19. *Molecular Polarisation and Molecular Interaction. Part V. The Apparent Dipole Moments of Mesidine, Aminodurene, and Methylmesidine in Benzene and Dioxan Solutions.*

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Measurements of the dielectric constants, specific volumes, and refractive indices of dilute solutions at 25° show that the apparent dipole moments of mesidine, aminodurene, and methylmesidine are 1·45, 1·45, and 1·22 D, respectively, in benzene solution and 1·57, 1·57, and 1·26 D, respectively, in dioxan solution. The lower values relative to those for aniline and methylaniline are interpreted as indicating that mesomerism is inhibited appreciably with mesidine and aminodurene and to a considerable extent with methylmesidine. Comparison of the two series confirms that a large increase in molecular polarisation accompanies hydrogen bonding only when mesomeric effects are possible in at least one of the molecular species involved. Possible reasons for the inhibition of resonance in mesidine and aminodurene but not in 2 : 4 : 6-tribromoaniline or in mesitaldehyde are discussed.

In Parts I, II, and IV (*J.*, 1949, 753, 2663; 1950, 3532) it was shown that the apparent molecular polarisations of aniline, *p*-chloro- and 2 : 4 : 6-tribromo-aniline, methylaniline, and diphenylamine are all much higher in dioxan than in benzene solution, whilst for *NN*-dimethyl- and 2 : 4 : 6-tribromo-*NN*-dimethyl-aniline and *n*- and *tert.*-butylamine there is little difference between the values in the two solvents. These higher molecular polarisations and the consequent higher apparent dipole moments in dioxan solution were attributed to hydrogen bonding between the amino-hydrogen atoms of the primary and secondary arylamines and the oxygen atoms of the dioxan molecules. Large increases in the apparent dipole moment have also been observed with diphenylamine in the presence of triethylamine or of pyridine (Part IV) and with alcohols in the presence of pyridine (*Chem. and Ind.*, 1948, 29). These results suggested that an appreciable increase in molecular polarisation results from hydrogen bonding only when at least one of the species involved has a highly polarisable electronic system. For the arylamines this polarisation is most likely to occur through an increase in the mesomeric effect of the amino-group, which in turn implies that the molecules must be able to adopt a structure in which the amino-hydrogen atoms approach coplanarity with the aromatic ring.

This raises a particular interest in amines for which steric inhibition of resonance may occur. Birtles and Hampson (*J.*, 1937, 10) and Ingham and Hampson (*J.*, 1939, 981) found the dipole moments of aminodurene and mesidine in benzene to be 1·39 and 1·40 D, respectively, values appreciably less than that for aniline. On the other hand, the moment of bromodurene differed but little from that of bromobenzene, a circumstance which led Ingham and Hampson to infer that it was the steric effect of the *o*-methyl groups in hindering the formation of resonance structures involving N=C double bonds which caused the moments of aminodurene and mesidine to be less than that of aniline.

It was observed in Part II, however, that the dipole moment of 2 : 4 : 6-tribromoaniline in benzene is considerably greater than that of aniline, whilst the apparent value in dioxan solution is much greater than that in benzene, suggesting that the hydrogen-bonding of the amino-hydrogen atoms results in an increased mesomeric effect. It was therefore of interest to study the apparent dipole moments of mesidine and aminodurene in dioxan as well as in benzene, and also to determine the apparent moments in the two solvents of methylmesidine, which would be expected to form hydrogen bonds to the dioxan molecules but with which there should be very considerable inhibition of the mesomeric effect. No previous measurements on this compound have been reported.

EXPERIMENTAL

Materials.—Benzene and dioxan were purified as described in Part I (*loc. cit.*).

Mesidine. Nitromesitylene, prepared from mesitylene by Powell and Johnson's method (*Org. Synth.*, 1943, Coll. Vol. II, p. 449), was reduced with iron in the presence of a little water and a trace of acetic acid. The product, after addition of ammonia, was extracted with alcohol, the extract being acidified with hydrochloric acid and evaporated. The mesidine hydrochloride was twice recrystallised, and the base, liberated by sodium hydroxide, was distilled under reduced pressure and dried (CaO); it had b. p. 227°/762 mm. (lit., 227—230°).

