TEMPERATURE

Turning now to the effect of temperature upon the rotation of the menthyl esters in solution, it might have been anticipated that an increase of temperature, in so far as it would tend to break up association complexes and diminish molecular orientation generally would have the same effect as diluting the esters with a non-polar medium. GRAPH VIII showing the effect of temperature upon the rotatory power of the six esters in dekalin indicates that little or no evidence of such a change can be observed. It is obvious however, that there is a steady change in the slope of the Graphs as we pass from the highly active nitro compound to the least active ester, the methoxy derivative. At the one extreme, the rotation falls with rise of temperature, and at the other, the rotation rises.

One explanation of these changes is suggested by the work of EBERT (Leipziger Vortrage, 1930, 60) mentioned on page 19 of the introduction. It has already been stated (cf. page 19) that the influence of substituents in the ortho-position of the benzoic esters, is probably largely a spatial effect. Rise of temperature will result in an increased molecular vibration which in turn may be supposed to/

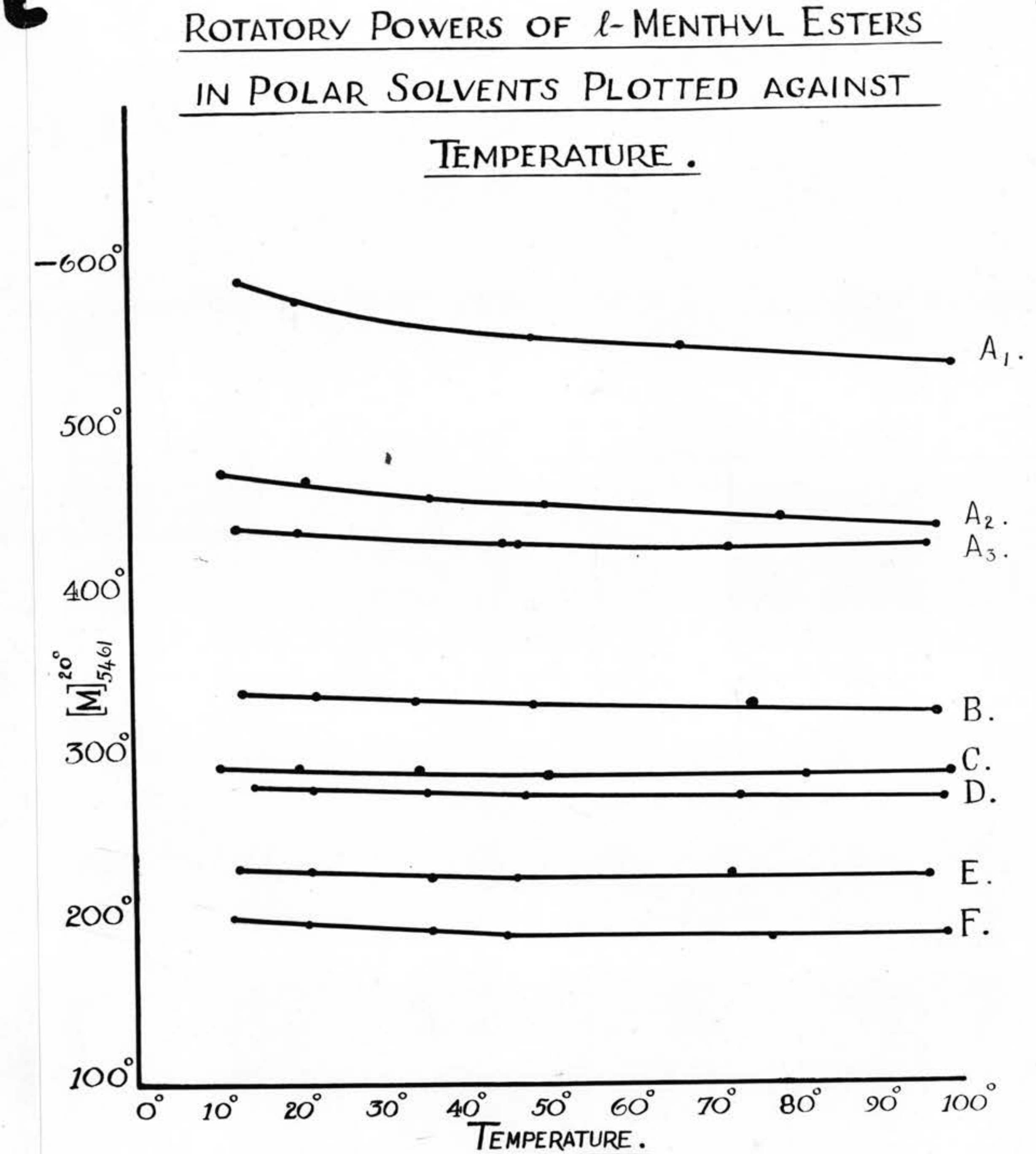
GRAPH VIII



A .... ℓ -Menthyl o-nitrobenzoate.
B .... ℓ -Menthyl hydrogen phthalate.
C .... ℓ -Menthyl salicylate.
D .... ℓ -Menthyl benzoate.
E .... ℓ -Menthyl o-chlorobenzoate.
F .... ℓ -Menthyl o-methoxybenzoate.

to lead, on Ebert's views, to an increase in the average mean distance between the $-COOC_{10}H_{19}$ group and the substituent group in the ortho position. If now, the introduction of the ortho substituent has an exalting effect upon the rotation of the unsubstituted ester, then it might be expected that a rise of temperature would cause a fall in rotation. The nitro- and carboxy- derivatives fall into this category and as may be seen, the appropriate temperature Curves each indicate a definite fall in rotation, with increasing temperature. As is to be expected on this hypothesis, the nitro-ester, which has the highest rotatory power, shows a more rapid fall than the less active menthyl hydrogen phthalate. A similar explanation would seem to hold for the nitro-ester in bromobenzene and benzonitrile, Curves A_1 and A_2, on GRAPH IX. Where, however, the normal effect of the ortho-substituent is to lower the rotation, then a rise of temperature on Ebert's observations should result in a rise of rotation. The chloro- and methoxy- esters both show such a rise, the latter in keeping with its very low rotatory power, as compared with *l*-menthyl benzoate, showing the greater change with increase of temperature. *l*-Menthyl benzoate shows an increasing rotation to the extent of 12° while/

GRAPH IX



ROTATORY POWERS OF *l*-MENTHYL ESTERS IN POLAR SOLVENTS PLOTTED AGAINST TEMPERATURE.

