102. Studies in Solvent Action. Part VI. Optical Rotatory Powers of β-Octanol, d-Amyl Alcohol, and their Derivatives.

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SUFFICIENT evidence has now been accumulated to show that the rotatory powers of optically active esters in solution are in many cases intimately related to the electrical (dipole) character of the solvent, a conclusion which is supported by the investigation of a variety of ester-types, both aliphatic and aromatic, substituted and unsubstituted (Rule and co-workers, J., 1931, 674, 2652; 1932, 1409, 2332). According to recent theories of optical activity (cf. W. Kuhn, *Trans. Faraday Soc.*, 1930, **26**, 293), the magnitude of the rotatory power of a compound depends upon the situation and circular dichroism of its absorption bands, especially those in the visible and near ultra-violet region, and upon their reaction towards other bands in the spectrum. One link between these theories and the above solvent influence is supplied by the work of Scheibe on the manner in which a change of solvent modifies the position of the characteristic absorption bands of a substance. Using ketones in the presence of a number of different solvents, he has shown (*Ber.*, 1926, **59**, 2619) that the typical ketonic band is displaced progressively towards the far ultra-violet region as the polarity of the solvent is increased, a change which might be expected on Kuhn's theory to lead to a continuous modification of the optical rotation. Kuhn also concludes (Freudenberg, " Stereochemie," 1932, p. 417) that the change in rotation may in certain cases result from an alteration in the anisotropic properties of the band without any appreciable change in its position.

Additional confirmation of a relationship between rotatory power and the polar condition of the solvent has been obtained (Rule and McLean, J., 1932, 1400) by determining the molecular rotation of an active ester in mixtures of benzene with various alcohols. By a simple mathematical treatment of the experimental figures, it has been shown that the characteristically irregular changes in the degree of polarisation of the alcohol, which occur as the latter is diluted with benzene, are accompanied by corresponding changes in the rotation of the ester dissolved in the mixture.

These polarimetric determinations have now been extended to a number of *sec.*-β-octyl and *d*-amyl * derivatives, including the alcohols, halides, and methyl ethers of both series, together with β-nitro-octane, *d*-amyl *o*-toluate, and the *o*-, *m*-, and *p*-toluic and methoxybenzoic esters of β-octanol. Methyl-*n*-butylacetic acid has also been examined in place of the β-carboxylic derivative of octane, which is not readily prepared in sufficient quantity for resolution. The majority of these compounds are not of the ordinary ester type, but are built up of a single polar substituent (OH, OMe, Cl, Br, NO_2, or CO_2H) united to a simple optically active hydrocarbon radical. Among these, special interest attaches to octyl alcohol, since 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; such changes should thus be traced more simply and certainly than was possible in using the above-mentioned three-component system. Considering the varied nature of the substituents present, it was also hoped that more definite information might be gained as to some of the causes leading to apparent abnormalities in the solvent influence. Very marked differences were observed in the manner in which the compounds reacted towards change of solvent, and some of the cases are therefore discussed individually. In the following tables space has been economised by giving the limiting values of α_{5461} in place of the full experimental data.

With octyl alcohol as the active solute, a definite polar influence is clearly evident among the aliphatic solvents: those of non-polar character give the highest rotations, whereas acetonitrile, the most strongly polar medium, gives a low value. In this respect the di- and the tri-substituted compound, methylene chloride and chloroform, are partial exceptions and yield solutions of relatively low activity. The tendency for these liquids

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TABLE I.

1-β-*Octanol*, $[M]^{20^{\circ}}_{5461}$ $-15{\cdot}3^{\circ}$ (t = 20°, c = 5, l = 4).

Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.	Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.
CS_2	− 20·3°	0	$C_6H_5{\cdot}CHO$	−20·5°	2·75
CCl_4	19·4	0	C_6H_6	19·2	0
C_6H_{14}	19·1	0	$C_6H_5{\cdot}CH_3$	19·2	0·5
CH_3I	17·1	1·66	$C_6H_5{\cdot}NH_2$	18·8	1·60
$CH_3{\cdot}OH$	17·0	1·64	$C_6H_5{\cdot}COMe$	18·6	2·97
$CH_3{\cdot}CO_2H$	16·6	1·4	$C_6H_5{\cdot}NO_2$	18·2	3·90
$CH_3{\cdot}CN$	14·8	3·05	$C_6H_5{\cdot}OMe$...............	18·1	1·25
$CHCl_3$	14·2	1·10	C_6H_5Br	17·9	1·50
CH_2Cl_2	13·9	1·61	C_6H_5Cl	17·8	1·52
			C_6H_5I	17·8	1·50
			$C_6H_5{\cdot}CN$	17·3	3·85

Limiting values of α_{5461}, − 2·14° and − 3·16°.

to rank with the more highly polar solvents has also been observed with menthyl methyl naphthalate as the active solute (Rule and McLean, J., 1931, 676).

Irregularities of a more pronounced nature occur in the aromatic series, although here also the non-polar hydrocarbons give highly active solutions. In this group exceptional positions are assumed by nitrobenzene and the ketonic compounds benzaldehyde and benzophenone, all of which are displaced towards the non-polar end of the table, notwithstanding the high values of their dipole moments. It is interesting and possibly significant that each of these solvents is believed to be capable of entering into co-ordination with the hydroxyl group of the alcoholic molecule (Sidgwick, " The Electronic Theory of Valency," p. 149) a process involving the formation of a new and highly polar link between solvent and solute and one likely to result in a modification of the rotatory power. No evidence of a displacement of this type, however, has been found in the case of *d*-amyl alcohol dissolved in benzaldehyde (p. 383).

