30. *Studies in Solvent Action. Part XII. Optical Rotatory Powers of* l-*Benzoin and* l-*Benzoin Methyl Ether in Solution.*

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The data already published in this series of communications show that the rotatory power of an optically active compound is profoundly modified by the association of the active compound with itself or with a solvent. This process is facilitated by the presence in the solvent and solute molecules of polar substituent groups. For a weakly polar solute dissolved in a large excess of solvent the association is mainly of solute–solvent type and varies with the polarity of the solvent, being of a high order of magnitude in strongly polar media and either very low or entirely absent in those of non-polar type. If the optically active molecules are strongly polar, they will in addition have a pronounced tendency to associate with themselves, both in the homogeneous state and when dissolved in a non-polar medium. In interpreting the optical changes it has been assumed that the electrical field exerted by a polar group upon the active molecule to which it is attached makes its own characteristic contribution towards the total rotatory power. Dipole association between this group and a neighbouring polar group—whether belonging to a similar molecule or to one of an added substance—would thus be expected to result in a diminution of the electrical contribution and in a corresponding alteration in optical rotation. In practice it has been observed that both the above types of association lead to optical displacements in the same direction, in accordance with the requirements of this hypothesis.

These investigations have now been extended by an examination of *l*-benzoin and its methyl ether. The former is chiefly of interest owing to its property of readily undergoing association in certain non-polar solvents: the methyl ether has a smaller power of self-association, but may yield dextro- or lævo-rotatory solutions according to the experimental conditions.

l-*Benzoin.*—A reliable comparison of the relative degrees of association of benzoin in different non-polar solvents is not easily achieved by use of the classical methods, as the solubility of the compound is low and the necessary measurements cannot be made at the same temperature. Determinations by the ebullioscopic method (see p. 144) have, however, been carried out in *cyclo*hexane, carbon tetrachloride, benzene, and carbon disulphide. In *cyclo*hexane the molecules of benzoin (*M.W.* 212) are found to be strongly associated even at low concentrations, the calculated molar weight rising rapidly from 238 at $c = 0{\cdot}371$ to 274 at $c = 1{\cdot}037$. In carbon tetrachloride and benzene the values rose steadily though less rapidly over similar ranges of concentration, but in carbon disulphide they remained constant within the experimental limits. The rotatory powers of *l*-benzoin dissolved in various solvents are given in Table I. For reasons already stated (J., 1931, 674—679) it is considered preferable to tabulate aromatic and aliphatic solvents separately.

In the present case the main factors controlling the magnitude of the optical rotation appear to be the refractive index of the medium and the degree of association of the active molecules with themselves or with molecules of the solvent. The refractive effect is revealed in the tendency of the rotatory powers to rise as the refractive index increases, a change which is in agreement with modern theories of optical activity although the relationship is often so dominated by polar and other factors as to be scarcely traceable. The polar influence is marked by the low rotations observed in strongly polar liquids and the high values found in those of less polar character.

TABLE I.

Molecular Rotations of l-*Benzoin in Solution.*

Solvent.	$[M]^{20°}_{5461}$.	μ.	$n^{20°}_{D}$.	Solvent.	$[M]^{20°}_{5461}$.	μ.	$n^{20°}_{D}$.
Acetaldehyde	−276°	2·7	1·332	Acetophenone	−460°	2·9	1·533
Acetone	314	2·8	1·359	Nitrobenzene	462	3·9	1·550
Acetonitrile	413	3·2	1·344	Benzaldehyde	513	2·7	1·545
Nitromethane	427	3·0	1·381	Benzonitrile	530	3·8	1·528
Methanol	427	1·7	1·328	Mesitylene	550	0	1·496
*cyclo*Hexane	464	0	1·427	Toluene	568	0·4	1·495
Methylene chloride	534	1·5	1·424	Benzene	571	0	1·501
Chloroform	545	1·0	1·446	Bromobenzene	619	1·5	1·560
Acetic acid	585	1·7	1·372	Chlorobenzene	627	1·5	1·525
Methyl iodide	625	1·3	1·530	Anisole	649	1·2	1·516
Carbon tetrachloride	633	0	1·461	Iodobenzene	700	1·2	1·618
Carbon disulphide	1064	0	1·628				

In the majority of cases $l = 2$ and $c = 2$ (approx.). For some solvents a lower concentration was necessary, *viz.*, methanol ($c = 1·012$), acetic acid ($c = 1·010$), *cyclo*hexane ($c = 0·056$; $l = 4$), carbon disulphide ($c = 0·522$), carbon tetrachloride ($c = 0·22$), nitrobenzene ($c = 1·037$), mesitylene ($c = 0·966$), toluene ($c = 0·81$), benzene ($c = 1·01$), bromobenzene ($c = 0·986$). Observed rotations varied from −0·49° (*cyclo*hexane) to −13·60° (iodobenzene). Values of the dipole moments, μ, and refractive indices of the pure solvents are also appended.