A_1.... *l*-Menthyl o-nitrobenzoate in C6H5Br.
A_2.... *l*-Menthyl o-nitrobenzoate in C6H5CN
A_3.... *l*-Menthyl o-nitrobenzoate in $C_6H_5NO_2$
B .... *l*-Menthyl salicylate in $C_6H_5NO_2$
C .... *l*-Menthyl hydrogen phthalate in $C_6H_5NO_2$
D .... *l*-Menthyl benzoate in $C_6H_5NO_2$
E .... *l*-Menthyl o-chlorobenzoate in $C_6H_5NO_2$
F .... *l*-Menthyl o-methoxybenzoate in $C_6H_5NO_2$

while the salicylic ester shows an even smaller change. When we come to consider the esters in nitrobenzene solution (cf. Tables 34-39) it is found that in every instance there is a small drop in the rotation value with rising temperature. In no case, however, is this greater than 14° and there is no apparent regularity in the data obtained. (cf. also GRAPH IX).

Only in the case of the nitro-, carboxy-, and chloro- esters does solution in dekalin result in an appreciable increase of the rotation value for the corresponding homogeneous esters. It is felt that in the remaining three esters the changes, consequent upon dissolving the optically active compounds in this solvent, are insufficient to warrant the drawing of conclusions. With regard to the recent generalisation of PATTERSON, DUNN, BUCHANAN & LOUDON, mentioned on page 33 of this Thesis, it should thus be found that rise of temperature in the case of the nitro-, carboxy- and chloro- esters, in dekalin, should result in a fall, or at most a slight increase, in rotatory power. As Tables 26, 27, and 30 indicate, this holds in a marked degree for the nitro-ester, where a rotation value of -581° at 13° is changed to one of -519° at 96°, and to a lesser extent for the carboxy/

carboxy ester. Possibly the chloro-ester may also be considered as coming within the scope of the above prediction, as it suffers a rise of only 16° when the dekalin solution is examined over a temperature range similar to that used for the nitro- and carboxy-esters.

When we consider the esters in nitrobenzene solution, it is found that this solvent depresses the value of the homogeneous nitro-ester to the extent of 53° and raises that of the methoxy ester by 25°. Nevertheless, raising the temperature of the nitrobenzene solutions of these esters to similar extents, results in a fall of rotation in both cases; again the carboxy-ester, which has, in nitrobenzene, an appreciably lower rotation value than in the homogeneous condition, also exhibits a slight fall under comparable conditions. Such results are clearly not in agreement with Patterson's generalisation. In this solvent then, it appears that some secondary influences are at work, and moreover, the extent to which these are exerted is such as to mask completely any regularities which might be interpreted in the light of Ebert's observations, or correlated with the results obtained in dekalin, and in general agreement with the work of PATTERSON and his co-workers.