In common with other hydroxy-compounds, octyl alcohol normally exists in a state of association. Since its solutions in highly polar solvents (*e.g.*, acetonitrile) exhibit a low rotatory power, an effect which has been attributed to the high degree of association between such solvents and the solute, it may be concluded that association between two or more molecules of the alcohol will operate in the same sense in the homogeneous liquid. This is supported by the fact that the molecular rotation of the alcohol in the homogeneous state, $[M]^{20^{\circ}}_{5461}$ $-15{\cdot}3^{\circ}$, is much lower than that observed for dilute solutions in carbon disulphide, carbon tetrachloride, hexane, and the aromatic hydrocarbons, in which media a considerable proportion of the alcohol exists in the unimolecular condition.

The figures in Table II, referring to the alteration in the rotatory power of octyl alcohol as it is continuously diluted with benzene or hexane, illustrate this point in greater detail: as the dilution increases the optical rotation rises.

TABLE II.

d-β-*Octanol in various concentrations* (t = 20°).

In hexane (l = 4).			In hexane (l = 4).			In benzene (l = 2).			In benzene (l = 2).		
c.	f_2.	$[M]_{5461}$.	*c.*	f_2.	$[M]_{5461}$.	*c.*	f_2.	$[M]_{5461}$.	*c.*	f_2.	$[M]_{5461}$.
4·994	0·050	+19·6°	35·00	0·372	+16·91°	4·998	0·035	+19·3°	39·97	0·346	+15·46°
10·00	0·099	18·6	37·28	0·399	17·02	9·994	0·072	18·2	41·87	0·368	15·52
15·07	0·151	18·1	42·05	0·453	16·79	15·99	0·119	17·2	43·53	0·388	15·40
20·00	0·203	17·6	50·01	0·551	16·45	22·01	0·170	16·65	47·56	0·436	15·44
23·38	0·253	17·54	55·01	0·618	16·10	30·01	0·244	16·12	55·30	0·532	15·20
27·03	0·283	17·62	62·05	0·709	15·87	32·27	0·266	15·97	62·42	0·647	15·09
30·00	0·313	17·29	69·99	0·819	15·40	34·76	0·292	15·87	71·18	0·789	15·13
33·02	0·345	16·73	(Homog.*)	1·000	15·24	36·78	0·308	15·71	(Homog.)	1·000	15·24
						38·61	0·331	15·62			

* l = 2.

Limiting values of α_{5461}: in hexane 3·01° and 33·23°, in benzene 1·48° and 16·54°. The figures under f_2 (mol. fraction of *d*-*β*-octanol in mixture) are calculated from the weights of alcohol and solvent employed.

Lange has observed that under similar treatment the electrical polarisation of an alcohol in solution does not always vary continuously with the composition of the mixture, but may pass through a well-defined maximum [*Z. Physik*, 1925, **33**, 174 (2—6)]. Unfortunately, no data relating to the polarisation changes of β-octyl alcohol are available in the literature, although a number of isomeric octanols were recently examined by Smyth and Stoops (*J. Amer. Chem. Soc.*, 1929, **51**, 3330). But when the above molecular rotations are plotted as in Fig. 1, it is seen that well-marked deviations from the main curve occur in hexane solution between the concentrations $f_2 = 0{\cdot}2$ and 0·7, which apparently take the form of two maxima at $f_2 = 0{\cdot}28$ and 0·4 and of a minimum at 0·35. With benzene as solvent the disturbances are scarcely perceptible, though the sharp minimum in the hexane curve is possibly repeated on a much diminished scale at a corresponding point on the benzene diagram. It may be noted that the minima previously observed in the rotatory power of *l*-menthyl methyl naphthalate (*loc. cit.*) dissolved in mixtures of an alcohol with benzene or hexane were also more accentuated when hexane was employed as the non-polar component, probably owing to its lower dielectric constant. We may therefore conclude that these alterations in rotatory power reflect the changes taking place in the electrical condition of the molecules of octyl alcohol in the solution. Their irregular character indicates an additional reason for the existence of minor displacements in solvent effect such as those referred to under Table I.

FIG. 1.

Rotatory power of d-*β-octanol in hexane and benzene.*

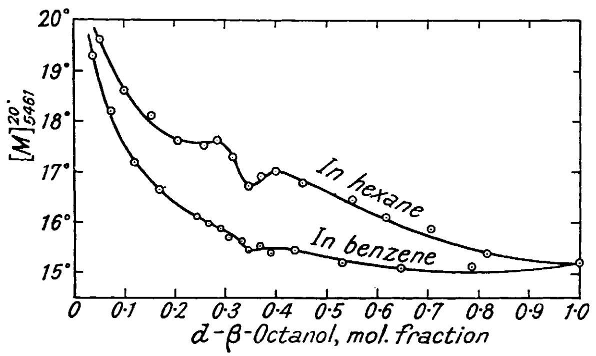

TABLE III.

Methyl d-β-*Octyl Ether* (t = 20°, *c* = 4, l = 2).

Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.	Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.
CCl_4	+ 17·5°	0	C_6H_5I	+ 27·6°	1·50
CS_2	+ 16·9	0	C_6H_5Br	+ 21·6	1·50
C_6H_{14}	+ 13·7	0	C_6H_6	+ 20·0	0
(Homog.)	+ 13·1	—	C_6H_5Cl	+ 19·2	1·52
CH_3I	+ 11·9	1·66	$C_6H_5{\cdot}CH_3$	+ 19·1	0·5
$CH_3{\cdot}OH$	+ 9·9	1·64	$C_6H_5{\cdot}OMe$	+ 18·6	1·25
$CH_3{\cdot}CO_2H$	+ 9·35	1·40	o-$C_6H_4Cl_2$	+ 18·6	2·24
$CH_3{\cdot}CHO$	+ 9·3	2·71	$C_6H_5{\cdot}CHO$	+ 16·7	2·74
$CH_3{\cdot}CN$	+ 8·3	3·05	$C_6H_5{\cdot}CN$	+ 15·4	3·85
CH_2Cl_2	+ 3·95	1·61	(Homog.)	+ 11·0*	—
$CHCl_3$	+ 3·8	1·10	$C_6H_5{\cdot}NO_2$	+ 10·5	3·90
$CH_3{\cdot}NO_2$	− 0·35	3·78			

Limiting values of α_{5461} : aliphatic solvents − 0·02° and + 0·97°, aromatic solvents 0·60° and 1·54°.

