698. *Molecular Polarisation and Molecular Interaction. Part IV. The Molecular Polarisation of Diphenylamine in Solution in Benzene, Dioxan, and Mixtures of Benzene with Nitrobenzene, Triethylamine, and Pyridine.*

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From measurements of the dielectric constants, specific volumes, and refractive indices of dilute solutions at 25°, and on the assumption that the total distortion polarisation is given by $1{\cdot}05[R_D]$, the apparent dipole moment of diphenylamine has been determined as 1·01 D. in benzene and 1·26 D. in dioxan. The apparent molecular polarisation of diphenylamine at infinite dilution in benzene containing nitrobenzene is slightly less than in benzene alone, but in benzene–triethylamine and benzene–pyridine it is considerably greater than in benzene. The high values in these cases are attributed to hydrogen bonding of the hydrogen atom of the amine to the electron-donor nitrogen atoms of the triethylamine and pyridine, the particularly large effect in the presence of pyridine being associated with the highly mobile electron system of this compound.

IN Parts I and II (Few and Smith, *J.*, 1949, 753, 2663) it was shown that the apparent dipole moments of aniline, methylaniline, and their nuclear-substituted derivatives are much higher for dioxan than for benzene solutions, whilst the moments of dimethylaniline and its derivatives and of *n*- and *tert.*-butylamine are almost equal in the two solvents. This evidence supported the view that large differences between the values of the moments in the two solvents are associated with hydrogen bonding between the hydrogen atoms of the primary or secondary amine group and the oxygen atoms of the dioxan molecule. The rather surprising result with the primary alkylamines was attributed to their less acidic character and to the fact that there is no possibility of resonance structures which would facilitate the bonding of the hydrogen atoms.

In view of these results it seemed probable that a very pronounced effect might be observed with diphenylamine, which has a relatively low dipole moment in benzene solution and for which, therefore, any increases in apparent moment in other solvents caused by hydrogen bonding should be more accurately determinable. It was also desirable to determine which other groupings, in addition to the ether grouping in dioxan and ethyl ether, are able to participate in the formation of hydrogen bonds with resultant increase in the molecular polarisation of an amine. In this connection the nitro-group, known to yield both inter- and intra-molecular hydrogen bonds with phenolic groups, was one natural choice, and, owing to its strong proton-accepting character, the tertiary aliphatic amine group was another. It has been observed that the presence of pyridine causes a very considerable increase of the apparent molecular polarisation of alcohols (Cleverdon and Smith, *Chem. and Ind.*, 1948, 29, and unpublished results), so it was also of interest to test its effect in the case of amines.

To study the effects of these groupings it was necessary to work with ternary systems, as the dielectric constants of pure liquid compounds suitable for the purpose are so high that a change in the apparent molecular polarisation of a proton-donating solute might be obscured by other factors. The molecular polarisation of diphenylamine in benzene and dioxan solution has therefore been studied. In addition, measurements have been made with solutions of diphenylamine in mixtures of benzene with nitrobenzene, triethylamine, and pyridine at concentrations such that the solvent mixture had a dielectric constant not greater than about 2·7.

The results are summarised in Table I, where the symbols have the same significance as in the previous communications. In each case the molecular polarisation and molecular refraction of the diphenylamine have been calculated on the usual arbitrary assumption that the values for the solvent remain constant, a supposition which is unjustified for the solvent mixtures but which serves to illustrate the difference in behaviour in the various cases. The values of μ in column 6 are derived on the common assumption that $P_{E+A} = 1{\cdot}05[R_D]$, and those in column 7 on the assumption that $P_{E+A} = [R_D]$.

TABLE I.

Diphenylamine in various solvents.

Solvent.	α.	β.	$P_{2\infty}$, c.c.	R_D, c.c.	μ (D.) ($P_{E+A} = 1{\cdot}05[R_D]$).	μ (D.) ($P_{E+A} = [R_D]$).
Benzene	1·132	−0·2480	81·22	57·3	1·016	1·082
Dioxan	1·808	−0·0707	94·24	58·8	1·261	1·317
2·8951 wt.-% Nitrobenzene in benzene	0·959	−0·2369	79·90	57·3	0·983	1·052
11·7083 wt.-% Triethylamine in benzene	1·476	−0·2808	93·14	57·2	1·273	1·327
6·1812 wt.-% Pyridine in benzene	2·080	−0·2273	110·00	57·5	1·559	1·604

The only previously recorded measurement of the dipole moment of diphenylamine appears to be that of Leonard and Sutton (*J. Amer. Chem. Soc.*, 1948, **70**, 1565), who found the value in benzene solution to be 1·04 D. if the total distortion polarisation is taken as equal to $[R_D]$, or 0·99 D. if it is taken as $1{\cdot}05[R_D]$. The present result for benzene solution is in reasonable agreement with this observation.