SUMMARY AND CONCLUSION

INFLUENCE of SOLVENTS and of CONCENTRATION.

An investigation has been made of the solvent influences exerted by liquids of the same molecular type (monosubstituted benzenes and substituted derivatives of methane) upon the rotatory powers of the six ℓ-menthyl o-substituted benzoates prepared in the experimental part of this Thesis. In the case of ℓ-menthyl o-nitrobenzoate and ℓ-menthyl hydrogen phthalate, excellent agreement between rotatory power and dipole moment of solvent employed, was found to exist: the rotation being highest in those solvents of low and zero dipole moment, and lowest in those of high dipole moment (cf. RULE & co-workers, J.C.S., 1931,674,2652; 1932,1409,2332). Indications of a similar relationship were given by ℓ-menthyl salicylate in solution: here, however, in general, an inverted order of effects was noted, the highest rotations being recorded in those solvents of highest dipole moment. Of the remaining three esters, ℓ-menthyl o-chlorobenzoate was found to give changes in solution similar to, although less marked, than those of the nitro and carboxy- esters, while ℓ-menthyl benzoate and ℓ-menthyl o-methoxybenzoate gave results which/

which were small and indeterminate. The fact that the three esters which contain the most polar ortho-substituents, viz., NO_2, COOH, and OH are those which give the most definite solvent and concentration effects is, it is thought, significant.

Solvents of two types, viz., those derived from the parent hydrocarbon benzene and those from methane, were employed in the above investigations. In general, those of the former type gave the more regular results, a fact which, it is suggested, is due to the stabilising influence of the rigid aromatic nucleus and to the greater tendency of the esters to exist in the associated state in non-polar aliphatic solvents.

A graphical method of showing these results indicated that the diagrams obtained on plotting molecular rotation against the dipole moment of the solvent, although showing similar irregularities for certain solvents, differed chiefly in their angle of slope. The rotatory power of the highly active nitro ester fell off rapidly as the polarity of the solvent increased; the rate of change was somewhat less with the carboxy ester, and still less, and in the opposite direction, for the less active salicylate. Apart from these variations, no very specific effects towards solvent influence are shown when the ortho-hydrogen/

ortho-hydrogen atom in menthyl benzoate is replaced by NO_2, COOH, OH, Cl or OMe.

When various di-substituted benzenes were used, admixed with benzene, as solvents, it was found that *o*-$C_6H_4Cl_2$, which has a high dipole moment, behaved as a strongly polar medium. It thus depressed the rotation of *l*-menthyl *o*-nitrobenzoate to a greater extent than an equivalent molecular proportion of the corresponding monosubstituted halogen compound. The para-compound has zero dipole moment, nevertheless, it was found that it behaved as a relatively strong polar solvent. This peculiarity is explained on the assumption that in p-dichlorobenzene the oppositely oriented chloro-groups are held so far apart by the rigid benzene ring that they can, in large measure, exert their influences independently towards an adjacent optically active molecule. This same explanation should hold for p-dinitrobenzene, which also has a zero dipole moment. Owing to the low solubility of the dinitro-compounds in benzene, the range of values obtained when m- and p-dinitrobenzenes were used as component solvents, was slight, because of the small mole fraction of these substances present in the solution. The results obtained were consequently not so decisive as in the case of the di-substituted halogen/

halogen compounds, but indicated clearly that p-dinitrobenzene does function as a polar substance in spite of its zero dipole moment. These conclusions are in general agreement with those of RULE & HILL (loc. cit.) and RULE & McLEAN (loc. cit.).

Following a suggestion of Rule (cf. RULE, SMITH & HARROWER, loc. cit.) we were enabled, from a consideration of the various solvent influences, to predict, with considerable accuracy, the effect that an increasing concentration of the solute, in a non-polar medium, would have upon the rotation. Thus, the concentration Curves of ℓ-menthyl o-nitrobenzoate, ℓ-menthyl hydrogen phthalate and ℓ-menthyl o-chlorobenzoate all indicated a definite decrease of rotation with increasing concentration of solute in non-polar solvents; while ℓ-menthyl salicylate under similar conditions, manifested, as anticipated, the opposite effect. Hence it may be concluded that the nitro and carboxy esters exhibit diminished rotations, either through association with a highly polar solvent, or by self-association when the concentration in a non-polar solvent is increased. With the salicylate the direction of these optical changes is reversed. The rotation-concentration Graph for menthyl salicylate in hexane also showed a decided upward/