* This sample was not optically pure.

From the results of molecular-weight determinations it is usually supposed that ethers have little tendency to undergo association, and at first sight the wide range of molecular rotations for methyl octyl ether in Table III is surprising. Nevertheless, the fact that the ether exhibits higher rotations when dissolved in non-polar aliphatic solvents may be interpreted as indicating that the molecules in the homogeneous ether are to some extent oriented with respect to each other,* and in such a manner as to lead to a diminution in rotatory power.

Except for a downward displacement of methylene chloride and chloroform in the aliphatic series, which recalls a similar abnormality in the influence of these compounds on the rotation of octyl alcohol, there is a close agreement between the polarity of the solvents and the rotatory power. In nitromethane the depression in activity is so great

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* Throughout this paper the term association is used to indicate any departure from an entirely random orientation of the molecules.

that the rotation is reversed in sign. Aromatic solvents on the whole yield more highly active solutions, among which those given by the halogen derivatives, chloro-, bromo-, and iodo-benzene, are unusually high in relation to their polar properties. Apart from these three exceptions, the aromatic solvents also influence the rotatory power in the inverse order of their dipole moments.

TABLE IV.

d-β-*Chloro-octane* (t = 20°, c = 5, l = 2).

Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.	Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.
$CH_3{\cdot}CN$	+ 57·7°	3·05	$C_6H_5{\cdot}CN$	+ 55·0°	3·85
$CH_3{\cdot}OH$	56·8	1·64	(Homog.)	(53·5)	—
$CH_3{\cdot}NO_2$	55·9	3·78	$C_6H_5{\cdot}NO_2$	52·8	3·90
$CH_3{\cdot}CO_2H$	55·0	1·40	$C_6H_5{\cdot}CHO$	51·6	2·74
C_6H_{14}	54·8	0	*o*-$C_6H_4Cl_2$	49·6	2·24
*cyclo*Hexane	54·0	0	C_6H_5Cl	49·1	1·52
(Homog.)	(53·5)	—	C_6H_5Br	48·3	1·50
CH_2Cl_2	53·3	1·61	$C_6H_5{\cdot}OMe$	47·6	1·25
$CHCl_3$	52·7	1·10	$C_6H_5{\cdot}CH_3$	46·2	0·5
CCl_4	52·6	0	C_6H_6	46·1	0
CH_3I	50·1	1·66	C_6H_5I	46·0	1·50
CS_2	48·1	0			

Limiting values of a_{5461}, 3·10° and 3·88°.

d-β-*Bromo-octane* (t = 20°, c = 5, l = 4).

Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.	Solvent.	$[M]_{5461}$.	$\mu \times 10^{18}$.
$CH_3{\cdot}CN$	+ 85·8°	3·05	(Homog.)	(+ 78·7°)	—
$CH_3{\cdot}OH$	85·0	1·64	$C_6H_5{\cdot}CN$	78·7	3·85
$CH_3{\cdot}NO_2$	82·9	3·78	$C_6H_5{\cdot}NO_2$	77·6	3·90
$CH_3{\cdot}CO_2H$	82·7	1·40	$C_6H_5{\cdot}CHO$	76·2	2·74
C_6H_{14}	80·5	0	*o*-$C_6H_4Cl_2$	73·1	2·24
(Homog.)	(78·7)	—	C_6H_5Cl	72·8	1·52
*cyclo*Hexane	77·3	0	C_6H_5Br	71·5	1·50
$CHCl_3$	77·3	1·10	$C_6H_5{\cdot}OMe$	71·4	1·25
CCl_4	76·7	0	$C_6H_5{\cdot}CH_3$	69·8	0·5
CH_3I	74·4	1·66	C_6H_6	69·5	0
CS_2	72·7	0	C_6H_5I	69·5	1·50
			s-$C_6H_3(CH_3)_3$	69·3	0

Limiting values of a_{5461}, 7·16° and 8·92°.

The experimental results obtained with octyl chloride are identical in almost every detail with those given by the bromide, apart from the higher rotatory power of the latter, and the compounds may therefore be discussed together. In two important respects these halides differ from all the other simple octyl derivatives under examination. Not only are the observed rotations of a much higher order of magnitude, but they tend to vary *directly* with the polarity of the solvent, so that the highest rotations are given in the most highly polar media.

For the aromatic series, the correspondence between optical activity and dipole moment is almost complete; iodobenzene alone forms an exception and gives a lower rotation than was to be expected from its polarity. A number of irregularities occur among the aliphatic solvents, the most notable of which are the low rotation observed in methyl iodide and the high value in methyl alcohol. Chloroform and methylene chloride again give low values, although their position with respect to carbon tetrachloride indicates that here also the general arrangement of the chloro-compounds among themselves is such that the more polar solvent yields the more active solution.