As was expected, the apparent dipole moment of diphenylamine in dioxan solution is higher than in benzene, the difference being about the same as was observed in the case of aniline. In the benzene–triethylamine mixture the value was about the same as in dioxan, but the apparent moment was much greater still in the benzene–pyridine mixture, although the pyridine concentration was relatively lower than that of the triethylamine. At first sight this is surprising, since it might be expected that triethylamine, a much stronger base than pyridine, would exert a greater attraction upon the hydrogen atoms of the NH groups. However, the greater increase in molecular polarisation observed in the presence of pyridine need not indicate that the degree of hydrogen-bonding association is greater in this case, but may be associated with the much higher electron mobility in the pyridine, compared with the triethylamine molecule, leading to greater electronic shifts when association occurs. The relative behaviours of pyridine and triethylamine appear to bear some relation, in fact, to the previously observed difference between the primary aromatic amines and the butylamines in dioxan solution. With pyridine and diphenylamine both molecules have mobile electronic systems, whereas with dioxan and aniline or triethylamine and diphenylamine only one of the molecular types has any great electron mobility, and with dioxan and the butylamines the electrons are relatively immobile in both constituents. On the other hand, the fact that simple aliphatic alcohols show an even greater increase of molecular polarisation in the presence of pyridine than does diphenylamine may be due a greater degree of hydrogen bonding in the case of the alcohols.

It was rather surprising that the apparent molecular polarisation of diphenylamine at infinite dilution in the benzene–nitrobenzene mixture was slightly lower than in benzene, and the values at finite concentrations lower than would be expected in benzene solutions of equal dielectric constant. When, however, the results are recalculated as solutions of nitrobenzene in benzene–diphenylamine mixtures, the molecular polarisations of which are assumed to remain unchanged in the presence of nitrobenzene, the derived values of the molecular polarisation of nitrobenzene are almost exactly equal to the figures obtained by Jenkins (*J.*, 1934, 480) and by the author (unpublished) in solutions of equal dielectric constant in benzene alone. This illustrates the error which may be introduced in assuming that the molecular polarisation of a polar solvent remains constant, and indicates that the lower apparent dipole moment of diphenylamine in this solvent mixture is due to the variation in the molecular polarisation of the nitrobenzene. At the same time it must be inferred that at the concentrations studied there is in this system no hydrogen bonding which leads to an enhancement of the polarisation.

It is also worthy of note that the molecular refraction of diphenylamine is appreciably higher in dioxan than in benzene, whilst in the mixtures of benzene with nitrobenzene, triethylamine, and pyridine the value is, within the limits of experimental error, the same as in pure benzene. It was also found in Part II that the differences in molecular refraction in different solvents do not follow the differences in molecular polarisation. The measurements then made indicated that the molecular refraction could be higher in dioxan than in benzene for solutes which showed no such abnormality in molecular polarisation and which could not associate with dioxan by hydrogen bonding. The present results show that the molecular refraction may be normal in systems in which the molecular polarisation is abnormally high, presumably owing to hydrogen bonding. It must therefore be inferred that the factors involved in the variation of the molecular refraction with solvent differ from those concerned with molecular polarisation.

EXPERIMENTAL.

Materials.—Benzene and dioxan were purified as described previously (*J.*, 1949, 753).

Commercial "pure" diphenylamine was redistilled twice under reduced pressure; the solidified product, crushed and stored over phosphoric oxide, had m. p. 53·5°.

Nitrobenzene from thiophen-free benzene was redistilled under reduced pressure, fractionally crystallised four times, redistilled again, and dried (Na_2SO_4, followed by P_2O_5); it had m. p. 5·7°

Triethylamine was purified by recrystallisation of the hydrochloride, followed by liberation of the base with calcium oxide. The product was dried (BaO) and redistilled; it had b. p. 89·4°.

Reagent-grade pyridine was refluxed with potassium permanganate, to oxidise homologues, dried (KOH), fractionally distilled, and stored over BaO; it had b. p. 115·5°.

TABLE II.

Polarisation data for solutions of diphenylamine in various solvents.

