CCCLXX.—*Studies in Solvent Action. Part II. Rotatory Powers of* d-*β-Octyl Hydrogen Phthalate and its Methyl Ester.*

By H. GORDON RULE and JOHN M. HILL.

IN view of the regular manner in which the rotatory power of *d*-β-octyl sodium phthalate is affected by the presence of added salts, it was considered of interest to examine the behaviour of the compound towards organic solvents. Striking variations have already been established in the case of *l*-menthyl methyl naphthalate (Rule and McLean, this vol., p. 674), the rotation of which is depressed by polar solvents to an extent depending upon the polarity of the medium.

It is now found that octyl hydrogen phthalate undergoes similar variations in solvents derived from benzene, but that the effects in simple aliphatic solvents are less regular. The observed data are contained in Table I, in which the rotatory powers are arranged in descending order of magnitude. Dipole moments, μ (in e.s.u.), are those given in Debye's " Polare Molekeln " (1929) except where otherwise stated.

In benzene solvents the rotatory powers vary from 150° to 74°, and arrange themselves approximately in the same order as the dipole moments of the liquid media. Benzaldehyde is displaced to a small extent, apparently owing to the presence of benzoic acid or an intermediate product of oxidation, since the rotatory power is still lower when measured in benzaldehyde which has been allowed to stand for several days after distillation (compare also the low value obtained for acetic acid). As in the case of *l*-menthyl methyl naphthalate, the lowest values are observed in strongly polar solvents, indicating that the changes are probably due to deformation, possibly accompanied by dipole association between solvent and solute, which will have the effect of lowering the internal electrical field exerted by the polar substituents in the active compound. A small part of the diminution in optical activity, however, may be attributed to increased ionisation in the solvents of high dielectric constant. *o*-Dichlorobenzene, in which the adjacent CCl-dipoles reinforce each other's field, is found to occupy the expected position in the table; the case of *p*-disubstituted derivatives is discussed later. Further, a comparison of benzaldehyde (76·3°) and benzophenone (109·8°) illustrates the steric influence of the methyl group in hindering the approach of the polar groups in solvent and solute, thus leading to a higher rotatory power. Several examples of this type have already been discussed in connexion with *l*-menthyl methyl naphthalate.

TABLE I.

(1) d-β-*Octyl hydrogen phthalate in benzene solvents* (l = 2).

Solvent.	c.	$\alpha^{20°}_{5461}$.	$[M]^{20°}_{5461}$.	$\mu \times 10^{18}$.
$C_6H_5{\cdot}CH_3$	5·020	5·43°	150·5°	0·4
C_6H_6	5·000	5·21	145·0	0
$C_6H_5{\cdot}OMe$	5·004	4·53	126·0	1·16
C_6H_5Br	5·000	4·26	118·6	1·5
C_6H_5I	5·000	4·21	117·2	1·25 (1·5 ?)
C_6H_5Cl	5·000	4·15	115·5	1·55
$C_6H_5{\cdot}NH_2$	5·018	3·87	107·3	1·51 (1·60)
o-$C_6H_4Cl_2$	5·000	3·76	104·6	2·25]
$C_6H_5{\cdot}CN$	5·000	2·88	80·2	3·84
$C_6H_5{\cdot}NO_2$	5·016	2·83	78·5	3·90
$C_6H_5{\cdot}CHO$	5·000	2·74	76·3	2·75
($C_6H_5{\cdot}CHO$*	5·000	2·67	74·3)	
[$C_6H_5{\cdot}CO{\cdot}CH_3$	5·020	3·96	109·8	2·97]

Maximum range of rotation, 76°.

* Several days after distillation.

(2) d-β-*Octyl hydrogen phthalate in methane solvents* (l = 2).

[$C_2H_5{\cdot}OH$	5·024	5·85	162·0	1·74]
$CH_3{\cdot}OH$	5·004	5·56	154·6	1·73
CH_3I	5·024	5·48	151·8	1·66
CCl_4.....................	4·012	4·32	149·8	0
$CHCl_3$	5·000	5·38	149·7	1·10
$CH_3{\cdot}CHO$	5·000	5·15	143·3	2·72
CS_2	5·000	5·10	141·9	0
CH_2Cl_2	5·000	5·05	140·5	1·61
$CH_3{\cdot}CO{\cdot}CH_3$	5·000	5·04	140·3	2·97
$CH_3{\cdot}CO_2H$	5·000	4·98	138·5	0·74 (1·4*)
$CH_3{\cdot}CN$	5·020	4·89	135·6	3·94 (3·1)
$CH_3{\cdot}NO_2$	1·014	0·92	126·2	3·78 (3·05)

Maximum range of rotation, 36°.