Aminodurene. Durene was brominated by Smith and Moyle's method (*J. Amer. Chem. Soc.*, 1933, **55**, 1676), and the resulting bromodurene nitrated as described by Smith and Tenenbaum (*ibid.*, 1935, **57**, 1293). The bromonitrodurene was reduced to aminodurene with tin and hydrochloric acid in glacial acetic acid solution (Birtles and Hampson, *loc. cit.*), and after addition of sodium hydroxide the base was steam-distilled and recrystallised from alcohol; it had m. p. 72·0° (lit., 71—75°).

Methylmesidine. Mesidine was methylated with methyl sulphate (Ullmann, *Annalen*, 1903, **327**, 104), the product being purified through the nitrosamine, which was reduced with stannous chloride. After addition of sodium hydroxide the amine was steam-distilled and dried (CaO); it had b. p. 229°/755 mm. (Ullmann gives 228—229°/730 mm.).

Experimental Methods.—The dielectric constants and specific volumes were determined as in the previous investigations, and refractive indices for the Na-*D* line were measured with a Hilger Abbé refractometer.

Results.—The measurements are recorded in Table 1, where the symbols have their usual significance. The parameters α, β, and ν (the limiting values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, at zero concentration) and the values of $P_{2\infty}$ and $[R_D]$ derived from them are given in Table 2. The values so deduced are in each case in accord with those calculated from the measurements at each concentration. The dipole-moment values given under μ are calculated on the assumption that $P_{E+A} = [R_D]$, and those under μ' are based on the arbitrary assumption that $P_{E+A} = 1{\cdot}05[R_D]$.

DISCUSSION

Previous values for the dipole moments in benzene of mesidine (1·40 D; Ingham and Hampson) and aminodurene (1·39 D; Birtles and Hampson) are slightly lower than those now reported. This is explained partially by the use of the older values of the universal constants in their calculations. It is confirmed, however, that these moments are appreciably less than the dipole moment of aniline, lying between the latter and the value for primary alkylamines. This comparison is illustrated by the data collected in Table 3,

TABLE 1.

$100w$	ε	v	n_D	p (c.c.)	P_2 (c.c.)	r (c.c.)	R_2 (c.c.)
			Mesidine in benzene.				
0·0000	2·2725	1·14458	1·4979	0·34090	—	0·33544	—
1·6399	2·3023	1·14296	1·4987	0·34597	87·9	0·33542	45·2
3·2272	2·3316	1·14142	1·4994	0·35089	88·0	0·33537	45·0
4·5604	2·3573	1·14012	1·5000	0·35515	88·3	0·33533	45·0
6·0510	2·3850	1·13865	1·5007	0·35964	88·0	0·33529	45·0
7·4051	2·4111	1·13733	1·5013	0·36383	88·0	0·33525	45·0
			Mesidine in dioxan.				
0·0000	2·2041	0·97280	1·4199	0·27862	—	0·24612	—
0·8987	2·2267	0·97338	1·4212	0·28250	96·1	0·24694	45·5
1·8117	2·2499	0·97400	1·4225	0·28645	96·1	0·24777	45·5
3·0125	2·2808	0·97476	1·4241	0·29164	96·1	0·24879	45·2
4·9594	2·3313	0·97594	1·4270	0·29997	95·9	0·25057	45·4
6·0854	2·3810	0·97715	1·4299	0·30802	96·1	0·25237	45·7
			Aminodurene in benzene.				
0·0000	2·2725	1·14458	1·4980	0·34090	—	0·33550	—
1·1313	2·2915	1·14326	1·4986	0·34406	92·6	0·33545	49·5
1·7447	2·3017	1·14255	1·4989	0·34574	92·3	0·33542	49·4
2·3942	2·3125	1·14180	1·4992	0·34750	92·1	0·33542	49·6
3·0243	2·3233	1·14106	1·4997	0·34926	92·1	0·33543	49·7
3·6502	2·3340	1·14032	1·5000	0·35099	92·1	0·33540	49·6
			Aminodurene in dioxan.				
0·0000	2·2040	0·97280	1·4200	0·27860	—	0·24618	—
1·0580	2·2285	0·97317	1·4216	0·28273	99·9	0·24710	49·8
2·2988	2·2578	0·97353	1·4234	0·28759	99·9	0·24812	49·3
3·3422	2·2826	0·97394	1·4250	0·29172	100·1	0·24905	49·6
4·0675	2·3000	0·97425	1·4261	0·29454	100·0	0·24968	49·6
			Methylmesidine in benzene.				
0·0000	2·2725	1·14460	1·4980	0·34090	—	0·33550	—
0·8998	2·2826	1·14394	1·4982	0·34260	79·0	0·33543	48·9
1·4678	2·2887	1·14353	1·4983	0·34363	78·4	0·33538	48·8
1·9701	2·2946	1·41322	1·4984	0·34462	79·1	0·33533	48·8
3·2848	2·3095	1·14228	1·4987	0·34710	79·1	0·33522	48·8
5·2360	2·3322	1·14082	1·4991	0·35081	79·1	0·33502	48·7
			Methylmesidine in dioxan.				
0·0000	2·2050	0·97286	1·4200	0·27879	—	0·24619	—
0·8247	2·2172	0·97370	1·4210	0·28104	82·3	0·24691	49·7
1·6415	2·2294	0·97455	1·4219	0·28326	82·3	0·24758	49·4
2·3728	2·2406	0·97526	1·4228	0·28531	82·6	0·24825	49·7
3·0135	2·2500	0·97587	1·4236	0·28702	82·4	0·24880	49·6
5·6023	2·2888	0·97855	1·4265	0·29406	82·3	0·25104	49·6