$100w_2$.	ε_{12}.	v_{12}.	p_{12}, c.c.	P_2, c.c.	n_D.	r_{12}, c.c.	$[R_D]$, c.c.	$\Delta\varepsilon/w_2$.	$\Delta v/w_2$.
				Benzene.					
0·0000	2·2725	1·14458	0·34090	—	1·4979	0·33544	—	—	—
0·9951	2·2838	1·14218	0·34230	81·51	1·4992	0·33548	57·40	1·14	—0·241
1·1451	2·2853	1·14182	0·34251	81·48	1·4994	0·33549	57·43	1·14	—0·241
2·0527	2·2959	1·13962	0·34378	81·42	1·5007	0·33558	57·89	1·141	—0·242
3·6007	2·3137	1·13566	0·34585	80·99	1·5028	0·33554	57·23	1·144	—0·248
4·5748	2·3254	1·13297	0·34717	80·89	1·5040	0·33548	56·89	1·156	—0·254
8·4862	2·3714	1·12351	0·35245	80·74	1·5091	0·33552	56·92	1·165	—0·248
				Dioxan.					
0·0000	2·2041	0·97280	0·27862	—	1·4199	0·24612	—	—	—
1·1092	2·2243	0·97202	0·28171	94·32	1·4225	0·24726	58·72	1·82	—0·070
1·7986	2·2365	0·97150	0·28355	93·56	1·4241	0·24796	58·92	1·81	—0·072
2·1898	2·2436	0·97126	0·28463	93·57	1·4250	0·24834	58·80	1·804	—0·070
3·5765	2·2686	0·97024	0·28835	93·17	1·4283	0·24976	58·87	1·803	—0·071
5·4512	2·3023	0·96897	0·29331	92·73	1·4326	0·25167	58·87	1·802	—0·070
12·3027	2·4245	0·96413	0·31041	90·87	1·4484	0·25837	58·48	1·792	—0·070
				2·8951 *wt.-% Nitrobenzene in benzene.*					
0·0000	2·6928	1·13489	0·40938	—	1·4989	0·33317	—	—	—
1·9123	2·7111	1·13039	0·41056	79·74	1·5015	0·33331	57·61	0·96	—0·235
4·6431	2·7374	1·12385	0·41261	79·37	1·5050	0·33333	56·99	0·961	—0·238
9·7746	2·7869	1·11174	0·41500	79·00	1·5123	0·33375	57·39	0·963	—0·237
				11·7083 *wt.-% Triethylamine in Benzene.*					
0·0000	2·3047	1·17248	0·35536	—	1·4838	0·33533	—	—	—
2·4215	2·3401	1·16563	0·35991	91·93	1·4872	0·33537	57·00	1·464	—0·283
5·9217	2·3902	1·15582	0·36600	90·53	1·4923	0·33551	57·25	1·444	—0·281
7·2390	2·4090	1·15221	0·36822	90·17	1·4943	0·33556	57·28	1·441	—0·280
8·1676	2·4218	1·14957	0·36964	89·70	1·4955	0·33552	57·14	1·434	—0·281
				6·1812 *wt.-% Pyridine in benzene.*					
0·0000	2·7038	1·13642	0·41163	—	1·4993	0·33384	—	—	—
2·0745	2·7464	1·13176	0·41642	108·73	1·5020	0·33400	57·73	2·053	—0·225
2·6876	2·7585	1·13031	0·41771	107·90	1·5028	0·33402	57·58	2·031	—0·227
5·5482	2·8150	1·12375	0·42359	106·14	1·5065	0·33414	57·38	2·004	—0·228

Methods.—The dielectric constants and specific volumes were determined by the methods described in Part I, but the refractive indices were measured with a Hilger Abbé refractometer. The apparent molecular polarisation at infinite dilution ($P_{2\infty}$) and apparent dipole moment (μ) were deduced by the same methods as previously.

Results.—The experimental results are recorded in Table II, where the symbols have the same significance as previously.

TABLE III.

Nitrobenzene in diphenylamine–benzene.

Diphenylamine, wt.-%	0·0000	1·9682	4·7749	10·0367
100 w_2	2·8951	2·8397	2·7606	2·6122
[illegible] (calc.)	2·2725	2·2949	2·3269	2·3905
v_1 (calc.)	1·14458	1·13970	1·13274	1·11969
p_1 (c.c.)	0·34090	0·34362	0·34737	0·35463
p_{12} (c.c.)	0·40938	0·41056	0·41216	0·41500
P_2 (c.c.)	333·3	332·5	331·7	328·2
P_2 in benzene (c.c.)	333·3	332·6	331·0	328·0

Table III shows the results for the system nitrobenzene–benzene–diphenylamine re-evaluated as solutions of nitrobenzene in benzene–diphenylamine mixtures. The values of ε_1 and v_1 for these " solvents " are derived from the parameters deduced from the measurements on the benzene–diphenylamine system, whilst the figures denoted P_2 in benzene are the molecular polarisation values of nitrobenzene in benzene at such a concentration as to yield a dielectric constant equal to that of the solution in question.

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