Aromatic solvents illustrate the polar influence very clearly, as the variations in their refractive indices are on a smaller scale than those occurring among the aliphatic derivatives. The depression in rotatory power produced by highly polar liquids is also evident from a general survey of the aliphatic and aromatic solvents employed. Thus, although the refractive indices, $n^{20°}_{D}$, of the four highly polar benzene derivatives from acetophenone to benzonitrile all lie between the relatively high limits 1·528 and 1·550, the corresponding rotatory powers of their solutions follow immediately after those of the most strongly polar aliphatic solvents and assume a position between methanol ($n^{20°}_{D}$ 1·328) and methylene chloride ($n^{20°}_{D}$ 1·424). Here the polar influence outweighs that due to the refractive power.

Among non-polar liquids, *cyclo*hexane yields solutions of the lowest rotatory power, as was to be anticipated from the fact that benzoin is most strongly associated in this solvent. A displacement in the same direction is also observed with the hydrocarbons mesitylene, toluene, and benzene. In carbon disulphide no appreciable association of the solute could be detected at low concentrations by the ebullioscopic method, and the solution has a very high rotatory power in agreement with its high refractive index and non-polar character.

Weakly polar solvents, it may be noted, also yield solutions of relatively high optical activity. In such media the intermolecular forces are assumed to be sufficiently powerful to prevent the aggregation of *l*-benzoin molecules at low concentrations, but not strong enough to depress the rotatory power greatly by the formation of solute–solvent complexes. To take a concrete example, the degree of solvation which occurs in the weakly polar methyl iodide is regarded as producing an optical depression of the same order as that due to the self-association of the benzoin molecules in carbon tetrachloride solution. Neither of these solutions shows a rotatory power as high as that which would be given by *l*-benzoin if it could exist in the truly unimolecular state at the same temperature in a non-polar medium. In some respects the case of *l*-benzoin resembles that of *d*-β-nitro-octane (Rule, Smith, and Harrower, J., **1933**, 376), which is very strongly associated and exhibits its highest rotations in solvents of intermediate polarity. With the latter compound, however, no refractivity effect could be traced, probably owing to the extremely high polarity of the nitro-group and its greater tendency to undergo association in solvents of all kinds.

TABLE II.

l-*Benzoin Methyl Ether in Solution* (l = 2, c = 4).

Solvent.	$[M]^{20°}_{5461}$.	μ.	$n^{20°}_{D}$.	Solvent.	$[M]^{20°}_{5461}$.	μ.	$n^{20°}_{D}$.
Methanol	−352°	1·7	1·328	Aniline	−374°	1·6	1·586
Acetic acid	−344	1·7	1·372	Benzonitrile	−146	3·8	1·528
Nitromethane	−320	3·0	1·381	Benzaldehyde	−125	2·7	1·545
Acetaldehyde	−243	2·7	1·332	Nitrobenzene	−117	3·9	1·550
Acetonitrile	−236	3·2	1·344	Acetophenone	−109	2·9	1·533
Chloroform	−214	1·0	1·446	*o*-Dichlorobenzene	− 8·0	2·2	1·549
Methylene chloride	−178	1·5	1·424	Anisole	+ 6·6	1·2	1·516
Acetone	−102	2·8	1·359	Bromobenzene	+ 35	1·5	1·560
Methyl iodide	+ 27	1·3	1·530	Chlorobenzene	+ 35	1·5	1·525
Carbon tetrachloride	+316	0	1·461	Iodobenzene	+ 43	1·2	1·618
Carbon disulphide	+370	0	1·628	Benzene	+138	0	1·501
*cyclo*Hexane	+373	0	1·427	Toluene	+190	0·4	1·495
				Mesitylene	+269	0	1·496

