XCIII.—*Studies in Solvent Action. Part I. Influence of Polar Solvents on the Rotatory Power of* l-*Menthyl Methyl Naphthalate.*

By H. GORDON RULE and ANDREW MCLEAN.

IN earlier communications of these series, evidence has been brought forward indicating that the optical rotation of a dissymmetric compound is dependent upon the magnitude and disposition of the dipoles within the molecule.* Optical activity is thus one of the many properties which may be treated according to the theory of dipoles. In discussing the disturbing influence of electrical forces on the behaviour of a molecule, Debye refers among other causes to that exerted by the fields of neighbouring molecules. Such fields may arise from adjacent molecules of the optically active substance or from those of an added solvent. So far, little or no definite progress has been made in elucidating the connexion between the molecular structure of a solvent and its effect upon the rotatory power of an optically active substance dissolved in it. The problem is obviously one of an intricate nature, but the success already achieved in tracing the polar influence of substituents forming a part

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* It has been assumed that the optical activity is not so much a function of the polarisation of the molecule as a whole (*i.e.*, with respect to a uniform external field) as of the arrangement of the individual dipoles around the asymmetric atom. This represents a fundamentally different standpoint from that more recently suggested by Betti (*Trans. Faraday Soc.*, 1930, **26**, 345), who correlates the rotatory power directly with the molecular polarisation.

of the asymmetric molecule has encouraged the hope that similar methods would reveal the existence of a polar factor in solvent effect.

A first step in this direction was made during the investigation of the rotatory powers of β-octyl esters of various monosubstituted acetic acids when dissolved in liquid media (Rule and Mitchell, J., 1926, 3202), as the result of which it was suggested 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" (J., 1927, 58). Although no general regularities were detected for the solvents as a whole, it was observed that among several closely related liquids, *viz.*, the monosubstituted benzenes, C_6H_5X, the rotatory powers for variations of X were given by $CH_3>H>OEt>Cl>Br>I$. This is a polar series, the arrangement of which is almost the exact reverse of that representing the influence of the same substituents when present in the optically active molecule, *viz.*, $I>Br>Cl>OMe>CH_3>H$. In the latter case, the more highly polar the substituent the higher is the rotation of the ester, whereas in the solvent molecule the direction of the change is reversed, highly polar solvents giving a low value.

Further confirmation of a polar influence exerted by the solvent molecule was indicated in the properties of *l*-menthyl esters of peri-substituted naphthoic acids, among which the nitro-group greatly raises the rotation of *l*-menthyl 1-naphthoate, whilst chlorine and the methoxyl group lower the activity (Rule, Spence, and Bretscher, J., 1929, 2516). It was noted that, whether the substituent increased or decreased the rotatory power, its characteristic influence tended to be exhibited to the maximum degree in hydrocarbon solvents. Highly polar solvents, on the other hand, appeared to diminish the effect of the peri-substituent.

The discovery of an ester, *l*-menthyl methyl naphthalate (see this vol., p. 669), with a rotatory power extremely sensitive to solvent structure has now led to a detailed investigation of this phenomenon. As regularities in solvent influence among the β-octyl acetates were only observed with liquids of similar molecular constitution, the solvents selected in the present case are restricted to four main types, *viz.*, simple derivatives of the four hydrocarbons methane, ethane, benzene, and naphthalene. In the first instance the rotatory power of the *l*-menthyl methyl naphthalate was determined in each solvent at a concentration of approximately $c = 4$. The observed data together with the dipole moments of the solvents are given in Tables I and II, the arrangement being in order of increasing rotatory powers. Solvents in parentheses strictly belong to another series, but are included to show the influence of an additional alkyl group.

TABLE I.

Rotatory Powers of l-*Menthyl Methyl Naphthalate in Solvents derived from Methane and Benzene.*

Solvent.	$[M]^{20^\circ}_{5461}$.	$\mu \times 10^{18}$.	Solvent.	$[M]^{20^\circ}_{5461}$.	$\mu \times 10^{18}$.
$CH_3\cdot NO_2$	-219°	3·78	$C_6H_5\cdot CN$	-372°	3·85
$CH_3\cdot CN$	239	3·05	$C_6H_5\cdot NO_2$	423	3·89
CH_2Cl_2	267	1·61	$C_6H_5\cdot CHO$	432	2·75
CH_2Br_2	277	1·89	$[C_6H_5\cdot COMe]$	[454]	[2·97]
$CH_3\cdot CHO$	316	2·71	$o\cdot C_6H_4Cl_2$	433	2·24
CH_3I	336	1·66	$C_6H_5\cdot NH_2$	443	1·60
$CHCl_3$	362	1·10	C_6H_5Cl	463	1·52
$CH_3\cdot OH$	383	1·64	C_6H_5I	465	1·50
$CH_3\cdot CO_2H$	423	0·75	C_6H_5Br	466	1·50
$CHBr_3$	429	1·3	$C_6H_5\cdot OMe$	466	1·25
CS_2	437	0	C_6H_6	543	0
CCl_4	563	0	$C_6H_5\cdot CH_3$	546	0
$C(NO_2)_4$	651	0	$s\cdot C_6H_3Me_3$	583	0
C_5H_{12}	651	0	C_6H_{12}	688	0
C_6H_{14}	653	0			
C_7H_{16}	653	0			

(Rotatory powers in a number of other solvents will be found in the text.)

Influence of Dipoles.—*l*-Menthyl methyl naphthalate, it will be seen, undergoes exceptionally large variations in rotatory power with change of solvent, the molecular rotations $[M]^{20^\circ}_{5461}$ ranging from -219° in nitromethane to -788° in decalin. One of the most striking points which emerge from the above tables is the close relationship existing between the dipole moment of the solvent and the rotatory power of the dissolved ester. In all four series the rotation is lowest in strongly polar solvents and highest in those of zero dipole moment. Solvents of intermediate polarity fall, on the whole, into the order of their dipole values, but with this class some displacements * are observed. A particularly interesting com-

TABLE II.