Further confirmation of the optical effects arising in this case from solution in highly polar solvents is obtained by diluting the homogeneous *l*-octyl chloride with increasing proportions of a non-polar liquid. It is not necessary to reproduce the full experimental details, but the results may be briefly summarised. With benzene as diluent, the rotatory power falls from $[M]_{5461}$ — 55·4° for the homogeneous liquid to — 47° at low concentrations ($c = 5$), the change being represented by a smooth curve without maximum or minimum. An effect in the same sense follows when the non-polar solvents carbon disulphide, carbon tetrachloride, or toluene are employed. The use of hexane brings about a very small rise in value from — 60·0° to — 61·6°, but on the other hand when *l*-octyl bromide is used as the active solute in hexane solution the rotation falls from — 78·7° to — 77·3°. Hence it may be assumed that the normal effect of orientation is to raise the rotatory power. Since it appears probable that the rotation of the halides is largely controlled by the halogen atoms which are directly linked to the asymmetric carbon atom, we must conclude that the specific influence of these atoms is enhanced when the active molecules are brought into closer proximity to one another. An optical change of this kind might be imagined to arise if the molecules oriented themselves in the manner (+ —) (+ —) instead of in the more usual arrangement corresponding to dipole association, because in this case the fields mutually reinforce each other. No evidence, however, has been obtained from polarisation measurements which would indicate an orientation of this type among the halides (Smyth, *Chem. Reviews*, 1929, **6**, 567) although it has been observed frequently among alcohols at intermediate concentrations in a non-polar medium. Viewing the matter from another angle, it is not yet possible to discuss the influence of an increasing polarity of the solvent upon the position or anisotropic properties of the absorption bands of the active halides. But the opposite trend of the optical displacement in polar solvents as compared with that found for the remaining octyl derivatives suggests that the mechanism of the solvent effect may vary from one case to another.

TABLE V.

Rotatory Powers of β-*Nitro-octane* (t = 20°, l = 2).

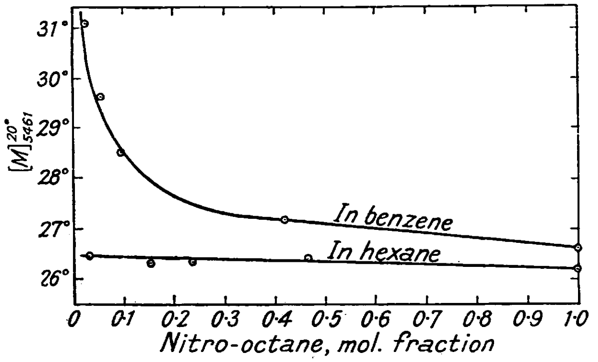
In benzene.			In benzene.			In hexane.			In hexane.		
c.	f_2.	$[M]_{5461}$.	*c.*	f_2.	$[M]_{5461}$.	*c.*	f_2.	$[M]_{5461}$.	*c.*	f_2.	$[M]_{5461}$.
3·998	0·023	31·1°	53·71	0·420	27·16°	3·994	0·033	26·5°	50·07	0·467	26·40°
9·346	0·055	29·6	(Homog.)	1·000	26·58	17·98	0·152	26·30	(Homog.)	1·000	26·18
15·80	0·095	28·53				27·27	0·237	26·33			

f_2 = Mol. fraction of nitro-octane. Limiting values of α_{5461} are 1·33° and 30·83°.

Owing to the fact that β-nitro-octane can only be prepared in very small yields it was decided to examine the change in rotatory power on diluting the compound with benzene and hexane respectively, and thereafter to investigate the influence of as many other solvents as was possible with the material available.

FIG. 2.

Rotatory power of d-β-*nitro-octane in hexane and benzene.*



The diagrams (Fig. 2) obtained by plotting the values of the rotatory powers in hexane and benzene against the mol. fractions of nitro-octane present in solution are very different in form. The values for hexane fall on an almost horizontal straight line, whereas those for benzene lie on a smooth curve which rises steeply at low concentrations, indicating that the rotatory power increases as the degree of association of the nitro-compound diminishes. It thus appears that hexane is not capable of breaking up the association complexes appreciably even at high dilutions, but that the addition of benzene is accompanied by a gradual disruption of the aggregates, a change which becomes more definite at very low concentrations. Although it is not possible to determine the exact point at which the benzene curve meets the vertical axis, the nitro-compound in the unimolecular state in this solvent would evidently possess a molecular rotation $[M]_{5461}$ higher than 35°. It may be noted that the form of the rotation–dilution diagram for nitro-octane in benzene resembles that of the polarisation–dilution diagram given by Debye ("Polare Molekeln," p. 49) for nitrobenzene in the same solvent.

TABLE VI.

d-β-*Nitro-octane in Solution* (c = 4, t = 20°, l = 2).

Solvent.	$C_6H_5{\cdot}OMe$.	C_6H_5Cl.	C_6H_6.	$C_6H_5{\cdot}NO_2$.	C_6H_{14}.	(None).
$[M]_{5461}$	35·5°	31·5°	31·1°	27·2°	26·9°	(26·7°)
$\mu \times 10^{18}$	1·25	1·52	0	3·90	0	—

Limiting values of a_{5461} in solution : 1·35° (hexane) and 1·79° (anisole).

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 compound 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 will not allow the rotation to rise to its maximum value owing to the depressive influence of association between the nitro- and the methoxyl group. 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 rotation lower, although not so low as that found in nitrobenzene. On this hypothesis benzene fails to effect a complete separation of the solute molecules at moderate dilutions, and in hexane a considerable degree of association occurs even at the lowest concentration ($c = 4$) for which the optical rotation was determined. This supposition is supported by molecular-weight determinations recorded in the literature for nitro-derivatives (cf. Mascarelli and Benati, *Gazzetta*, 1909, **39**, ii, 652; Auwers, *Z. physikal. Chem.*, 1893, **12**, 689) and by the following values obtained for inactive nitro-octane ($M = 159$) in *cyclo*hexane and benzene.

Solvent.	Wt. of solute, g.	Depression of f. p.	*c*.	*M*.
*cyclo*Hexane, 20 c.c.	0·1284	0·901°	0·64	187
(15·52 g.)	0·4657	3·108	2·33	196
	0·6248	4·100	3·12	200
Benzene, 15 c.c.	0·4197	0·978	2·8	162
	1·348	2·983	8·3	170

The exact interpretation of molecular-weight values deduced by such methods as the above is still a matter for discussion, but the figures indicate that at $c = 4$, the lowest concentration at which it is practicable to determine the rotatory powers, nitro-octane is very considerably associated in *cyclo*hexane solution (extrapolated value of M, 205), whereas in benzene the association is of a much smaller order of magnitude. In this connexion it is probable that *any tendency of the solute molecules to assume a definite orientation towards one another will be more clearly exhibited in polarimetric than in cryoscopic data.* A similar conclusion in respect of the degree of polarisation has been arrived at by Smyth (*Chem. Reviews*, 1929, **6**, 573), who writes that a " molecular orientation too slight to be apparent in its effect upon most physical properties of liquids may have a considerable effect upon the polarisation."