α_{5461} varied from 0·23° in anisole to 13·29° in *cyclo*hexane. Owing to the low rotatory powers in *o*-dichlorobenzene, a concentration of $c = 10$ was used; the rotation in this solvent was found to be negative for λ_{6563}, λ_{5893}, and λ_{5761}, but positive for λ_{4861} and λ_{4358}.

l-*Benzoin Methyl Ether.*—Preliminary determinations of the molecular weight of *l*-benzoin methyl ether in *cyclo*hexane and benzene by the ebullioscopic method indicated very little self-association. The compound is readily soluble in all types of solvents to form solutions varying from a high lævo- to a high dextro-rotation, and it will be observed (Table II) that, with the sole exception of aniline, all solvents giving higher negative rotations than — 150° possess low refractive indices. The relationship between refractive index and rotatory power is, however, irregular, as may be seen from the positions in the table occupied by the highly refractive compounds aniline (— 374°), iodobenzene (+ 43°), and carbon disulphide (+ 370°), and also from the very high dextrorotations recorded in the remaining non-polar liquids, all of which have refractive indices of intermediate values. In fact, among the aromatic solvents as a group, no definite refractive influence is visible, although there is a clear connexion between rotatory power and the polarity of the medium.

Whereas all the strongly polar solvents give lævorotatory solutions, aniline at the head of the list occupies a higher position than corresponds to its dipole moment. This is probably to be attributed to an abnormal electronic coupling between its amino-group and the ketonic group of the benzoin ether. The rotatory powers in aniline were found to fall very slowly, owing either to combination between solvent and solute or to racemisation in the weakly basic medium. The general resemblance between hydroxy- and amino-groups may account for the similarly high rotations found for the hydroxylic solvents methanol and acetic acid. With both aliphatic and aromatic solvents, however, the compounds of non-polar character are sharply differentiated from adjacent solvents in the tables by the very highly dextrorotatory nature of their solutions. *l*-Benzoin methyl ether has also been examined in the homogeneous state at temperatures ranging from 55° to 100°. When extrapolated to 20°, the determinations give a value for $[M]_{5461}$ of approximately — 99°. Thus the rotatory power of the ketonic ether in the absence of any solvent is practically identical with that found for a solution in either of the ketonic solvents acetone (— 102°) or acetophenone (— 109°). In view of the widely differing refractive indices of these two liquids, this coincidence further emphasises the importance of the chemical character of the solvent in its influence upon the rotatory power.

Influence of Concentration.—The molecular rotatory powers for *l*-benzoin in Table I indicate a fall in the negative rotation as the degree of association is raised by dissolution of the compound in strongly polar solvents. A similar change is therefore to be anticipated when solutions of *l*-benzoin are examined at increasing concentrations in a non-polar solvent. This is found to be the case; *e.g.*, in benzene solutions, $[M]^{20°}_{5461}$ falls from —571° at $p = 1·146$ to — 559° at $p = 2·831$.

Concentration effects over a wider range are, however, readily investigated with the more soluble *l*-benzoin methyl ether. From Table II it is seen that a rise in the degree of association of this compound, as brought about by solution in solvents of greater dipole moment, corresponds to an increase in the negative rotatory power. In agreement with this relationship, a rise in the concentration of a solution in benzene displaces the dextrorotation towards the negative region :

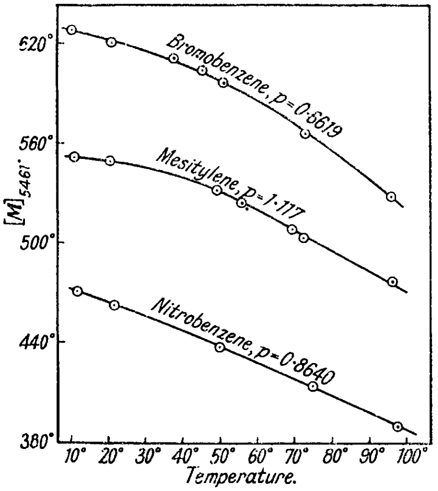
l-*Benzoin Methyl Ether in Benzene.*

c	0·643	4·02	12·02	25·05	Homog. state *
$[\alpha]_{5893}^{20°}$	+50·9°	+ 47·0°	+ 39·1°	+26·7°	−35·4°
$[M]_{5461}^{20°}$	—	+138°	+115°	+80·1°	−99°

* Extrapolated from the data obtained for the fused ether (see later). The value at c = 0·643 is that recorded by Wren for 15° (J., 1909, **95**, 1584).