Rotatory Powers of l-*Menthyl Methyl Naphthalate in Solvents derived from Ethane and Naphthalene.*

Solvent.	$[M]^{20^\circ}_{5461}$.	$\mu \times 10^{18}$.	Solvent.	$[M]^{20^\circ}_{5461}$.	(In C_6H_6).*	$\mu \times 10^{18}$.
$C_2H_5\cdot NO_2$	-282°	4·03	$C_{10}H_7\cdot NO_2$	—	-442°	3·62
$COMe_2$	365	2·72	$C_{10}H_7\cdot CN$	—	449	—
$[Et\cdot COMe]$	[392]	[2·70]	$C_{10}H_7\cdot OMe$	-497°	508	—
C_2H_5Br	360	1·78	$C_{10}H_7Cl$	552	512	1·59
C_2H_5I	383	1·70	$C_{10}H_7Br$	553	510	1·58
$C_2H_5\cdot OH$	439	1·70	$C_{10}H_7\cdot CH_3$	586	545	—
Et_2O	495	1·15	$C_{10}H_{18}$	788	625	0

* See p. 677.

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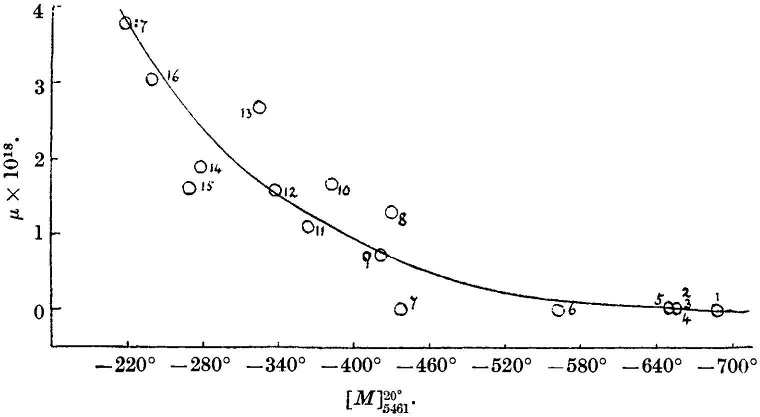
* In addition to the varying degree of association of the solvent, some irregularity is probably caused by the modification (deformation) of the solvent dipoles in the field of the solute.

parison is furnished by the nitro-derivatives of the methane series. Nitromethane ($\mu = 3{\cdot}78 \times 10^{-18}$) is one of the most polar solvents examined and has the greatest effect in depressing the activity of the ester; on the other hand, tetranitromethane, although containing four nitro-groups, yields a highly active solution in agreement with its non-polar properties ($\mu = 0$). Similarly, a high rotation is recorded in carbon tetrachloride ($\mu = 0$), whereas chloroform ($\mu = 1{\cdot}10$) and methylene chloride ($\mu = 1{\cdot}61$) give progressively lower values.

FIG. 1.

Rotatory powers of l-*menthyl methyl naphthalate in solvents of the methane type.*



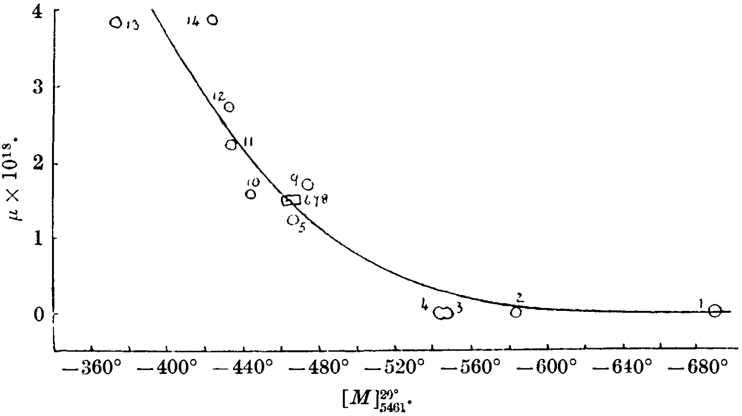
1. cyclo*Hexane.*
2. *Heptane.*
3. *Hexane.*
4. *Pentane.*
5. *Tetranitromethane.*
6. *Carbon tetrachloride.*
7. *Carbon disulphide.*
8. *Bromoform.*
9. *Acetic acid.*
10. *Methyl alcohol.*
11. *Chloroform.*
12. *Methyl iodide.*
13. *Acetaldehyde.*
14. *Methylene bromide.*
15. *Methylene chloride.*
16. *Acetonitrile.*
17. *Nitromethane.*

As several of the naphthalene derivatives under examination were solids, a more complete comparison was effected by employing them in the form of a mixture containing a 0·6 mol. fraction of benzene. It may be noted that among the homogeneous solvents the halogen compounds are displaced above the ether, but that dilution with benzene tends to bring them into a lower position, presumably owing to a breakdown of the association complexes. Naphthalene proved to be too sparingly soluble in benzene for inclusion in this series.