TABLE 2.

	$10^3\alpha$	$10^4\beta$	$10^3\nu$	$P_{2\infty}$ (c.c.)	$[R_D]$ (c.c.)	μ (D)	μ' (D)
Mesidine in benzene	1800	−980	139	88·0	45·0	1·45	1·41
Mesidine in dioxan	2504	642	411	96·1	45·5	1·57	1·53
Aminodurene in benzene	1665	−1165	164	92·4	49·6	1·45	1·41
Aminodurene in dioxan	2315	343	427	100·1	49·6	1·57	1·53
Methylmesidine in benzene ...	1110	−712	63	79·1	48·8	1·22	1·17
Methylmesidine in dioxan ...	1495	1013	336	82·3	49·6	1·26	1·22

TABLE 3.

	$P_{2\infty}$ (c.c.) in :		μ (D) in :			
	benzene	dioxan	benzene	dioxan	ΔP (c.c.)	$\Delta\mu$ (D)
Aniline [1]	78·3	95·1	1·53	1·77	16·8	0·24
Mesidine [4]	88·0	96·1	1·45	1·57	8·1	0·12
Aminodurene [4]	92·4	100·1	1·45	1·57	7·7	0·12
2 : 4 : 6-Tribromoaniline [2]	116·7	139·5	1·73	2·00	22·8	0·27
n-Butylamine [2]	61·1	60·1	1·34	1·33	−1·0	−0·01
Methylaniline [1]	93·2	106·7	1·68	1·86	13·5	0·18
Diphenylamine [3]	81·2	94·2	1·08	1·32	13·0	0·24
Methylmesidine [4]	79·1	82·3	1·22	1·26	3·2	0·04
Dimethylamine [4]	43·3	—	1·17	—	—	—
Dimethylaniline [1]	94·1	97·8	1·61	1·66	3·7	0·05

[1] Part I. [2] Part II. [3] Part IV. [4] This paper. [5] Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374.

in which, for convenience, all the moments quoted are calculated on the assumption that $P_{E+A} = [R_D]$. In dioxan solution the apparent dipole moments of mesidine and aminodurene are each 0·12 D higher than in benzene solution, but this difference is less than was found for aniline or 2 : 4 : 6-tribromoaniline.

On the other hand, the dipole moment of methylmesidine in benzene is very much lower than that of methylaniline, and very little higher than that of dimethylamine, suggesting that in this compound resonance is almost completely suppressed sterically, as has been found with dimethylmesidine (Ingham and Hampson, *loc. cit.*) and 2 : 4 : 6-tribromodimethylaniline (Part II, *loc. cit.*). Further, the apparent moment of methylmesidine in dioxan solution is only 0·04 D greater than in benzene. As there is no *a priori* reason to believe that the tendency towards hydrogen bonding should be so much less than for methylaniline it would appear that the increase in apparent moment accompanying hydrogen bonding in these amines is intimately associated with the mesomeric effect of the amine molecule. This observation, therefore, supports the view (Part IV) that a large increase in molecular polarisation and consequently in apparent dipole moment accompanies hydrogen bonding only when a large increase in the mesomeric effect can occur. When such is impossible, as with alkylamines in dioxan, no abnormality in the apparent dipole moment is observed. These results suggest, in fact, that comparative polarisation measurements in benzene and dioxan solutions could be used to test for the existence or otherwise of a mesomeric effect in amines, phenols, and other proton-donor molecules which are too complex to permit the satisfactory interpretation of their dipole moments in benzene alone.