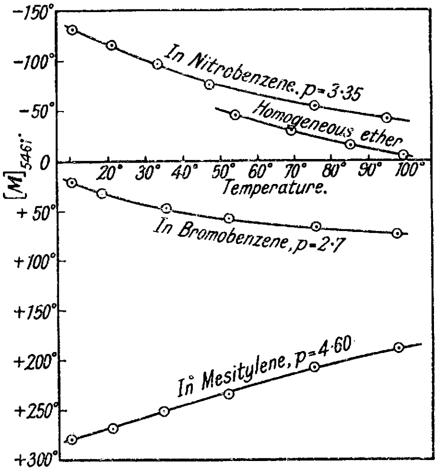
Influence of Temperature.—It has been pointed out (Rule, J., 1933, 1222) that the theory of dipoles allows a prediction to be made as to the relative slopes of the temperature–rotation curves for highly polar and for non-polar solvents, in those cases where a definite relationship is traceable between the polarity of a solvent and the rotatory power of the solution. Since the degree of dipole association between solvent and solute generally diminishes as the temperature rises, it follows that the characteristic optical displacement due to a highly polar solvent will also diminish. The T–R curves for polar and non-polar solvents will therefore tend to converge with rise of temperature.

FIG. 1.



Rotatory power of l-*benzoin in solution.*

FIG. 2.



Rotatory power of l-*benzoin methyl ether.*

Owing to the association of the optically active molecules with one another, *l*-benzoin exhibits somewhat abnormal rotatory powers when dissolved in the majority of non-polar solvents. The above prediction should, however, hold equally well if a weakly polar solvent capable of disrupting the solute–solute complexes is substituted for one of non-polar type. This is illustrated in Fig. 1, which shows the influence of a rise in temperature upon the rotatory powers of *l*-benzoin in the three solvents bromobenzene, mesitylene, and nitrobenzene. It will be observed that the curve for the strongly polar nitrobenzene converges towards that for the weakly polar bromobenzene, the difference in the values of $[M]_{5461}$ falling from 156° at 20° to 131° at 100°. The curve for the non-polar solvent mesitylene occupies an intermediate position.

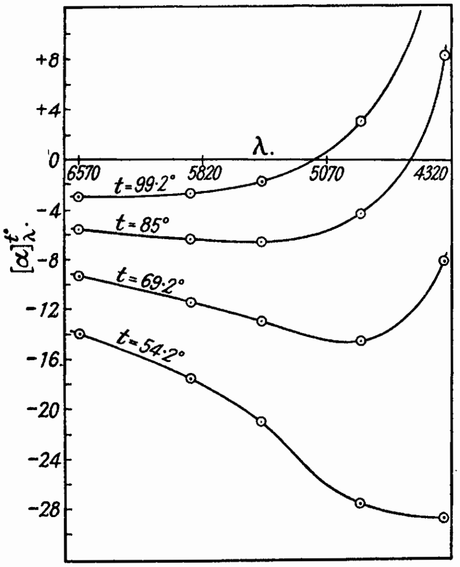
l-Benzoin methyl ether (Fig. 2) shows the effect even more clearly, since in this case the degree of association of the solute molecules in non-polar solvents is small and the comparison can be made under more favourable conditions. Here the curves for nitrobenzene, bromobenzene, and mesitylene are arranged in the order of their dipole moments and converge rapidly with rise of temperature, apparently trending towards positions on the positive side of the diagram. The curve for the homogeneous optically active compound, which as a ketonic ether may be assumed to have a dipole moment not far removed from 2·9, falls into its proper place below that of nitrobenzene and is inclined in the same general direction.

In cases where a definite influence due to the refractive index of the medium is visible at low temperatures, this should become still more clearly defined as the temperature is raised and the degree of association falls. No such tendency can be traced in the above very limited data.

Nature of the Dispersion.—The diagram obtained by plotting the rotatory powers of *l*-benzoin against the wave-length of light in the visible region shows the dispersion in all solvents to be normal and complex. For bromobenzene and chlorobenzene the dispersion curves lie close together and cut one another in the neighbourhood of λ_{4845}; a similar intersection about λ_{5520} occurs with acetophenone and nitrobenzene.

l-Benzoin methyl ether in solution exhibits a more interesting type of dispersion, the curves lying partly in the negative and partly in the positive region (see data in experimental section). In *o*-dichlorobenzene ($c = 10$) the rotatory powers are negative for wave-lengths longer than 4935 A., and positive for shorter wave-lengths up to λ_{4358}. For the methyl ether in the homogeneous state between 55° and 100° the dispersion is either highly complex or anomalous according to the conditions, as is illustrated in Fig 3. This complexity in the optical properties, however, does not appreciably disturb the relationship existing between the rotatory power and the polarity of the solvent.