When the rotatory powers of the ester in a given series of solvents are plotted against the dipole moments of the solvents, the points approximate to a smooth curve (Figs. 1 and 2). A closer agreement than that found is scarcely to be expected. If, as seems probable, the influence of a solvent is chiefly related to its power of influencing the internal fields of the asymmetric compound by deformation or dipole association, the change in rotation must depend to some extent upon the volume and form of the solvent molecule as well as upon its constituent dipoles. In addition, polar liquids are themselves normally more or less associated. Dipole moments are therefore evaluated by examining the compound in question dissolved in a non-polar medium and extrapolating the experimental figures to extreme dilution, in which state the polar compound usually exists in the form of single molecules. Rotatory powers, on the other hand, are usually determined by using the homogeneous polar solvents in the associated state. The operation of these two factors is discussed separately in the following pages, and gives valuable information regarding the manner in which the intermolecular forces are modified by the structure of the solvent molecules.

FIG. 2.

Rotatory powers of l-*menthyl methyl naphthalate in benzene derivatives.*



1. cyclo*Hexane.*
2. *Mesitylene.*
3. *Toluene.*
4. *Benzene.*
5. *Anisole.*
6. *Chlorobenzene.*
7. *Iodobenzene.*
8. *Bromobenzene.*
9. o-*Chlorotoluene.*
10. *Aniline.*
11. o-*Dichlorobenzene.*
12. *Benzaldehyde.*
13. *Benzonitrile.*
14. *Nitrobenzene.*

Influence of Molecular Volume and Structure.—Homologous and isomeric solvents. The influence of the size of the solvent molecule is revealed by a comparison of the rotatory powers of the ester in corresponding derivatives of the four series under investigation, *e.g.*, the halides, methyl iodide (— 336°), ethyl iodide (— 383°), iodobenzene (— 465°), and bromonaphthalene (— 553°). All these solvents have an electric 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 the 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.

A more direct screening of the dipole occurs in certain cases where a hydrogen atom in the vicinity of a polar group is replaced by a more bulky hydrocarbon radical. For example, acetaldehyde, acetone, and methyl ethyl ketone each have the same dipole moment, $\mu = 2{\cdot}7 \times 10^{-18}$, but as the polar ketonic group becomes more and more screened, the rotation of the ester in these solvents rises progressively from − 316° to − 365° and finally to − 392°. Benzaldehyde (— 432°) and acetophenone (— 454°) illustrate the same change. The small effect due to an additional alkyl group in a non-polar molecule may be seen in the similar values obtained for pentane, hexane, and heptane on the one hand, and benzene and toluene on the other.

In order to establish this point more definitely, the rotatory powers were also determined 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 the polar C–Cl group becomes increasingly screened as we pass from the normal, through the *iso*-, to the tertiary chloride :

Solvent.	$[M]_{5461}^{20^\circ}$.	B. p.
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$	−450·1°	77°
$(CH_3)_2CH{\cdot}CH_2Cl$	−464·0	68
$(CH_3)_3CCl$	−511·2	51

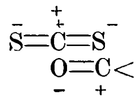
In agreement with the above conclusions the rotatory power was found to be lowest in the normal and highest in the tertiary isomeride, the behaviour of the latter being almost that of a non-polar liquid. As was to be expected from its molecular structure, *iso*butyl chloride allies itself much more closely to the normal chloride than to the tertiary compound, a relationship which may also be observed in the boiling points of the three liquids.

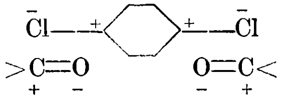
In the three isomeric chlorotoluenes the rotatory powers of the ester arrange themselves in order of the dipole moments of the solvents :

	$[M]_{5461}^{20^\circ}$.	$\mu \times 10^{18}$.
o-Chlorotoluene	− 502°	1·39
m-Chlorotoluene	− 497	1·60
p-Chlorotoluene	− 433	1·74

Chlorobenzene, as was to be expected, gives an intermediate value (— 463°) in agreement with its moment (1·52). The displacement in the relative positions of chlorobenzene and *m*-chlorotoluene may be ascribed to the increased bulk of the hydrocarbon radical in the latter.

Non-polar solvents. Surprisingly large variations occur in the rotatory powers determined in non-polar solvents. It is improbable that changes of this magnitude are to be explained by the varying degree of association of the optically active ester in solution (see also p. 686), but among solvents, the non-polarity of which is due to a symmetrical arrangement of substituent dipoles, other factors may come into operation. Although such molecules are non-polar with reference to a uniform external field, they may exert a definite force on a point charge or dipole in their immediate neighbourhood. Carbon disulphide and *p*-dichlorobenzene, for example, would appear to be so constituted as to permit some degree of dipole association. In the case of the former, however, the two oppositely oriented dipoles are so close to one another that the field exerted by the one at a near-by point is almost completely annulled by that due to the other. The polar properties of a solvent of this type, if they exist at all, will be extremely weak. On the other hand, in *p*-dichlorobenzene the CCl-dipoles are separated by two carbon atoms and may to a large extent be expected to function individually. On this assumption *p*-dichlorobenzene will provide approximately twice the dipole concentration of the monosubstituted compound, chlorobenzene. The disubstituted molecule will thus behave as a strongly polar substance towards other molecules in its immediate neighbourhood.





These conclusions are supported by an examination of the rotatory powers in the solvents under consideration. In aliphatic hydrocarbons and tetranitromethane the rotatory power of the ester is — 653°, carbon tetrachloride giving a somewhat lower value (— 563°). Carbon disulphide (— 437°) falls into line with the feebly polar liquids bromoform (— 429°) and acetic acid (— 423°) in its influence on the rotation. On the other hand, *p*-dichloro- and *p*-dinitro-benzene group themselves with the strongly polar solvents, as may be seen from the following table. As some of these derivatives are solids, a comparison was effected by using them mixed with benzene.

Rotatory Powers of Ester (c = 4) *in Mixtures containing Benzene.*

(f_2 = 0·4).	$[M]^{20°}_{5461}$.	Δ.	$\mu \times 10^{18}$.	(f_2 = 0·015).	$[M]^{20°}_{5461}$.	Δ.	$\mu \times 10^{18}$.
C_6H_5Cl	— 501°	42°	1·52	$C_6H_5{\cdot}NO_2$	— 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.