upward inflexion between c = 35 and c = 60. It has been pointed out that the existence of such an inflexion for the salicylate is in general agreement with the results of RULE, SMITH & HARROWER (loc. cit.) for octyl alcohol. A similar type of effect was noted by PATTERSON & McDONALD (J.C.S., 1908, 937) for ethyl tartrate in benzene. These irregularities would seem to be characteristic of compounds containing a hydroxy group. In the case of the two remaining esters, *l*-menthyl benzoate and *l*-menthyl o-methoxybenzoate, somewhat small and irregular solvent influences were reflected in concentration Curves of no very definite inclination. The above assumption, supplemented by a consideration of molecular screening in the cases of the chloro-, methoxy and the unsubstituted menthyl benzoate, furnished a satisfactory explanation of the observed data.

A further consideration of Rule's suggestion leads to another interesting conclusion. *l*-Menthyl o-substituted benzoates, due to the large proportion of hydrocarbon radicals in the molecules, are, bulk for bulk, relatively less polar than solvents of the benzene or methane type containing a similar substituent group. Thus, in such highly polar solvents as nitrobenzene/

nitrobenzene and nitromethane, it should be found for example, that the nitro ester possesses a rotation lower than that of the homogeneous active liquid. On the other hand, in hydrocarbon media, such as benzene or hexane, the ester, at high dilution, largely exists in the unassociated state, and may be regarded as exhibiting a rotatory power more truly characteristic of the molecular structure than that observed in the homogeneous condition, or in the presence of polar solvents. This rotation value therefore, will be higher than that of the homogeneous ester. The series of solvents employed in the present investigations of solvent effect, ranged from non-polar hydrocarbons to the very highly polar nitro- and cyano-compounds. It might then be anticipated that the esters in the homogeneous state would all posses rotatory powers intermediate in value between those observed in solvents of the two extreme, polar and non-polar, types. The experimental results indicate that for each of the six esters examined, this generalisation holds.

l-Menthyl salicylate has been made the subject of a special explanation. On the observations of SIDGWICK, and SIDGWICK & EWBANK (loc. cit.) it is postulated that the abnormal results obtained with this ester, are partly due to the fact that it exists in/

in the form of a co-ordinated compound, in which the hydroxy and ketonic groups in the ortho position to each other, are concerned. It is considered probable, in view of the molecular weight values quoted in the literature for methyl salicylate in naphthalene, that some at least of the menthyl salicylate molecules are in the un-co-ordinated state, and therefore, free to participate in ordinary molecular association. To explain the maximum observed in the rotation-concentration diagram for this ester in hexane, it is suggested that the kind of association which takes place is that indicated by DEBYE in his polarisation researches, in which the dipoles orient themselves in the form $(- \; +)(- \; +)$, as well as in the form $\begin{matrix}(+ & -)\\(- & +)\end{matrix}$

That the hydroxyl group leads to abnormalities when present in the solvent molecule, as well as in that of the solute, is shown by the Graph illustrating the optical variations undergone by ℓ-menthyl o-nitrobenzoate when examined in a binary solvent mixture of n-hexane and n-butyl alcohol. It was found, as anticipated, that a minimum in the deduced rotation Curve of the nitro ester, corresponded to a maximum in the polarisation Curve of the n-butyl alcohol mixture, and it is concluded that abnormalities in polarisation are reflected in corresponding anomalies/

anomalies in the rotation of the optically active solute. These results, and those obtained by the examination of the same ester in the binary solvent mixture of benzene-carbon tetrachloride and benzene-carbon disulphide, are shown to be in agreement with the similar researches of Rule and McLean on *l*-menthyl methyl naphthalate.

In view of the type of esters examined in this Thesis, the following observations of W. KUHN (Stereochemie, Freudenberg, 1932, page 420-421) are of particular interest. He points out that substitution in the phenyl grouping of *l*-menthyl and *l*-octyl benzoates, almost certainly produces a greater change in the absorption spectra of the unsubstituted compound, than does a similar substitution in the corresponding esters of acetic acid. Furthermore, he observes that these same substituents have a very much greater effect in altering the rotatory power of the unsubstituted benzoate than that of the unsubstituted acetate. When it is remembered that the absorption bands of the unsubstituted benzoate are already very close to the visible region of the spectrum one may assume with certainty that change in the rotatory power of *l*-menthyl and *l*-octyl benzoate, following upon substitution in the phenyl residue, may be referred back to alteration in the nature and position of the absorption bands/

bands which are characteristic of the phenyl group. Such an assumption gives additional justification for the suggestion (cf. page 33.) that the present work on solvent influences can be correlated with the theories of KUHN, via the researches of SCHEIBE.