* C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 1824.

In aliphatic solvents a similar tendency is evident, although there are here numerous exceptions. The five lowest positions are again occupied by strongly polar liquids, with acetonitrile and nitromethane at the foot of the list, but the arrangement of the remainder of the table reveals no regularities. From the abnormally low rotation found in carbon disulphide, it may be suggested that two separate solvent influences are at work : one propagated through the chemically active carboxyl group, and probably representing the main effect, and a secondary one through the less active octyl ester grouping. The investigation of octyl acetate and of the corresponding esters of monosubstituted acetic acids (Pickard and Kenyon, J., 1914, **105**, 835; Rule and R. K. S. Mitchell, J., 1926, 3203) has shown that these compounds are affected in a remarkably similar and very irregular manner by aliphatic solvents, a similarity which must be ascribed to the presence of the carboxy-ester complex common to all the active compounds. In every case an abnormally low rotatory power was observed in carbon disulphide, in which the rotation was usually reversed in sign. Aromatic solvents on the other hand gave definite evidence of a polar influence. Probably the considerable variation in molecular form and volume of the methane derivatives is one factor bearing upon these differences. The smaller steric hindrance offered by the less bulky molecules would be expected to facilitate their effective approach to the already well-screened dipoles of the $CO_2C_8H_{17}$-group.

On the above assumption of a dual route of propagation it would be anticipated that the secondary influence could be made more prominent by repressing the chemical activity of the free carboxyl group, *e.g.*, by converting the phthalate into its *methyl* ester. In the latter compound the ester groups are of similar polarity and differ principally in the greater steric hindrance offered by the *sec.*-octyl than by the methyl radical. The rotatory powers observed with the methyl ester are given in Table II.

As in the case of the acid ester, the rotatory power of methyl octyl phthalate dissolved in benzene derivatives varies regularly in accordance with the polarity of the medium. Anisole is slightly displaced with respect to benzene, but the remaining solvents fall into positions corresponding to their dipole moments. In view of the small difference between the values in benzene and anisole solutions, as compared with the considerable gap between those for benzene and bromobenzene, it would appear that the higher rotations in anisole and toluene are due to the presence of the methyl group in the side chain of the solvent molecule. Aliphatic solvents in general give higher rotations for both esters, and although the acid ester could not be examined in hexane owing to its insolubility, the diester in this solvent was found to exhibit a high rotatory power. Anisole and toluene are not only partly aliphatic in character, but the polar nature of the former is to some extent masked by the screening influence of the methyl group. A similar two-fold influence is shown in the much higher rotation given by acetophenone as compared with benzaldehyde.

Among the methane solvents, it is not even possible to trace the limited polar influence which was evident in the case of the acid ester. At present no suggestion is advanced to account for the divergent properties of the two series of solvents, except to draw attention to a contributary factor in the more pronounced variations in molecular form and volume which obtain among the aliphatic compounds. Such variations will necessarily affect the ease with which the polar groups in solvent and solute can approach one another, and so lead to irregularities. On the other hand, the greater bulk and rigidity of the benzene ring in the aromatic solvents tend to minimise differences due to the structures of the attached substituents.

TABLE II.

(1) *Methyl* d-β-*octyl phthalate in benzene solvents* (l = 2).

Solvent.	c.	$\alpha^{20°}_{5461}$.	$[M]^{20°}_{5461}$.	$\mu \times 10^{18}$.
$C_6H_5{\cdot}CH_3$	5·040	3·87°	112·2°	0·4
$C_6H_5{\cdot}OMe$	5·048	3·71	107·4	1·16
C_6H_6	5·048	3·60	104·2	0
C_6H_5Br	5·052	3·07	88·8	1·5
$C_6H_5{\cdot}NH_2$	5·040	3·06	88·7	1·51
C_6H_5I	5·044	3·02	87·5	1·50 (1·25)
C_6H_5Cl	5·046	2·99	86·6	1·55
o-$C_6H_4Cl_2$	5·044	2·76	80·0	2·25
$C_6H_5{\cdot}CHO$	5·050	2·72	78·7	2·75
$C_6H_5{\cdot}CN$	5·048	2·64	76·4	3·84
$C_6H_5{\cdot}NO_2$	5·052	2·58	74·6	3·90
[$C_6H_5{\cdot}CO{\cdot}CH_3$	5·052	3·45	99·8	2·97]

Maximum range of rotation, 37·6°.