FIG. 3.



Optical rotatory dispersion of homogeneous l-*benzoin methyl ether.*

EXPERIMENTAL.

l-Benzoin was prepared from amygdalin by way of *d*-mandelonitrile (Smith, *Ber.*, 1931, **64**, 427). Yields were similar to those recorded by this worker, the purified product having m. p. 131—132° and $[\alpha]_D^{16°} = -119·2°$ in acetone ($c = 2·76$) (Smith quotes $-119·4°$ for $c = 2·50$). Methylation of *l*-benzoin was effected according to Wren (*loc. cit.*) by means of dry silver oxide and methyl iodide in acetone. The resulting methyl *l*-benzoin had the same rotatory power as that found by Wren.

Solvents were purified in the manner described in earlier papers of this series. Refractive indices are taken from "Critical Constants" and refer to the D-line, the corresponding values for λ_{5461} not being generally available. No correction has been made for the changes in refractive index produced by the addition of optically active solute, which will in any case be small in magnitude.

Observed Optical Rotations.

l-Benzoin ($l = 2$, $t = 20°$, all rotations negative).

Solvent.	c.	α_{6563}.	α_{5893}.	α_{5461}.	α_{4861}.	α_{4358}.
Acetaldehyde	2·328	−3·78°	−4·96°	−6·07°	−8·68°	−12·86°
Acetone	2·764	5·07	6·59	8·18	11·84	17·90
Acetonitrile	2·262	5·53	7·14	8·82	12·64	18·85
Nitromethane	2·306	5·76	7·47	9·29	13·33	20·05
Methyl alcohol	1·012	2·55	3·30	4·08	5·86	8·68
Methylene chloride	2·288	7·41	9·56	11·77	16·72	24·62
Chloroform	2·212	7·18	9·39	11·55	16·43	24·03
Acetic acid	1·010	3·57	4·56	5·57	7·86	11·41
Methyl iodide	2·216	8·30	10·66	13·08	18·53	27·01
Carbon tetrachloride	0·220	0·84	1·09	1·32	1·86	2·73
Carbon disulphide	0·522	3·32	4·28	5·24	7·44	10·75

Solvent.	*c*.	α_{6563}.	α_{5893}.	α_{5461}.	α_{1861}.	α_{4358}.
Acetophenone	2·036	5·53°	7·15°	8·83°	12·57°	18·57°
Nitrobenzene *	1·037	1·38	1·80	2·26	3·27	—
*cyclo*Hexane	0·047	—	—	0·42	—	0·950
	0·056	—	—	0·49	—	1·13
Benzaldehyde	2·314	6·87	9·01	11·19	16·10	24·03
Benzonitrile	2·324	7·28	9·40	11·61	16·52	24·35
Mesitylene	0·966	1·54	1·99	2·51	3·54	5·19
Toluene	0·810	2·72	3·54	4·34	6·16	9·03
Benzene	1·012	3·37	4·43	5·44	7·69	11·24
Bromobenzene	0·986	1·80	2·33	2·88	4·14	6·1
Chlorobenzene	2·068	7·70	9·95	12·24	17·35	25·37
Anisole	2·082	7·98	10·36	12·75	17·97	26·23
Iodobenzene	2·058	8·59	11·05	13·60	19·19	28·23

* $t = 21·5°$.

l-Benzoin methyl ether ($l = 2$, $t = 20°$).