Among the chloro-compounds, the depression in rotatory power produced by the *o*-compound, in which the two CCl-dipoles are oriented in the same direction and thus reinforce one another's field, is almost as great as that given by the *p*-compound, where the increased effect is due to the doubled frequency with which the individual dipoles come into play. In each of the dichloro-derivatives the depression approximates to twice that observed for chlorobenzene under the same conditions. Similarly the depressions recorded for *m*- and *p*-dinitrobenzene are approximately twice that found for nitrobenzene. It therefore appears that in the *m*- and *p*-compounds the dipoles are capable of acting independently towards neighbouring molecules. Further confirmation of this explanation is furnished by the rise in the melting points of the isomeric dichloro- and dinitro-derivatives as the substituent groups are moved away from each other, a change which has been attributed to the increasing degree of molecular association.

Degree of Association of the Solvent.—It has already been suggested that one of the main factors governing the influence of a solvent on the rotatory power is its polarity as measured by the electric moment, but that modifications may be introduced owing to its characteristic molecular structure and degree of association.

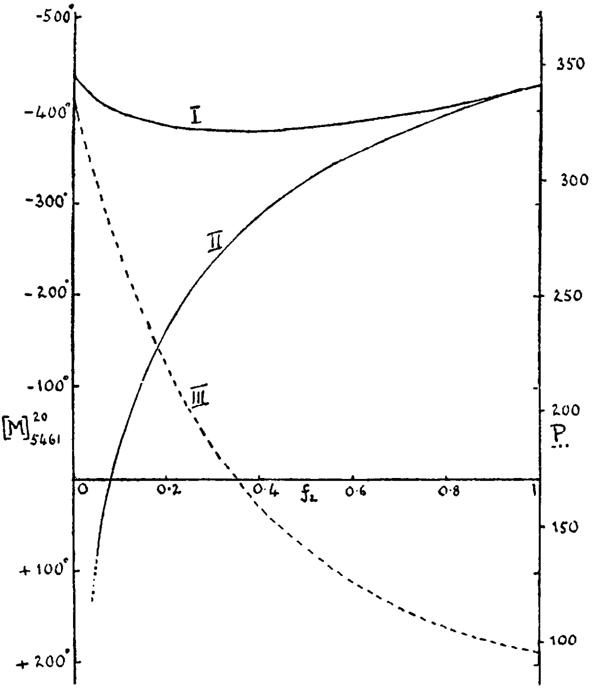
In the majority of cases the association of a polar compound leads to the formation of more or less unstable complexes of lower dipole moment, which may be progressively dissociated to single molecules of higher moment by dilution with a non-polar medium such as benzene or carbon disulphide. It should therefore be possible to trace this process polarimetrically in the present instance, as the depression in rotatory power (after correction for the proportion of non-polar solvent present) should become more pronounced with increasing dilution.

l-Menthyl methyl naphthalate has approximately the same rotatory power in nitrobenzene as in carbon disulphide solution, and in mixtures of these two solvents the dissociation of the nitrobenzene complexes is evident without applying any correction for the molarity of the polar liquid in the mixture. The molecular rotations found for the ester ($c = 4$) in such mixtures are shown diagrammatically in Fig. 3, Curve I. It will be seen that as nitrobenzene is replaced by carbon disulphide the rotations fall steadily to a minimum about 60° lower than the value for the pure liquids, and finally rise steeply to the figure for homogeneous carbon disulphide. Similar although less pronounced changes of this kind have been observed for mixtures of benzene with various polar solvents. Mixtures of benzene with carbon tetrachloride or carbon disulphide on the other hand give practically straight-line graphs.

In his monograph "Polare Molekeln," Debye has divided polar compounds into three main categories according to the type of polarisation–dissociation diagrams they give after elimination of the contribution due to the non-polar solvent. These three groups are illustrated by reference to nitrobenzene, ether, and alcohol, which are represented respectively by a steeply rising curve, a straight line, and a rising curve leading to a maximum and followed by a fall (see Curve III in Figs. 3, 4, 5). It was therefore considered of interest to investigate the form of curves obtained for the rotatory power of *l*-menthyl methyl naphthalate in such mixtures, using a similar means of eliminating the rotation contributed by the benzene or carbon disulphide solution.

Fig. 3.

l-*Menthyl methyl naphthalate in mixtures of carbon disulphide and nitrobenzene.*



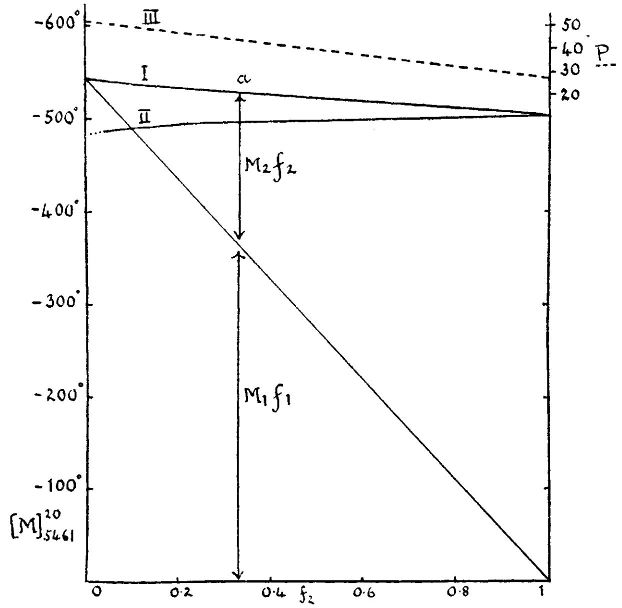
I. *Experimental rotation curve.*
II. *Rotation curve deduced for nitrobenzene alone.*
III. *Polarisation of nitrobenzene alone.*

The procedure may be explained by reference to the benzene–ether diagram in Fig. 4. Negative rotations are plotted vertically and mol.-fractions of polar solvent in the mixture horizontally. In each case the left-hand vertical axis represents a solution in the pure non-polar solvent, and the right-hand axis a solution in the pure polar liquid.

