514. *The Dipole Moments of Some Derivatives of Diphenylmethanol and Related Compounds.*

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From measurements of the dielectric constants, refractive indices, and specific volumes of solutions in benzene at 25° the following apparent dipole moments have been deduced; diphenylmethanol 1·60, *p*-methoxy- 2·03, *op*-dimethoxy- 2·69, *mp*-dimethoxy- 2·11, and *p*-phenoxy-diphenylmethanol 1·91, *op'*-ditolylmethanol 1·73, *op*-dimethoxybenzophenone 4·16, and diphenylchloromethane 1·85 D.

THE measurements recorded here were commenced some years ago, when it was considered possible that the different behaviours of the esters of diphenylmethanol derivatives on hydrolysis (alkyl–oxygen and acyl–oxygen fission) might be reflected in the dipole moments of the alcohols. No very distinct displacement of the apparent moments in a direction parallel with the hydrolytic behaviour of the esters was found, but as there are no recorded moments of any of the compounds studied except diphenylchloromethane, the measurements have some interest in other connexions. The results are summarised in Table I, where α and β are the limiting values of $\Delta\varepsilon/w_2$ and $\Delta v/w_2$, respectively, at zero concentration, and the other symbols have their usual significance. The value obtained for diphenylchloromethane is in accord with that reported by Weissberger and Sangewald (*Z. physikal. Chem.*, 1933, *B*, **20**, 150), although they found $P_{2\infty}$ and $[R]$ to be 138 and 64·0 c.c., respectively.

TABLE I.

	α.	β.	$P_{2\infty}$, c.c.	$[R]$, c.c.	μ (D). $P_{E+A} = [R]$.	μ (D). $P_{E+A} = 1{\cdot}05\,[R]$
Diphenylmethanol	1·80	−0·2498	111·5	56·7	1·64	1·60
p-Methoxydiphenylmethanol	2·38	−0·2774	151·2	63·7	2·07	2·03
op-Dimethoxydiphenylmethanol	3·51	−0·3031	222·5	71·5	2·72	2·69
mp-Dimethoxydiphenylmethanol	2·28	−0·3050	165·9	(71·5)	2·15	2·11
p-Phenoxydiphenylmethanol	1·77	−0·2955	161·3	83·1	1·96	1·91
op'-Ditolylmethanol	1·78	−0·2108	130·0	(67·7)	1·78	1·73
op-Dimethoxybenzophenone	8·10	−0·3141	429·0	71·8	4·18	4·16
Diphenylchloromethane	2·17	−0·2927	134·2	61·3	1·89	1·85

The molecular polarisations of the alcohols, particularly of diphenyl- and *p*-methoxydiphenyl-methanol, show a tendency to decrease at the lowest concentrations, and the plot of $\Delta\varepsilon/w_2$ against w_2 is not linear. Extrapolation of the results by any method is therefore subject to inaccuracies. This behaviour has been found to be common with alcohols, and is attributable to association which increases with increasing concentration. It may be expected, however, that extrapolation of the results for low concentrations should yield approximate values for the monomer.

Owing to this circumstance, and to the fact that some of the compounds studied probably have high atomic polarisations and a considerable solvent effect, any inferences which might be drawn from the rather complex vectorial analyses of these moments would be hazardous. Qualitatively, however, it is of interest to note that the dipole moment of diphenylmethanol is less than that reported for benzyl alcohol (1·69) * and much lower than for triphenylmethanol (2·11), whereas the value for diphenylchloromethane lies intermediately between those for benzyl chloride (1·82) and triphenylchloromethane (1·925) and is almost equal to that of methyl chloride (1·86). The remaining moments determined are consistent with other data; *e.g.*, the value of *p*-phenoxydiphenylmethanol is slightly lower than that of the *p*-methoxy-analogue, as is to be expected from the lower moment of diphenyl ether (1·1) as compared with anisole (1·23).

EXPERIMENTAL.

Materials.—Diphenylmethanol was prepared by reduction of vacuum-redistilled commercial benzophenone with zinc dust and sodium hydroxide in ethyl alcohol (*Org. Synth.*, 1941, *Coll. Vol.* **1**, 90). The crude product, extracted with light petroleum (b. p. 60—80°) in a Soxhlet apparatus and recrystallised twice from light petroleum, had m. p. 68·2°.

* All dipole moments quoted are taken from the Massachusetts Institute of Technology Tables (1948) and are values (in Debye units) for benzene solution.

TABLE II.

Polarisation data for benzene solutions.