For methylmesidine the difference between the apparent moments in dioxan and benzene solutions is approximately the same as for dimethylaniline, and hence may be attributed to a normal solvent effect, although the possibility that it is due to an increase in a small mesomeric effect in the methylmesidine molecule cannot be excluded. Although it is impossible on steric grounds for the methylamino-group to become coplanar with the ring, it has been realised to an increasing extent recently that appreciable π-bonding can occur, for instance between the two ring systems of derivatives of diphenyl, even when the planes of the two rings are inclined at a considerable angle to one another (Guy, *J. Chim. phys.*, 1949, **46**, 469; Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854).

This view lends particular interest to the apparent dipole moments of mesidine and aminodurene in the two solvents. As pointed out by Hampson and his co-workers, the values in benzene solution suggest that the contribution of the mesomeric form is less than for aniline, and this conclusion is supported by the relatively smaller increases in apparent dipole moment observed in dioxan solution. One of the problems remaining to be solved, however, is the difference in behaviour of mesidine as compared with 2 : 4 : 6-tribromoaniline, for which the moment in benzene is appreciably greater than that of aniline and for which the moment in dioxan is increased almost proportionately to that of aniline. In Part II it was suggested that the $-I$ effects of the bromine atoms favoured the double-bonded structure and therefore caused the moment to be greater than that of aniline. However, in view of the results with mesidine and aminodurene it would have been expected that the bromine atoms, being only slightly smaller than the methyl group, would have had at least some slight effect in inhibiting the mesomeric effect.

Possible reasons for this difference in behaviour include: (i) Mutual repulsion of the hydrogen atoms. (ii) Displacement of the C–X bonds in the trisubstituted compounds from their symmetrical positions: a slight effect of this type would increase considerably the dipole moment of a symmetrical trihalogenoaniline but would have little effect for mesidine, in which the corresponding group moments are smaller; if this were the cause, however, it would not be expected that the difference between the moments in dioxan and in benzene would be more than twice as great for 2 : 4 : 6-tribromoaniline as for mesidine. (iii) Formation of hydrogen bonds between the methyl groups and nitrogen atoms in mesidine and aminodurene (Watson, *Ann. Reports*, 1939, **36**, 219); this may occur with amines, but the extension of this view to embrace hydrogen bonding between methyl groups and the oxygen atoms of a nitro-group seems improbable, as (*a*) this would be expected to increase the mesomeric effect in nitromesitylene and nitrodurene rather than decrease it, and (*b*) if this form of hydrogen bonding occurred one would expect similar bonding between the amino-hydrogen atom of diphenylamine and the oxygen atoms of nitrobenzene; no increase of polarisation arising from such cause could be detected (Part IV).

It is noteworthy that, in benzene solution, acetophenone has a dipole moment of 2·88 D, whereas the moments of acetylmesitylene and aminodurene are 2·71 and 2·68 D, respectively, indicating that in the last two compounds mesomerism is suppressed (Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310). This view is supported by the higher Raman C=O frequency of acetylmesitylene and aminodurene (1699 cm.$^{-1}$) as compared with acetophenone (1684 cm.$^{-1}$) (Saunders, Murray, and Cleveland, *ibid.*, p. 3121; 1942, **64**, 1181). On the other hand, the dipole moment of mesitaldehyde (2·96 D) is actually greater than that of benzaldehyde (2·92 D) and much greater than the moments of aliphatic aldehydes (~2·5 D), suggesting that in this case there is no steric inhibition of resonance; this is confirmed by the fact that the C=O frequency of mesitaldehyde is 1687 cm.$^{-1}$.

It seems unlikely that the coplanarity of the amino-group with the ring should be inhibited by *o*-methyl groups on purely spatial grounds, whereas that of the aldehyde group is not. In extension of Watson's suggestion, weak hydrogen bonding of the methyl hydrogen atoms to the oxygen atom of the aldehyde group would be at least as possible as bonding to the nitrogen atom of an amino-group, and this would tend to increase the mesomeric effect. In the absence of proof of the formation of hydrogen bonds by methyl groups, however, this problem must remain open.

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