(2) *Methyl* d-β-*octyl phthalate in methane solvents* (l = 2).

C_6H_{14}	5·050	4·90	141·8	0
$CH_3{\cdot}CHO$	5·046	4·73	137·0	2·72
$C_2H_5{\cdot}OH$	5·048	4·65	134·6	1·72
$CH_3{\cdot}CO_2H$	5·044	4·58	132·7	0·74 (1·4)
$CH_3{\cdot}CO{\cdot}CH_3$	5·050	4·56	131·9	2·97
CH_3I	5·052	4·54	131·3	1·66
$CH_3{\cdot}OH$	5·040	4·48	129·9	1·73
$CH_3{\cdot}CN$	5·036	4·41	127·9	3·94 (3·1)
$CH_3{\cdot}NO_2$	5·042	4·24	122·9	3·78 (3·05)
CH_2Cl_2	5·054	3·95	114·2	1·61
CCl_4	5·040	3·78	109·6	0
$CHCl_3$	5·040	3·76	109·0	1·10
CS_2	5·050	3·22	93·2	0

Maximum range of rotation, 48·6°.

The rotation of the diester dissolved in carbon disulphide is seen to be abnormally low. This resemblance to the behaviour of octyl acetate supports the suggestion that, with the esterification of the carboxyl group in octyl hydrogen phthalate, an increasing proportion of the solvent influence is transmitted through the octyl ester complex $\cdot CO_2C_8H_{17}$. In so far as the regularities in benzene solvents are concerned, the esterification of the second carboxyl group reduces the maximum range of rotation to about half that observed for the acid ester.

Experiment has shown that disubstituted nitro- and chlorobenzenes also bring about a depression in rotatory power. As these compounds, apart from *o*-dichlorobenzene, are solids, their influence was determined by using them in benzene solution, and the observed molecular rotation was then compared with that found for pure benzene (values of $[M]_{5461}$ in benzene, $c = 5$: acid ester, 145·0°; diester, 104·2°). In Table III, f_2 = mole-fraction of polar solvent in benzene mixture, Δ = depression as compared with value in pure benzene.

TABLE III.

Rotations in mixtures of benzene and substituted benzenes ($c = 5, l = 2$).

	$\mu \times 10^{18}$.	f_2.	$\alpha^{20°}_{5461}$.	$[M]^{20°}_{5461}$.	Δ.
	d-β-Octyl hydrogen phthalate.				
$C_6H_5{\cdot}NO_2$	3·85	0·1555	4·35°	121·1°	23·9°
m-$C_6H_4(NO_2)_2$	3·80	0·1512	4·10	113·8	31·2
C_6H_5Cl	1·52	0·4113	4·65	129·4	15·6
o-$C_6H_4Cl_2$	2·25	0·4224	4·22	117·4	27·6
p-$C_6H_4Cl_2$	0	0·4250	4·82	134·1	10·9
	Methyl *d*-β-octyl phthalate.				
$C_6H_5{\cdot}NO_2$	3·85	0·1793	3·25	94·7	9·5
m-$C_6H_4(NO_2)_2$	3·80	0·1506	3·23	94·1	10·1
C_6H_5Cl	1·52	0·4221	3·34	96·4	7·8
o-$C_6H_4Cl_2$	2·25	0·4283	3·15	91·5	12·7
p-$C_6H_4Cl_2$	0	0·4345	3·35	97·0	7·2

(*p*-Dinitrobenzene proved to be too sparingly soluble for inclusion in the above tables, and for the same reason the *m*-isomeride could not be used in as high a concentration as was possible with the chlorobenzenes.)