KUHN (ibid.) also stresses the point that the phenyl group, in the above respect, is to be considered as a single unit, and that it has the faculty of transmitting, with facility, substituent influences which have an important bearing on rotatory power. BRIEGLEB has recently observed (Zeit. fur phys. Chem. 1932, B.16,249.Pt.II) that even among substances of zero dipole moment and which contain no polar groups, electrical differences are to be found which are due to the polarisation of the molecules and especially to a certain anisotropy of polarisability. This is found to be the case to a quite appreciable extent with benzene. Any set of conditions which alters the electrical equilibrium of the phenyl grouping, due to its anisotropic properties under the influence of an electrical field, will, it may be imagined, interfere with the transmissions of substituent influence. These conditions which bring about a deformation of the normal configuration of the phenyl/

phenyl grouping (e.g. the presence of highly polar solvent molecules) will, at the same time, have some specific effect upon the substituent group itself. Both of these effects will make their contribution towards the rotation actually observed.

The added complexity which considerations such as the above introduce into the study of the *l*-menthyl o-substituted benzoates, is at once apparent.

It has already been suggested that the main features encountered in an examination of *l*-menthyl o-substituted benzoates in numerous solvents, and at varying concentrations in non-polar solvents, can be accounted for by the postulation of an association of solute molecules with each other and with the molecules of the solvent employed. The more strongly polar the solvent, the greater is this tendency towards the formation of solute-solvent complexes supposed to be. Non-polar solvents, on the other hand, tend, in large measure, to break down the solute-solute complexes which may exist in the homogeneous active ester. In the esters containing the less polar substituent groups, Cl and OMe, in the ortho-position, an additional consideration, namely that of screening, was taken into account.

The above conclusions are of particular interest since WALDEN (Ber. 1905, 38.1.389), in an extensive review of the earlier work done in connection with the/

the rotatory powers of optically active compounds, remarks that the influence of solvents in affecting the rotation of an optically active solute, is probably twofold. It is due to (a) its power of affecting the degree of association of the solute molecules with each other, and (b), a constitutive factor. Despite the argument of many workers in this field to the effect that the degree of association is not related to the magnitude of the rotatory power, the evidence advanced by Rule, Smith and Harrower, and that contained in the present Thesis, goes far to confirm the accuracy of Walden's views. We now realise that the constitutive factor is the electrical structure of the solvent, which controls not only its power of altering the degree of association between solute molecules, but also, its ability to bring about association between solute and solvent.

INFLUENCE of TEMPERATURE

It was anticipated that rise of temperature would diminish the degree of association and thus have the same effect upon rotation as diluting the esters with a non-polar medium. This was not found to be the case and, to account for the observed facts, use is made of a conclusion of EBERT'S (cf. page 19) which involves an increase in the mean distance between/

between the two groups in the ortho position with increasing temperature. It seems possible that any changes in the degree of association brought about by variation in temperature are, in the present cases, small in their effect upon the rotatory power, compared with the influence of configurational changes in the mean positions of the molecule. Ebert's views account satisfactorily for the case of the six *l*-menthyl o-substituted benzoates in the non-polar solvent dekalin. A rise of temperature appears to affect the rotatory power of these esters in dekalin in a graded sense, as we pass from the highly active nitro ester, for which a rise of temperature leads to a pronounced fall in rotation, to the least active methoxy ester, the rotation of which rises with increasing temperature. Thus, the high rotation brought about by the introduction of the nitro, or carboxy groups, into the ortho position, falls off with rise of temperature. Similarly, the lowering in the rotation caused by the presence of the o-methoxy group, tends to disappear. Both of these changes are in the direction to be expected, if, as assumed by Rule, the optical effects are mainly due to the substituent influence transmitted directly through space. The phenomena observed in dekalin are also correlated in part, with the generalisation of/

of PATTERSON, DUNN, BUCHANAN and LOUDON (cf. page 33) to the effect, that for a solvent which raises the rotatory power the value will be diminished by an increase in temperature. It is suggested that in nitrobenzene solution, secondary influences come into play, which completely mask any regularities existing between temperature change and variation of rotation.

I offer my sincere thanks to Dr Rule for his most valuable attention and guidance throughout the course of these researches, and, at the same time, desire to express my appreciation of that most refreshing spirit of enthusiasm with which his unfailing interest was always imbued.