The rotatory powers of α-methyl-*n*-hexoic acid in the above solvents are seen to vary only within narrow limits. As the acid becomes less associated at higher dilutions the rotation rises somewhat, the change being insignificant in hexane but more definite in benzene, as is to be expected from the greater dissociating power of the latter solvent. Slightly higher values are found in ether and acetone, in which the carboxylic aggregates may be assumed to be partly replaced by association complexes composed of acid and solvent. In ether the values appear to fall at low concentrations, giving a maximum at about $f_2 = 0{\cdot}1$. The limited range of the observed rotations may be attributed to the very strong tendency of the acid molecules to undergo association, either with one another, as occurs in the benzene and hexane solutions, or with a polar solvent; in either case it

TABLE VII.

*α-Methyl-*n*-hexoic Acid * in Solution* (t = 20°, l = 2).

Hexane.		Benzene.		Ether.		Acetone.	
f_2.	$[M]_{5461}$.	f_2.	$[M]_{5461}$.	f_2.	$[M]_{5461}$.	f_2.	$[M]_{5461}$.
0·045	+ 33·7°	0·013	+ 35·3°	0·023	+ 33·3°	0·026	+ 36·6°
0·079	33·6	0·031	35·4	0·053	34·3	0·048	36·4
0·173	33·5	0·068	34·9	0·072	34·7	0·055	36·3
0·344	32·85	0·122	34·5	0·094	35·1	0·132	35·75
0·536	32·69	0·196	34·1	0·147	34·96	0·217	35·21
0·719	32·44	0·283	33·78	0·207	34·70	0·412	34·21
1·000	32·17	0·447	33·15	0·334	33·56	0·566	33·61
($d_{4°}^{20°}$ = 0·915)		0·667	32·65	1·000	32·15	1·000	32·15
		1·000	32·14				

Limiting values of *α* are 1·03° and 40·87°.

* The sample of acid used was not optically pure (see p. 386).

may be concluded that the rotatory power will be considerably less than that corresponding to the unimolecular compound in a non-polar medium.

TABLE VIII.

Molecular Rotatory Powers $[M]_{5461}$ *of* sec.-β-*Octyl Toluates and Methoxybenzoates in Solution* (t = 20°, l = 2, c = 4).

		Toluates.			Methoxybenzoates.		
Solvent.	$\mu \times 10^{18}$.	*o*-.	*m*-.	*p*-.	*o*-.	*m*-.	*p*-.
*cyclo*Hexane	0	+ 84·9°	+ 104·1°	+ 114·7°	—	+ 101·5°	+ 124·9°
Mesitylene	0	76·5	—	115·8	—	—	129·2
C_6H_6	0	71·1	95·8	111·9	+ 29·6°	91·4	125·5
$C_6H_5{\cdot}CH_3$...............	0·4	71·0	101·5	116·2	34·4	98·4	128·9
$C_6H_5{\cdot}OMe$	1·25	69·7	106·9	118·3	32·0	104·4	134·2
C_6H_5Cl	1·52	61·0	92·7	104·7	26·1	90·0	117·0
C_6H_5Br	1·50	60·0	91·9	104·5	24·8	89·0	117·1
C_6H_5I	1·50	54·5	89·0	102·4	18·7	83·5	116·0
o-$C_6H_4Cl_2$	2·24	57·2	88·1	97·7	19·1	87·8	107·0
$C_6H_5{\cdot}CHO$	2·74	56·4	90·1	101·3	18·1	88·4	113·4
$C_6H_5{\cdot}CN$	3·85	56·8	89·0	99·3	21·1	88·1	111·9
$C_6H_5{\cdot}NO_2$	3·90	63·9	97·9	98·9	22·0	92·0	110·3
(Homog. ester)		(81·2)	(111·4)	(122·5)	(38·2)	(111·4)	(136·4)

The six *sec.*-β-octyl toluic and methoxybenzoic esters behave in a similar manner towards change of solvent and may therefore be included in one table by arranging the solvents in order of increasing polarity. On the whole, there is a definite tendency for solvents of low dipole moments to yield solutions of high activity and *vice versa*. Nitrobenzene behaves abnormally towards *o*- and *m*-substituted esters, giving somewhat higher values than correspond to its position in the polar scale, and displacements of the same kind are found with anisole.

Attention may be directed to the case of the *o*-methoxybenzoic ester, in which the presence of a weakly polar methoxyl group in the ortho-position brings about a pronounced fall in rotatory power as compared with the unsubstituted *d*-octyl benzoate, for which in the homogeneous state $[M]_{5461} = 92°$. Since the rotation suffers a still greater depression when the compound is dissolved in strongly polar solvents, it is improbable that any considerable part of the solvent influence operates by way of dipole association between the medium and the methoxyl group, a process which might be expected to nullify the original effect of the ortho-substituent and yield a more highly active solution. Hence the effect may be assumed to be propagated either through the more polar carboxyl group or, since this is largely screened by the bulky hydrocarbon radicals, through the benzene nucleus which exists in a state of induced polarisation as a result of the attached polar substituents.

One aim of the present investigation was to ascertain whether any inference as to the configurational relationships existing between the octyl alcohols and their halides could be drawn from the optical changes undergone by these compounds in solution. As has already been seen in Table IV, octyl chloride and bromide are affected in an unusual sense by an increase in the polarity of the solvent medium, but the direction of the change does not appear to throw any light on the point under discussion. The complexity of the problem is emphasised by the following data referring to some of the corresponding derivatives of *d*-amyl alcohol, which differs from β-octanol principally in being a primary alcohol and in having the asymmetric atom situated one remove from the hydroxyl group. Only a few typical aromatic solvents were examined on account of the limited amount of the active material available.