As in the case of the *l*-menthyl methyl naphthalate previously investigated, the tendency is for each polar group in the disubstituted benzenes to exert an individual influence upon the optically active phthalates. All three esters register a greater depression of rotatory power in the presence of *m*-dinitrobenzene than in that of nitrobenzene, although these two substances have practically the same dipole moment. Similarly, *p*-dichlorobenzene, despite the fact that it is completely non-polar with respect to a uniform external field, behaves as a comparatively strongly polar compound towards the localised charges in the solute molecules. The phthalates are affected by *p*-dichlorobenzene to about the same extent as by chlorobenzene, this being a somewhat smaller change than was found for the naphthalic ester. *o*-Dichlorobenzene, as already stated, produces a marked diminution in rotatory power.

Solvent Effect and the Influence of Added Electrolytes.—In the case of *d*-octyl hydrogen phthalate, the change in rotation of the acid ester on solution in strongly polar solvents is in the same direction as that undergone by the sodium salt in the presence of intensely charged kations, both being towards an increased negativity. It would be a matter of considerable interest to determine how far this correlation of the two effects is a general one, and to what extent it holds when the optically active molecule contains other polar groups in addition to the carboxyl complex.

The detailed experimental evidence necessary for a decision on this point is not yet available. On the hypothesis advanced by Darmois, however, tartaric acid and its ion exhibit an increased positive rotation under the influence of the highly positive fields exerted by Ba^{++}, Ca^{++}, Cs^{+} and Rb^{+}. This may be compared with the tendency towards an increased positivity indicated by the following observations of Přibram (*Ber.*, 1889, **22**, 6) on the rotatory power, $[\alpha]_D$, of tartaric acid in alcohol, to which was added an equal volume of various organic liquids :

EtOH + $C_6H_5{\cdot}NO_2$	+3·79°	EtOH + C_6H_6	−4·11°
,, + $Et{\cdot}NO_2$	+3·17	,, + $C_6H_5{\cdot}CH_3$	−6·19
,, + $Me{\cdot}C_6H_4{\cdot}NO_2$	−0·69	,, + Xylene	−6·52
,, + EtBr	−3·62	,, + C_6H_5Cl	−8·09

Although chlorobenzene forms an exception, among the remaining solvents there is no doubt that the highly polar compounds shift the rotation towards positive values.

Information bearing upon the behaviour of malic, methoxysuccinic, and mandelic acids in the presence of solvents is very scanty, but what is available appears to indicate the existence of a parallel in these cases also.

EXPERIMENTAL.

Solvents required for this investigation were purified by the methods described by Rule and McLean (*loc. cit.*). *Methyl* d-β-*octyl phthalate* was prepared by adding an excess of methyl iodide in small portions to dry finely divided silver *d*-β-octyl phthalate, with thorough shaking after each addition, as a considerable evolution of heat occurs. After a further 5—6 hours on a mechanical shaker, the bottle containing the reaction mixture was opened, the contents extracted with sodium-dried ether and filtered from silver salts. The ethereal solution was washed with aqueous alkali, and finally with water, and then dried over calcium chloride. Ether and methyl iodide were removed in a vacuum and the resulting crude methyl ester was maintained in a vacuum desiccator at 30—40° for one day to remove the last traces of the volatile liquids. The ester cannot be distilled, as it decomposes at moderate temperatures, and it was therefore employed without further purification. The homogeneous liquid gave $\alpha_{5461}^{20^\circ}$ + 42·27° ($l = 2$) (Found: C, 70·1; H, 8·5. $C_{17}H_{24}O_4$ requires C, 69·8; H, 8·3%).

Summary.

The variation in the rotatory power of octyl hydrogen phthalate and its methyl ester in solution may be summarised as follows.

(*a*) In solvents derived from benzene the rotations vary with the polarity of the medium; the higher the dipole moment of the latter, the lower are the observed rotations.

(*b*) The influence of aliphatic simple solvents is irregular.

(*c*) A screening of the dipole by the alkyl group is noted on comparing benzaldehyde with acetophenone.

(*d*) *m*- and *p*-Disubstituted benzenes bring about considerable depressions in rotatory power, even though the compounds of the latter type may have zero dipole moments. In such cases the polar groups appear to be so far removed from one another as to function individually.

(*e*) The depressions in the rotatory power of sodium octyl phthalate caused by the kationic charges of added electrolytes may be compared to the depressions undergone by octyl hydrogen phthalate in the presence of solvents containing dipoles A similar relationship exists in the case of tartaric acid and its ion, where both effects operate to bring about an increase in positive rotation.

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