$100w_2$.	ε_{12}.	v_{12}.	p_{12}, c.c.	P_2, c.c.	n.	r_{12}, c.c.	$[R]$, c.c.
0·0000	**2·2725**	**1·14458**	0·34090	—	1·4980 *	0·33550	—
					1·5021 †	0·33785	
			Diphenylmethanol.				
1·6514	2·3022	1·1405	0·34521	110·9	—	—	—
1·8538	2·3072	1·1399	0·34595	112·9	—	—	—
3·5307	2·3390	1·1358	0·35050	112·9	—	—	—
3·8758	2·3451	1·1351	0·35139	112·7	—	—	—
4·9149	2·3669	1·1324	0·35445	113·6	—	—	—
1·4848	2·2995	1·14089	0·34485	111·5	1·4991 *	0·33504	56·2
3·1834	2·3322	1·13664	0·34953	112·8	1·5005 *	0·33459	56·5
4·6670	2·3615	1·13291	0·35365	113·1	1·5019 *	0·33428	57·0
6·2586	2·3934	1·12897	0·35805	113·3	1·5031 *	0·33378	56·7
			p-Methoxydiphenylmethanol.				
1·4904	2·3084	1·14045	0·34634	151·3	1·4991 *	0·33491	63·5
2·7313	2·3391	1·13697	0·35088	151·4	1·5001 *	0·33446	63·7
4·0296	2·3712	1·13349	0·35556	151·0	1·5010 *	0·33394	63·6
6·6676	2·4410	1·12607	0·36538	151·7	1·5032 *	0·33298	63·8
			op-Dimethoxydiphenylmethanol.				
2·2835	2·3527	1·13757	0·35353	218·5	1·5040 †	0·33686	71·9
2·5805	2·3638	1·13676	0·35527	219·4	1·5042 †	0·33673	71·9
6·5392	2·5049	1·12483	0·37576	213·6	1·5071 †	0·33482	71·2
			mp-Dimethoxydiphenylmethanol.				
0·8264	2·2912	1·14206	0·34370	166·0	—	—	—
1·3713	2·3038	1·14040	0·34547	164·7	—	—	—
2·7888	2·3361	1·13607	0·35006	163·5	—	—	—
3·7375	2·3572	1·13317	0·35296	162·1	—	—	—
			p-Phenoxydiphenylmethanol.				
2·338	2·3149	1·13766	0·34668	161·9	—	—	—
2·804	1·136	1·13629	—	—	1·5008 *	0·33466	84·1
5·507	2·3758	1·12831	0·35476	163·1	1·5030 *	0·33354	82·6
8·294	2·4333	1·11995	0·36208	164·2	—	—	—
11·017	—	1·11208	—	—	1·5087 *	0·33178	83·1
			op'-Ditolylmethanol.				
0·528	2·2820	1·14343	0·34233	130·0	—	—	—
0·915	2·2879	1·14277	0·34324	126·7	—	—	—
1·870	2·3083	1·14069	0·34639	134·7	—	—	—
5·089	2·3664	1·13368	0·35477	130·3	—	—	—
			op-Dimethoxybenzophenone.				
1·8729	2·4250	1·13855	0·36665	415·6	1·5040 †	0·33715	73·8
2·8252	2·5043	1·13564	0·37927	411·6	1·5047 †	0·33648	70·1
5·4466	2·7149	1·12740	0·41007	390·3	1·5072 †	0·33565	72·1
8·8817	3·0128	1·11662	0·44863	376·4	1·5104 †	0·33420	71·9
			Diphenylchloromethane.				
5·1015	2·3850	1·1298	0·35685	132·5	1·5073 †	0·33638	62·6
6·1520	2·4125	1·1266	0·36064	134·2	1·5081 †	0·33586	62·0
11·6380	2·5474	1·1104	0·37785	133·5	1·5120 †	0·33321	60·4

* Sodium-D line. † Mercury green line.

p-Methoxydiphenylmethanol was prepared by interaction of phenylmagnesium bromide with anisaldehyde, the addition product being decomposed with ammonium chloride and ice. The dried ethereal extract was concentrated, and the carbinol precipitated with light petroleum. It was recrystallised from light petroleum.

The remainder of the solutes were kindly presented by Dr. J. Kenyon and his co-workers, and were recrystallised before use.

Thiophen-free benzene was fractionally crystallised, dried over phosphoric oxide, and redistilled immediately before use.

Apparatus and Methods.—For the second series of solutions of diphenylmethanol and for its *p*-methoxy-derivative the dielectric constants were measured with a heterodyne-beat apparatus, but for the remainder, which were studied during the war when other equipment was not obtainable, the apparatus used was similar to that described by Le Fèvre and Rayner (*J.*, 1938, 1921), but with the screened grid valve replaced by a pentode which increased the sensitivity. Specific volumes were determined with a pyknometer, and the refractive indices with a Pulfrich refractometer. All measurements were made at 25·0°.

Details of the measurements are shown in Table II, where the symbols used have their usual significance. The $P_{2\infty}$ values for the solutes shown in Table I were calculated by the method described previously (*Trans. Faraday Soc.*, 1949, **45**, 109) and are consistent with the P_2 values for finite concentrations. For *op'*-ditolylmethanol the molecular refraction was calculated from the bond refractions (Vogel *et al.*, *Chem. and Ind.*, 1950, 358), whilst for *mp*-dimethoxydiphenylmethanol the value was taken as equal to that for the *op*-isomer.

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