It will be seen that a straight line has been drawn from the point representing the rotation in pure benzene to the right-hand end of the horizontal axis, at which the concentration of benzene is zero. If now a perpendicular is dropped from any point *a* on the experimental rotation curve (I) to the horizontal axis, the intercept M_1f_1 between the above line and the axis will represent the contribution to the total rotatory power made by the benzene component of the mixture. By difference, M_2f_2 gives the rotation contributed by the polar (ether) component. On dividing M_2f_2 by the corresponding mol.-fraction, we obtain a molecular rotation corresponding to the particular degree of association in which the polar liquid is present in the mixture. By plotting a number of these calculated values against the mol.-fractions (Curve II),* we can thus follow the effect

FIG. 4.

l-*Menthyl methyl naphthalate in mixtures of benzene and ether.*



I. *Experimental rotation curve for mixed solvents.*
II. *Rotation curve deduced for ether alone.*
III. *Polarisation of ether alone.*

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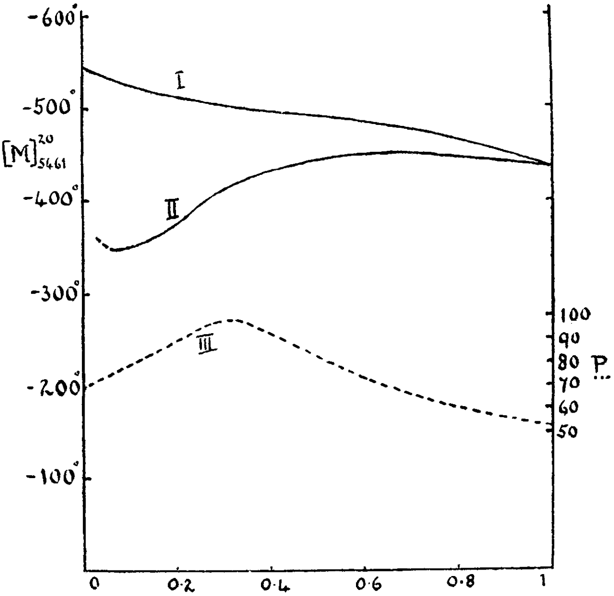
* In the following pages this type of diagram is referred to as a rotation–dissociation diagram.

of increasing dissociation of the polar liquid upon the rotatory power. The resulting curves are based on the assumption that the polar solvent is at all times distributed evenly throughout the mixture. Probably at very low concentrations the calculation will be inaccurate owing to the increasing tendency of the polar solvent molecules to cluster around the polar solute molecules. Such a tendency would lead to a greater depression in rotatory power and displace the left-hand end of Curve II downwards towards a positive value.

FIG. 5.

l-*Menthyl methyl naphthalate in mixtures of benzene and ethyl alcohol.*



I. *Experimental rotation curve for mixtures.*
II. *Deduced curve for alcohol alone.*
III. *Polarisation curve for alcohol alone.*

An examination of the diagrams for different solvents deduced in this manner leads to interesting comparisons. In the first place the general resemblance to Debye's polarisation–dissociation figures is clearly shown, an increase in the polarisation being accompanied by a fall in the rotatory power, in agreement with the relationship established in the preceding pages. For both properties the changes in ether are indicated by straight lines, in nitrobenzene by steep smooth curves, and in alcohol by curves leading to inflexions at low concentrations. Down to an alcohol concentration of 0·3 mol fraction a rising polarisation corresponds to a falling rotation. The maximum in the polarisation, however, does not coincide with a minimum in rotatory power. Probably a minimum rotation exists at concentrations below 0·1, but this is difficult to decide as considerable errors are involved in the calculation of Curve II at very low concentrations. Uniform scales for rotation and polarisation respectively have been adopted in all three figures, from which it will be seen that the resemblance between the deduced rotation and polarisation diagrams is not limited to similarity of form but extends also to the magnitude of the change represented. The results afford strong additional confirmation of the important part played by the solvent dipoles in modifying the rotatory power of a dissolved substance.

A number of similar mixtures were investigated, the data for which are recorded in the experimental section. It is found that the rotation–dissociation diagrams for carbon disulphide and carbon tetrachloride (on dilution in benzene) are represented by straight lines with a very slight trend towards the positive region at concentrations below 0·1. Nitromethane and acetonitrile in benzene give diagrams which are replicas of that calculated for nitrobenzene in carbon disulphide (Fig. 3). Acetophenone and acetone yield diagrams which fall comparatively steeply, but for methyl iodide (Table III, vi) the values rise to a maximum followed by a moderate fall. The authors do not attach any special significance to the actual figures deduced in this manner for extreme dilution, although it may be mentioned that nitrobenzene and nitromethane (Tables III, ix and i), which give solutions of strongly differing rotatory power when employed in the homogeneous state, extrapolate to approximately the same value (+ 250°) at infinite dilution. The acetone and acetophenone curves similarly cut the vertical axis in the same neighbourhood (— 80°).

Discussion of Results.