Solvent.	*c*.	α_{6563}.	α_{5893}.	α_{5461}.	α_{4861}.	α_{4358}.
Methyl alcohol	4·022	−7·68°	−10·10°	−12·53°	−17·97°	−27·05°
Acetic acid	4·020	−7·53	− 9·91	−12·25	−17·29	−25·36
Nitromethane	4·014	−5·39	− 7·20	− 9·04	−13·36	−20·75
Acetaldehyde	4·020	−5·35	− 7·05	− 8·66	−12·28	−17·95
Acetonitrile	4·006	−4·97	− 6·65	− 8·38	−12·32	−19·22
Chloroform	4·020	−4·84	− 6·24	− 7·63	−10·75	−15·45
Methylene chloride	4·018	−3·91	− 5·14	− 6·32	− 8·88	−12·84
Acetone	4·030	−2·18	− 2·89	− 3·65	− 5·46	− 8·51
Methyl iodide	4·036	+0·35	+ 0·62	+ 0·98	+ 2·06	+ 5·14
Carbon tetrachloride	4·026	+6·46	+ 8·82	+11·25	+17·46	+30·23
Carbon disulphide	4·012	+7·58	+10·25	+13·15	+20·34	+35·07
Benzonitrile	4·064	−3·21	− 4·23	− 5·26	− 7·64	−11·57
Benzaldehyde	4·010	−2·79	− 3·65	− 4·45	− 6·36	− 9·08
Nitrobenzene †	4·018	−1·25	− 1·67	− 2·07	− 2·96	—
Acetophenone	4·016	−2·17	− 3·16	− 3·88	− 5·98	− 7·97
o-Dichlorobenzene	10·04	−0·90	− 0·91	− 0·80	+ 0·03	+ 3·88
Anisole	4·008	+0·05	+ 0·11	+ 0·23	+ 0·79	+ 2·53
Bromobenzene *	3·984	+0·25	+ 0·37	+ 0·58	+ 1·17	+ 2·80
Chlorobenzene	4·020	+0·58	+ 0·89	+ 1·26	+ 2·35	+ 5·35
Iodobenzene	4·026	+0·71	+ 1·06	+ 1·53	+ 2·94	+ 6·76
Benzene	4·022	+2·81	+ 3·78	+ 4·91	+ 7·84	+14·34
Toluene	4·022	+3·82	+ 5·24	+ 6·76	+10·52	+18·49
Mesitylene †	4·021	+2·77	+ 3·75	+ 4·84	+ 7·39	+12·57
*cyclo*Hexane	4·022	+7·68	+10·32	+13·29	+20·18	+34·31

* $l = 1$, $t = 18·2°$. † $l = 1$.

Influence of Temperature.

l-Benzoin in nitrobenzene ($l = 1$, $p = 0·8640$).

Temp.	12°	21·5°	50°	74·5°	97·7°
$d_{4°}^{t°}$	1·209	1·200	1·173	1·150	1·129
α_{5461}	−2·32°	−2·26°	−2·09°	−1·94°	−1·79°

l-Benzoin in bromobenzene ($l = 1$, $p = 0·6619$).

Temp.	10·5°	21°	38°	45·5°	51°	73°	96·5°
$d_{4°}^{t°}$	1·504	1·491	1·469	1·460	1·452	1·424	1·393
α_{5461}	−2·95°	−2·88°	−2·80°	−2·76°	−2·70°	−2·51°	−2·30°

l-Benzoin in mesitylene ($l = 1$, $p = 1·117$).

Temp.	11°	20·5°	49·5°	55·5°	69·5°	72·5°	96·5°
$d_{4°}^{t°}$	0·8737	0·8655	0·8427	0·8379	0·8267	0·8245	0·8052
α_{5461}	−2·54°	−2·51°	−2·36°	−2·31°	−2·21°	−2·18°	−2·02°

l-Benzoin methyl ether in nitrobenzene ($l = 1$, $p = 3·354$).

Temp.	10·5°	21°	35·5°	47·2°	75·5°	94·5°
$d_{4°}^{t°}$	1·209	1·198	1·187	1·174	1·147	1·128
α_{6563}	−1·44°	−1·25°	—	−0·79°	—	−0·47°
α_{5893}	−1·91	−1·67	—	−1·09	—	−0·59
α_{5461}	−2·40	−2·07	−1·72°	−1·32	−0·92°	−0·68
α_{4861}	−3·55	−2·96	—	−1·78	—	−0·79

l-Benzoin methyl ether in bromobenzene ($l = 1$, $p = 2·699$).

Temp.	10·2°	18·2°	35·5°	52·2°	73·5°	97·2°
$d_{4^\circ}^{t^\circ}$	1·488	1·476	1·456	1·435	1·409	1·379
α_{6563}	+0·13°	+0·25°	+0·42°	+0·50°	+0·58°	+0·62°
α_{5893}	+0·25	+0·37	+0·59	+0·73	+0·83	+0·91
α_{5461}	+0·39	+0·58	+0·83	+1·00	+1·13	+1·22
α_{4861}	+0·89	+1·17	+1·57	+1·75	+1·96	+2·06
α_{4358}	+2·18	+2·80	+3·31	+3·67	+4·01	+4·18

l-Benzoin methyl ether in mesitylene ($l = 1$, $p = 4·604$).