TABLE IX.

Rotatory Powers, $[M]^{20^\circ}_{5461}$, *of* d-*Amyl Derivatives in Solution* (l = 4, c = 5).

Solvent.	$\mu \times 10^{18}$.	Alcohol.*	Methyl ether.	Bromide.	*o*-Toluate.
(None)	—	− 5·45°	+ 0·46°	+ 5·8°	+ 11·0°
C_6H_6	0	− 6·7	+ 0·8	+ 6·8	+ 10·1
$C_6H_5{\cdot}CH_3$	0·4	− 6·6	+ 0·9	+ 6·6	+ 10·8
$C_6H_5{\cdot}OMe$	1·25	− 6·2	+ 0·7	+ 7·2	+ 11·1
C_6H_5Cl	1·55	− 5·7	—	+ 6·9	—
$C_6H_5{\cdot}CHO$	2·75	− 5·6	—	—	—
$C_6H_5{\cdot}CN$	3·85	− 5·5	+ 0·1	+ 6·3	+ 13·7
$C_6H_5{\cdot}NO_2$	3·89	− 5·2	− 0·1	+ 6·1	+ 14·8

The experimental errors in these determinations are relatively large : α_{5461} varied from 0·02° for the methyl ether in $C_6H_5{\cdot}CN$ to 1·46° for the toluate in $C_6H_5{\cdot}NO_2$.

* Values for the alcohol were determined by Miss M. M. Barnett.

Although the observed optical changes are small, owing to the low rotatory powers of the active compounds, in every case the direction of the displacement is quite definite. On the basis of the above table we may divide the amyl derivatives into two groups, one comprising the lævorotatory alcohol and its dextrorotatory toluic ester, which are displaced in a positive sense as the polarity of the solvent increases, and the other including the ether and the bromide, which are displaced in a negative sense. It will be noted that these variations do not bear any simple relationship to those undergone by the corresponding octyl derivatives. Hence, although the optical rotation exhibited by each compound in solution is related to the dipole moment of the solvent employed, the direction of the change does not at present provide any means of determining the configurations of the active solutes, at all events in cases where the latter differ in chemical constitution. A similar difficulty has been encountered by earlier workers in attempts to make use of the effect of added salts in determining the configuration of active compounds.

DISCUSSION.

Each of the fifteen *sec.*-β-octyl and *d*-amyl compounds under examination exhibits rotatory powers in solution which are closely related to the dipole moment of the solvent, provided that monosubstituted derivatives of the same hydrocarbon are employed for the comparison. In eleven of these cases, *viz.*, octyl alcohol, the octyl and amyl ethers, amyl bromide, nitro-octane, and the six octyl toluic and methoxybenzoic esters, the magnitude of the optical rotation tends to vary in the *opposite* sense to the dipole moment of the medium. In the remaining four cases, *d*-amyl alcohol (regarded as a dextro-compound), amyl *o*-toluate, and octyl chloride and bromide, the reverse relation obtains, the highest rotations being given in highly polar solvents. α-Methyl-*n*-hexoic acid, which strictly does not belong to either of the above groups of active compounds, only showed very small differences in rotatory power, the values being somewhat higher in polar than in non-polar solvents.

In seeking for an explanation of these solvent effects in terms of the theory of dipoles, *we may take the case of an optically active liquid of simple structure, containing not more than one polar substituent,* and consider briefly the variations in the internal molecular field resulting from dilution with solvents of varying polarities. Where a polar substituent is present in the active molecule, it is assumed that the electrical field exerted by it upon the groups attached to the asymmetric atom represents one of the contributory factors governing the magnitude of the rotatory power. This field may be modified by variations in the degree and mode of association occurring between the active molecules or between those of the active compound and an added solvent, and also to a smaller extent by any variation in the average orientation of the molecules with respect to one another. In the majority of cases we are not yet in a position to predict with any certainty the direction in which the rotatory power of the compound will be displaced by solution in a highly polar solvent, but once this direction has been determined it should at all events be possible to correlate this effect with that arising from an increase in the concentration of the solute when dissolved in a hydrocarbon solvent.

From the data already obtained in these studies, it is suggested that optically active solutes may be divided into four main classes, according to the nature of the substituent groups present and their reaction towards the solvent.

Class I. Non-polar solutes. The chief representatives of this group are saturated hydrocarbons, the molecules of which in the homogeneous liquid may be regarded as assuming an almost entirely random orientation towards one another. This random arrangement may be expected to persist even when the compound is dissolved in solvents of a non-polar or polar character, so that, although in the latter case the internal field of the asymmetric molecule may suffer momentary changes under the influence of the polar groups in the solvent molecules, yet these fluctuations will tend to nullify one another in the aggregate. *Little or no variation in rotatory power is therefore probable when the compound passes from the homogeneous state into solution,* or when a change is made in the concentration. So far, no examples of this type have been examined.

Class II. Weakly polar solutes. Into this group fall compounds having low dipole moments, including the majority of unsaturated hydrocarbons, ethers, alcohols, esters and halogen derivatives. Many of these do not appear to undergo association when examined in solution by cryoscopic or ebullioscopic methods, but there is no doubt that the molecules tend to assume a definite orientation with respect to one another, as is shown by polarisation data. In a homogeneous optically active liquid of this type the molecular orientation would be expected to bring about some modification of the internal field and hence also of the rotatory power. Generally speaking, in the case of a substance possessing one weakly polar grouping, the mutual orientation of the molecules may be assumed partially to neutralise the polar field of the substituent and so to diminish its characteristic effect upon the rotatory power. Owing to the weakness of the intermolecular forces, when such a compound is diluted with a non-polar medium the molecules are largely separated from one another by the diluent. Under these conditions, the internal field due to the polar group is no longer diminished by mutual orientation and its full influence is exerted on the rotatory power. In the majority of monosubstituted optically active compounds having the substituent in close proximity to the asymmetric atom, the rotatory power is largely governed by the nature of the polar group; consequently, dilution with a non-polar medium commonly results in a rise in molecular rotation.