Previous investigations of menthyl 8-substituted 1-naphthoates have shown that very considerable alterations in rotatory power are caused by changes in the nature of the peri-substituent. The solvent influences under discussion are also on an unusually large scale and may therefore be intimately connected with disturbances of the mutual relationship existing between the two peri-groups. But if the solvent effects in the case of the di-ester are caused by deformation or dipole association, it is to be expected that changes in the same sense will be undergone by the unsubstituted *l*-menthyl 1-naphthoate, although probably in smaller degree. An examination of the ester gave the following data :

Rotatory Power of l-*Menthyl* 1-*Naphthoate in Homogeneous Solvents* ($c = 4$).

	$[M]^{20°}_{5461}$.	$\mu \times 10^{18}$.		$[M]^{20°}_{5461}$.	$\mu \times 10^{18}$.
C_6H_6	− 325°	0	CCl_4	− 280°	0
CS_2	313	0	$CHCl_3$	280	1·1
$CH_3{\cdot}CO_2H$	310	0·7	CH_3I	280	1·6
$CH_3{\cdot}OH$	302	1·6	$CH_3{\cdot}NO_2$	267	3·8
$CH_3{\cdot}CHO$	300	2·71	$CH_3{\cdot}CN$	249	3·9
C_6H_{14}	299	0			

As in the case of the di-ester there is here a tendency for the non-polar solvents to give high rotatory powers and for strongly polar ones to give low values. The effect is, however, much less pronounced, and the arrangement of solvents is subject to a number of exceptions. Chief among the latter may be noted the high positions occupied by the three strongly associated solvents acetic acid, methyl alcohol, and acetaldehyde. The relatively low rotation in hexane is all the more curious in view of the still lower figure (− 274°) found in decalin. Further information on this point might be gained from an extended investigation of *l*-menthyl naphthoate.

Peri-substituted derivatives of naphthalene, in which the groups attached to the 1- and 8-positions are of the same electrical type, will probably have a high dipole moment * and thus tend to exist in an associated state. It is, however, unlikely that the observed optical changes in the di-ester are due to variations in the degree of association. Rotatory powers $[M]^{20°}_{5461}$ in benzene measured over the maximum possible range ($c = 4$ to $c = 25$) only suffered an inappreciable change in value (− 543° to − 530°). At the former concentration there are present about 100 molecules of benzene to each molecule of ester. A rise in temperature was found to diminish the abnormally high rotatory power given in decalin solution, the value falling from − 788° at 20° to − 660° at 98°. An alteration in this sense is to be expected, as the increasing molecular vibration will lead to an increase in the mean distance between the peri-groups (compare Ebert, " Dipolmomente und chemische Struktur," p. 60 : Leipziger Vorträge, Debye).

For the present, therefore, the authors adopt the opinion advanced in the earlier part of this paper, that the observed effects are due to the influence of the solvent dipoles upon the internal field of the solute, acting either through deformation or dipole association. There is the further possibility that association may also lead to changes through the temporary formation of new asymmetric centres.

The simpler suggestion that the optical changes are caused by

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* 1 : 8-Dinitronaphthalene, $\mu = 7 \times 10^{-18}$, is the most polar substance listed in Debye's " Polare Molekeln."

variations in the electrostatic forces operating between the peri-groups, resulting from the variable dielectric constant of the medium, is apparently untenable in view of the powerful effect exerted by *p*-substituted-benzene solvents, which have low dielectric values.

Recent researches have tended more and more to bring the study of optical activity into fundamental relationship with that of absorption spectra. Reference need only be made to the investigations of Lowry and others on the Drude equation, and to the successful asymmetric decomposition of racemic compounds effected by W. Kuhn (*Z. physikal. Chem.*, 1930, *B*, **7**, 292) and Mitchell (J., 1930, 1892) by use of circularly polarised light following an examination of the absorption data. It is therefore a matter of interest that the screening of the carbonyl dipole by alkyl groups and the polar influence of solvents on ketones have already been demonstrated in the field of absorption spectra.

Scheibe (*Ber.*, 1926, **59**, 2617) finds that the characteristic absorption band of a ketone is displaced progressively towards the far ultra-violet when the compound is dissolved in liquids of increasing polarity. The arrangement of solvents for acetone is as follows :

$$CCl_4,\ C_6H_{14},\ Et_2O,\ EtOAc,\ \underrightarrow{CHCl_3,\ CH_2Cl_2,\ EtOH,}\ MeOH,\ CH_3{\cdot}CO_2H,\ H_2O.$$

Shift to shorter wave-length.

The magnitude of the observed displacement also diminishes progressively as the carbonyl group becomes more and more screened by substitution in the adjacent methyl groups, although the order of the solvents remains unchanged. Thus the shift is less for methyl *tert.*-butyl ketone than for acetone, and still smaller for hexamethylacetone. These examples present a complete parallel to the changes in rotatory power discussed on p. 679. If we assume the validity of Drude's equation in the case of an optically active keto-compound, such a displacement of the absorption band corresponds to a fall of rotatory power with increasing polarity of solvent.

With the object of further examining the theoretical points raised in this communication, a number of investigations are now in progress dealing with simpler optically active compounds, many of which contain only a single polar substituent.

EXPERIMENTAL.

Determinations of Rotatory Power.—The molecular rotations were determined at 20° in a 2-dcm. tube. Those in Tables I and II refer to the ester in a concentration of approximately $c = 4$, except that, owing to low solubility, smaller values of c were adopted in the case of nitromethane (2·3); methyl and ethyl alcohols (2·0); pentane, hexane, and heptane (1·95); mesitylene (2·4); *cyclo*hexane (2·0);

a-methylnaphthalene (2·0); α-chloronaphthalene (2·0); and decalin (2·0).