Temp.	9·5°	20·5°	34·5°	52°	75°	97·2°
$d_{4^\circ}^{t^\circ}$	0·8825	0·8735	0·8625	0·8480	0·8295	0·8110
α_{6563}	+2·92°	+ 2·76°	+ 2·59°	+ 2·35°	+2·08°	+1·84°
α_{5983}	+3·93	+ 3·71	+ 3·46	+ 3·15	+2·76	+2·44
α_{5461}	+5·00	+ 4·79	+ 4·43	+ 4·08	+3·51	+3·13
α_{4861}	+7·67	+ 7·30	+ 6·84	+ 6·27	+5·51	+4·83
α_{4358}	—	+12·44	+11·61	+10·73	+9·62	+8·63

l-Benzoin methyl ether, homogeneous state ($l = 0·5$).

Temp.	$d_{4^\circ}^{t^\circ}$.	α_{6563}.	α_{5893}.	α_{5461}.	α_{4861}.	α_{4358}.
54·2°	1·094	−7·64°	−9·64°	−11·48°	−15·18°	−15·71°
69·2	1·083	−5·07	−6·18	− 7·07	− 7·91	− 4·39
85·0	1·070	−3·00	−3·43	− 3·54	− 2·37	+ 4·47
99·2	1·059	−1·58	−1·43	− 0·94	+ 1·63	+11·37(?)

Determinations of Molecular Weight.—These were carried out by using the differential thermometer devised by Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314). In the following tables : c = concn./100 c.c. of solvent; Δt = elevation in b. p.

l-*Benzoin* (M.W. 212).

Wt. of solute, g.	c.	Δt.	M.	Wt. of solute, g.	c.	Δt.	M.
In benzene. Vol. 27·9 c.c.; b. p. 80·0°; K = 32.							
0·1356	0·4860	0·0754°	206	0·4688	1·680	0·2506°	214
0·2739	0·9817	0·1501	209	0·6570	2·355	0·3375	223
In carbon tetrachloride. Vol. 29·1 c.c.; b. p. 76·3°; K = 32·4.							
0·0786	0·2701	0·0444	196	0·2863	0·9840	0·1563	204
0·1761	0·6050	0·0990	198	0·3790	1·302	0·2018	209
In cyclo*hexane.* Vol. 28·4 c.c.; b. p. 81·3°; K = 27·5.							
0·1053	0·3708	0·0593	238	0·2946	1·037	0·1471	274
0·1992	0·7015	0·1091	246				
In carbon disulphide. Vol. 27·5 c.c.; b. p. 45·6°; K = 19·4.							
0·1784	0·6503	0·0574	219	0·3204	1·165	0·1033	215
0·2437	0·8861	0·0785	219				

l-Benzoin Methyl Ether (M.W. 226).

Wt. of solute, g.	c.	Δt.	M.	Wt. of solute, g.	c.	Δt.	M.
In benzene. Vol. 29 c.c.; b. p. 79·6°; K = 32.							
0·2361	0·8141	0·1156	225	0·4371	1·508	0·2164	223
0·3334	1·149	0·1673	220	0·5462	1·884	0·2668	226
In cyclo*hexane.* Vol. 28 c.c.; b. p. 80°; K = 27·5.							
0·2656	0·9705	0·1492	243	0·5547	1·981	0·2967	255
0·4179	1·492	0·2273	251				

Summary.

An examination of the optical rotatory powers exhibited by *l*-benzoin and its methyl ether when dissolved in a variety of solvents leads to the following conclusions.

1. The lævorotation of *l*-benzoin tends to rise in solvents of high refractive index and to fall in those of high dipole moment. Low rotations are also observed in certain non-polar solvents in which the solute molecules undergo appreciable self-association.

2. The lævorotation of *l*-benzoin methyl ether rises in strongly polar solvents : high dextrorotations are given in all non-polar media. In this case the refractive effect is irregular.

3. The optical changes in polar solvents are due to dipole-association between solvent and solute, and displacements in the same direction occur when the concentration of the solute in a non-polar medium is increased.

4. With rising temperatures the rotatory powers observed in highly polar solvents approximate more closely to those found in solvents of zero or low dipole moment, in agreement with the demands of the association hypothesis.

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