When the solute is dissolved in a strongly polar liquid, effects of a contrary nature are observed. Here the partial orientation of the molecules in the homogeneous solute is replaced by a still more definite arrangement due to the stronger polar forces of the solvent molecules. In a solution of this kind the normal result of dilution is a more complete neutralisation of the field due to the substituent in the active compound, leading in most cases to a diminished rotatory power. In the same way, solvents of intermediate polarity will produce changes lying between these extremes. From these considerations it is seen that *for dilute solutions the rotatory power should be closely related to the dipole moment of the solvent.* Apart from certain minor displacements, these conclusions are supported by the properties of the hydroxy-, methoxy-, ester, and halogen derivatives under discussion, although in several cases, which have already been specified, the direction of the optical change is in the reverse sense to that indicated above, the highest rotatory powers being observed in the presence of strongly polar solvents and low values in non-polar media.

Among solutes of this class, octyl alcohol, octyl methyl ether, and octyl chloride and bromide have been examined at various concentrations in a non-polar solvent, for the purpose of determining the change resulting from the increased molecular orientation which occurs as the concentration of the solute rises. In every case the displacement in optical activity is in the same sense as that produced by increasing the polarity of the solvent, a change which also corresponds to an increase in the degree of molecular orientation.

The variation in rotatory power, if any, which results when an optically active monosubstituted hydrocarbon (*e.g.*, *d*-octyl bromide) is diluted with a solvent of the same chemical type and containing the same substituent (*e.g.*, an alkyl bromide) would appear to depend primarily upon the molecular polarisations of the two media. If the solvent has a higher molecular polarisation than the active liquid, then the degree of orientation existing between solute and solvent molecules under the new conditions will be greater than that occurring between the active molecules before dilution. The addition of the solvent is thus equivalent to an increase in the polarity of the medium. Other factors, such as the creation of induced polarities in a hydrocarbon radical under the influence of polar groups in adjacent molecules, which appears to occur comparatively readily with aromatic nuclei, may also be expected to produce minor changes in the field and therefore in the rotatory power. At present, however, owing to the lack of the necessary data, these secondary effects cannot be estimated. But, considering the wide range of molecular polarisation values covered by the solvents employed in these investigations, it might be anticipated that the rotatory powers of all the active compounds in the homogeneous state would exhibit values intermediate in magnitude between the extreme limits observed for dilute solutions in non-polar and highly polar solvents respectively. This conclusion is borne out by the figures recorded in the tables for the various hydroxy-, methoxy-, halogen, and nitro-compounds investigated. *d*-Amyl bromide (Table IX) and *d*-nitro-octane (Table VI) which were only examined in aromatic solvents, form partial exceptions, but even in these cases the rotations for the homogeneous liquids differ from the lowest observed values in solution by no more than the experimental error involved in the determination. Since aliphatic solvents derived from methane generally lead to greater variations than monosubstituted benzenes, it is possible that these compounds would not have been exceptional had solvents of the former type been employed. On the other hand, the rotatory powers of the more complex toluic and methoxybenzoic esters, apart from the octyl and amyl *o*-toluates, all lie a few degrees above the highest values found in solution, thus indicating the existence of other factors influencing the magnitude.

Class III. Strongly polar solutes. In this group are included compounds such as nitro-, cyano-, and ketonic derivatives, all of which exhibit a strong tendency to undergo association even when dissolved in solvents of low or zero polarity. In such cases the considerations laid down under Class II still hold, modified, however, by the special characteristics of the highly polar compounds.

The rotatory power of the homogeneous compound in the liquid state will be strongly affected by the high degree of association existing between the molecules, and in the majority of cases this will result in a lowered optical rotation. *The changes following upon dilution with a solvent depend on the extent to which the latter is capable of breaking up these association complexes.* Nitro-compounds and many substances containing the ketonic grouping still remain more or less associated at high dilutions in *cyclo*hexane, hexane, or even benzene. Solutions of this kind therefore exhibit a rotatory power not far removed from that of the highly associated solute in the homogeneous state. When a weakly polar solvent is employed, the original solute complexes may become disrupted, leading either to the formation of new solute–solvent aggregates, or merely to a mutual orientation of solvent and solute molecules. In this event the rotation of the homogeneous liquid is considerably modified by the presence of the solvent, and in the majority of cases assumes a higher value. On dilution of the active solute with a highly polar solvent, however, the electrical state of the active molecules undergoes relatively little change, the highly associated solute aggregates being replaced by others formed by union between solvent and solute; this condition therefore resembles that occurring in hydrocarbon solvents. In illustration we may quote the case of nitro-octane, which exhibits very low rotations, not only in the homogeneous state and in nitrobenzene solution, but also when dissolved in hydrocarbons, although considerably higher values are obtained in the presence of weakly polar solvents.

Carboxylic acids are known to exist in the form of exceptionally stable association complexes, despite the relatively low dipole moments which have been assigned to them. It must be remembered, however, that the carboxyl group is a composite, containing as it does a ketonic and a hydroxylic dipole, both of which are of relatively high polarity. For this reason, the influence of the carboxyl group frequently classes it with the highly electronegative substituents, as is seen in its effect not only upon properties such as ionisation, chemical reactivity, and degree of association, but also in the behaviour of optically active acids in solution. From the values recorded in Table VII it will be noted that α-methyl-*n*-hexoic acid undergoes remarkably little alteration in rotatory power with change of solvent, a result which might have been expected if the carboxylic aggregates are not readily disrupted by non-polar or weakly polar solvents.