In the following tables relating to mixed solvents, f_2 denotes the mol.-fraction of the second solvent (a polar liquid in the majority of cases) which is being diluted with benzene or carbon disulphide (f_1); and the observed molecular rotation is given under $[M_{1,2}]_{5461}$. The final column contains the molecular rotations $[M_2]_{5461}$ representing the rotatory power in the second solvent after eliminating the component contributed by the non-polar diluent. These values are calculated from the graph as explained on p. 683.

TABLE III.

(i) *Benzene–Nitromethane.*

f_2.	*c*.	$\alpha^{20°}_{5461}$.	$[M_{1,2}]$.	$[M_2]$.
1·000	2·350	− 2·80°	—	−219°
0·541	4·004	− 7·81	−359°	−198
0·414	3·996	− 8·45	−389	−163
0·348	4·012	− 8·80	−404	−140
0·272	4·016	− 9·19	−421	− 90
0·211	4·012	− 9·73	−446	− 62
0·144	4·028	−10·12	−462	0
0·132	4·010	−10·26	−471	+ 15
0·119	4·004	−10·34	−475	+ 25
0·091	4·018	−10·70	−490	+ 55·5
0·063	3·992	−10·90	−502	+125
0·027	3·996	−11·33	−522	+185
0·000	4·004	−11·83	−543	—

(ii) *Benzene–Acetonitrile.*

f_2.	*c*.	$\alpha^{20°}_{5461}$.	$[M_{1,2}]$.	$[M_2]$.
1·000	3·992	− 5·19°	—	−239°
0·641	4·042	− 7·58	−345°	−233
0·373	4·042	− 9·17	−417	−189
0·300	4·010	− 9·18	−421	−160
0·254	4·042	− 9·25	−435	−130
0·210	3·994	− 9·83	−453	− 91
0·162	4·046	−10·20	−464	− 38
0·132	4·004	−10·34	−475	0
0·088	3·962	−10·54	−489	+ 56
0·062	4·010	−11·02	−506	+133
0·036	4·058	−11·37	−516	+225
0·000	4·004	−11·83	−543	—

(iii) *Benzene–Acetone.*

1·000	5·096	−10·12	—	−365
0·562	4·020	− 9·53	−436	−350
0·296	4·002	−10·41	−479	−327
0·237	4·020	−10·65	−488	−312
0·186	4·016	−10·85	−497	−289
0·126	3·992	−10·92	−502	−238
0·064	3·996	−11·37	−523	−167
0·030	4·006	−11·60	−533	−133
0·000	4·004	−11·83	−543	—

(iv) *Benzene–Methyl alcohol.*

1·000	1·968	− 4·09	—	−383
0·685	2·036	− 4·93	−446	−399
0·430	4·008	−10·49	−481	−388
0·286	4·010	−10·63	−488	−339
0·200	4·000	−10·82	−497·5	−305
0·149	4·012	−11·00	−504·5	−267
0·109	4·018	−11·16	−511	−227
0·092	3·988	−11·13	−513	−200
0·051	4·014	−11·48	−526	−160
0·000	4·004	−11·83	−543	—

(v) *Benzene–Ether.*

1·000	4·475	−12·04	—	−503
0·843	4·000	−11·16	−513	−500
0·663	4·008	−11·22	−515	−500
0·475	4·012	−11·45	−524	−498
0·214	4·000	−11·58	−533	−495
0·098	4·000	−11·61	−534	−490
0·000	4·004	−11·83	−543	—

(vi) *Benzene–Methyl iodide.*

1·000	4·464	− 8·15	—	−336
0·592	4·018	− 9·66	−442	−371
0·456	4·008	−10·12	−464	−370
0·358	4·012	−10·51	−482	−372
0·250	4·036	−10·97	−500	−372
0·150	4·000	−11·18	−514	−370
0·055	4·000	−11·54	−531	−355
0·000	4·004	−11·83	−543	—

(vii) *Benzene–Carbon tetrachloride.*

1·000	4·452	−13·63	—	−563
0·499	4·000	−12·07	−556	−566
0·245	4·004	−11·90	−547	−548
0·193	4·018	−11·84	−542	−545
0·144	3·980	−11·69	−541	−540
0·096	3·988	−11·72	−541	−533
0·000	4·004	−11·83	−543	—

(viii) *Benzene–Carbon disulphide.*

1·000	4·400	−10·44	—	−437
0·470	3·990	−10·63	−490·5	−438
0·253	3·980	−11·11	−514	−436
0·158	3·998	−11·39	−525	−438
0·106	3·992	−11·52	−531	−436
0·055	4·002	−11·67	−536·5	−433
0·000	4·004	−11·83	−543	—

TABLE III (*contd.*).

(ix) *Carbon disulphide–Nitrobenzene.*

f_2.	c.	$\alpha^{20^\circ}_{5461}$.	$[M_{1.\,2}]$.	$[M_2]$.
1·000	4·034	− 9·37°	—	− 427°
0·734	4·004	− 8·69	− 399°	− 385
0·511	4·000	− 8·33	− 383	− 330
0·386	3·990	− 8·20	− 378	− 285
0·224	4·004	− 8·31	− 382	− 182
0·105	4·012	− 8·60	− 394·5	− 55
0·065	4·006	− 8·79	− 404,	+ 29
0·000	4·400	− 10·44	− 437	—

(x) *Benzene–Ethyl alcohol.*

f_2.	c.	$\alpha^{20^\circ}_{5461}$.	$[M_{1,\,2}]$.	$[M_2]$.
1·000	2·000	− 4·77°	—	− 439°
0·870	2·022	− 5·01	− 456°	− 445
0·702	2·008	− 5·21	− 477	− 449
0·509	2·008	− 5·29	− 485	− 448
0·345	2·000	− 5·47	− 503	− 425
0·326	2·004	− 5·45	− 500·5	− 418
0·281	2·000	− 5·49	− 505	− 409
0·217	2·008	− 5·56	− 509	− 383
0·149	2·006	− 5·63	− 516	− 359
0·104	2·008	− 5·72	− 524	− 351
0·076	2·008	− 5·79	− 531	− 349
0·050	—	—	—	− 360
0·030	—	—	—	− 380
0·000	4·004	− 11·83	− 543	—

(xi) *Benzene–Acetophenone.*

f_2.	c.	$\alpha^{20^\circ}_{5461}$.	$[M_{1.\,2}]$.	$[M_2]$.
1·000	4·444	− 10·96	—	− 454
0·776	4·000	− 10·05	− 462	− 441
0·655	4·004	− 10·18	− 468	− 428
0·550	4·004	− 10·23	− 470	− 409
0·424	4·008	− 10·37	− 476	− 384
0·343	4·000	− 10·43	− 480	− 354
0·252	4·004	− 10·67	− 490	− 323
0·165	4·012	− 10·93	− 501	− 279
0·081	4·000	− 11·23	− 517	− 212
0·043	4·008	− 11·52	− 529	− 174
0·000	4·004	− 11·83	− 543	—

Materials.—The purest available solvents were used as starting materials and were then treated as follows :

Washed, dried over calcium chloride, and fractionated : nitromethane, nitroethane, methyl iodide, ethyl bromide, ethyl iodide, methylene chloride, methylene bromide, bromoform, carbon tetrachloride, benzaldehyde, anisole (gave no phenol reaction), chlorobenzene, bromobenzene, iodobenzene, α-methylnaphthalene, α-chloronaphthalene, α-bromonaphthalene, α-naphthyl methyl ether (gave no colour with diazotised aniline or with copper powder and carbon tetrachloride), decalin, *o*-dichlorobenzene (previously cooled to — 20° to freeze out traces of *p*-dichlorobenzene).

Dried and fractionated : acetonitrile, acetaldehyde, acetone (" purified by bisulphite "), aniline (" from sulphate "), toluene, mesitylene, methyl ethyl ketone.

Purified by repeated partial freezing, followed (except in the case of tetranitromethane) by drying and fractionation : acetic acid, m. p. 16° ; benzonitrile, m. p. — 12° ; nitrobenzene, m. p. 5·6—5·7° ; acetophenone, m. p. 20° ; benzene, m. p. 5·5° ; *cyclo*hexane, m. p. 4·1° ; tetranitromethane (Berger, *Compt. rend.*, 1910, **151**, 814) ; *o*-chlorotoluene, m. p. — 34·5°, b. p. 41°/11 mm. ; *m*-chlorotoluene, m. p. — 48°, b. p. 45·5°/12 mm. ; *p*-chlorotoluene, m. p. 7·5°, b. p. 45·5°/12 mm.

Hexane (" free from aromatic hydrocarbons ") was dried and fractionated ; pentane (b. p. 35—37°) and heptane (b. p. 98—98·5°) were first shaken with concentrated sulphuric acid.

The *n*- and *tert.*-butyl chlorides were washed, dried, and fractionated (*n*-compound, b. p. 77·2—77·4°; *tert.*-, b. p. 50·8—51·1°). *iso*Butyl chloride (b. p. 69—69·2°) was prepared and purified by the method of Michael and Zeidler (*Annalen*, 1912, **393**, 110).

Alcohol was dried over lime; ether was treated with sodium wire and fractionated.

The following were purified by repeated crystallisation until of constant melting point: *m*-dinitrobenzene (from alcohol, m. p. 89·9°); *p*-dinitrobenzene (from alcohol, m. p. 172·5°), α-naphthonitrile (from ligroin, m. p. 36—37°), α-nitronaphthalene (from alcohol, m. p. 56—57°), *p*-dichlorobenzene (from alcohol, m. p. 54°).

Summary.

The influence of solvents on the rotatory power of *l*-menthyl methyl naphthalate has been investigated with the following results.

1. The values of $[M]^{20°}_{5461}$ ($c = 4$) range from − 219° in nitromethane to − 788° in decalin.

2. In the majority of cases the fall in rotation varies with the polarity of the solvent, as determined by its dipole moment, and for a given polar substituent the influence becomes less pronounced as the molecular volume of the hydrocarbon radical increases. Hence the polar effects are best studied by comparing solvents of the same type, *i.e.*, those derived from the same parent hydrocarbon.

3. For solvents of the same type a rough approximation to a smooth curve is obtained when rotatory powers are plotted against dipole moments.

4. The depression caused by associated solvents such as nitrobenzene or acetone is greatly increased when the associated complexes are dissociated by dilution with a non-polar medium. By correcting the values found in such mixtures for the contribution due to the non-polar diluent, it is possible to follow polarimetrically the process of dissociation. The diagrams obtained in this way for nitrobenzene, ether, and alcohol (on dilution in benzene) agree in form and magnitude with the corresponding diagrams deduced by Debye for the change in polarisation undergone by the polar liquid.

5. Special effects are observed among homologous and isomeric solvents; *e.g.*, alkyl groups may exert a screening action on adjacent polar groups. Among the butyl chlorides, the depression in rotatory power becomes progressively smaller on passing from the normal through the *iso*- to the *tert.*-compound. On the other hand, *p*-dichloro- and *p*-dinitro-benzene (although of zero dipole moment) produce as large a depression as the *o*-compounds, apparently owing to the dipoles being so far removed in the former isomerides as to be capable of functioning individually towards neighbouring molecules.

6. It is assumed that the sensitivity of the di-ester towards

solvents is intimately connected with disturbances in the mutual relationship of the peri-groups, probably caused by electrical deformation or dipole association.

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