In addition, it seems probable that a similar explanation may be applied to certain abnormal values given by optically active solutes of *moderate* polarity in the presence of saturated hydrocarbon solvents. For example, reference to Table IV shows that octyl chloride and bromide yield solutions of intermediate activity in hexane and *cyclo*hexane, possibly owing to the fact that in these media the polar molecules do not assume an entirely random orientation.

Class IV. In this group may be placed compounds which, when brought into contact with certain solvents, suffer electronic rearrangement due to compound formation, co-ordination, ionisation, etc. Examples of this type are carboxylic acids dissolved in basic solvents, bases in alkyl halides, and ethers or ketonic derivatives in the presence of strong acids. The irregular changes found for octyl alcohol on progressive dilution with hexane may be traced to a similar origin, *viz.*, to alterations in the manner in which the alcohol molecules are associated with one another. On the other hand, the behaviour of octyl methyl ether, nitro-octane, and the octyl halides on dilution with non-polar solvents is represented by smooth curves without maxima or minima. These observations are in agreement with the polarisation changes which are characteristic of the types of organic compound in question.

No detailed analysis can be made of the actual direction of the optical displacement in any given case. Quite apart from the probability that these changes may be brought about by different mechanisms, a further complication is that, except in the halides, the more polar groups represent systems of two (or more) dipoles, *e.g.*, $\overset{+}{\mathrm{C}}\overset{-}{—}\mathrm{O}\overset{-}{—}\overset{+}{\mathrm{H}}$, $\overset{+}{\mathrm{C}}\overset{-}{—}\mathrm{O}\overset{-}{—}\overset{+}{\mathrm{Me}}$, which, at all events in the alcohol and ether, are oriented in opposite directions to one another.

EXPERIMENTAL.

The starting point in the prepn. of the following octyl derivatives was octyl alcohol ($\alpha_{5461}^{20^\circ}$ ± 9·60° to ± 9·67°, $l = 1$), obtained from the racemic hydrogen phthalate (Kenyon, J., 1922, **121**, 2540).

d-β-Octyl chloride was prepared from the *l*-alcohol by the method of McKenzie and Tudhope (*J. Biol. Chem.*, 1924, **62**, 551), $SOCl_2$ being used in the presence of C_5H_5N. Different prepns. had rotations varying from $\alpha_{5461}^{20^\circ}$ + 31·1° to 35·0° ($l = 1$). McKenzie and Tudhope record $\alpha_D^{20^\circ}$ + 29·2°; Houssa, Kenyon, and Phillips obtained a sample of $\alpha_D^{15^\circ}$ + 31·0°. Octyl bromide was prepared with the aid of PBr_3 (Shriner and Young, *J. Amer. Chem. Soc.*, 1930, **52**, 3337). It gave $\alpha_{5461}^{20^\circ}$ + 44·0° ($l = 1$), a considerably higher value than that found by the above authors, *viz.*, $\alpha_D^{20^\circ}$ + 29·8°.*

Methyl *d*-octyl ether was obtained by using a slight modification of Kenyon and McNicol's procedure (J., 1923, **123**, 14), any unchanged *d*-alcohol being removed by treating the ether with *p*-nitrobenzoyl chloride and dry C_5H_5N. The rotation of the product varied from $\alpha_{5461}^{20^\circ}$ + 6·14° to + 7·36° ($l = 1$). The above authors found + 7·14°.

β-Nitro-octane, prep. according to Shriner and Young (*loc. cit.*), had $\alpha_{5461}^{20^\circ}$ + 15·42° ($l = 1$). The authors do not give sufficient data for a comparison with their product.

α-Methyl-*n*-hexoic acid, m. p. 96°, was obtained by the malonic ester synthesis and purified by solution in C_6H_6, followed by pptn. with light petroleum. Resolution, which was incomplete

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* No polarimeter was available at this period for use with the D line, hence no direct comparison was made at this wave-length.

owing to the small amount of material, was effected by use of quinine (cf. Levene and Bass, *J. Biol. Chem.*, 1926, **70**, 211). The *d*-acid gave $[\alpha]_D^{20^\circ}$ 15·7° in Et_2O ($c = 5$). Levene and Bass record + 19·5° ($c = 5·5$).

The various octyl esters were redistilled from samples prepared by Rule and co-workers (J., 1926, 2116; 1928, 178).

(With J. HARROWER.) The following were prepared from *d*-amyl alcohol supplied by Prof. A. McKenzie. *d*-Amyl alcohol, 11 g., purified by distillation over Ca (b. p. 125—127°, $\alpha_{5461}^{19^\circ}$ − 5·05°, $l = 1$), was converted into the bromide by heating with HBr (Marckwald, *Ber.*, 1904, **37**, 1046), any unchanged alcohol being removed with conc. H_2SO_4. The bromide (4·8 g.) had $[\alpha]_D^{20^\circ}$ + 3·33°; Marckwald records + 3·68°. Methyl *d*-amyl ether was obtained by the method adopted for methyl octyl ether by Kenyon and McNicol (J., 1923, **123**, 17) from *d*-amyl alcohol (14 g.) in dry Et_2O, K (3·9 g.), and MeI (14 g.). This gave the methyl ether (4 g.), b. p. 91—94°/753 mm., and $\alpha_{5461}^{21^\circ}$ + 0·34° ($l = 1$) (Guye and Chavanne, *Bull. Soc. chim.*, 1896, **15**, 301, found $\alpha_D^{18^\circ}$ + 0·29°). *d*-Amyl *o*-toluate, prepared from the acid chloride, C_5H_5N, and *d*-amyl alcohol (2·8 g.), had $\alpha_D^{20^\circ}$ + 5·27° ($l = 1$) (Guye and Chavanne, *loc. cit.*, p. 291, record $\alpha_D^{20^\circ}$ + 4·51°, $l = 1$).

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