911. *Molecular Polarisation and Molecular Interaction. Part VII.* The Apparent Dipole Moments of Some Di- and Tri-substituted Anilines in Benzene and Dioxan.*

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The apparent dipole moments of 2 : 4- and 3 : 5-dibromoaniline, 2 : 4- and 3 : 5-dinitroaniline, 2 : 4 : 6-trinitroaniline, and 2-methyl-4-nitroaniline in benzene and dioxan have been determined from measurements on dilute solutions in these solvents. The interaction moments (μ_{int}) and the vectorial values of the additional moments in dioxan ($\Delta\mu_{\text{vect}}$) for these and allied amines have been calculated. For the disubstituted anilines μ_{int} and $\Delta\mu_{\text{vect}}$ follow the linear relation observed for *m*- and *p*-monosubstituted anilines. The values of μ_{int} for 2 : 4 : 6-tribromoaniline and 2 : 4 : 6-trinitroaniline are such as would be expected from the values for the corresponding mono- and di-substituted anilines, indicating that there is little or no steric inhibition of the mesomeric effect of the amino-group such as is observed with mesidine and aminodurene. For all aniline derivatives containing two *ortho*-groups, however, $\Delta\mu_{\text{vect}}$ is less than would be expected from the linear relationship.

THE apparent dipole moment of a primary aromatic amine in dioxan is invariably greater than in benzene.[1-3] The difference ($\Delta\mu$) has been interpreted as arising from hydrogen

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* Part VI, *J.*, 1957, 3217.

[1] Few and Smith, *J.*, 1949, 753.

[2] *Idem*, *J.*, 1949, 2663.

[3] Smith, *J.*, 1953, 109.

bonding between an amino-hydrogen atom and an oxygen atom of a dioxan molecule, and from an investigation of the system aniline–dioxan–benzene evidence has been obtained that in dilute solutions of aniline in dioxan a large proportion ($\sim$65%) of the amine molecules are hydrogen-bonded to a dioxan molecule.[4] For a number of *m*- and *p*-substituted anilines $\Delta\mu$ is greater than for aniline itself, and it is particularly large when the dipole moment in benzene exceeds appreciably the value calculated by vector summation of the group moments of the substituents. Such abnormal values of the moment in benzene solution may reasonably be assumed to arise from an " interaction moment " (μ_{int}) acting along an axis parallel to the line joining the carbon atoms carrying the amino-group and the other substituent, respectively. If it is further assumed that the increased moment in dioxan solution arises from an additional component to the moment ($\Delta\mu_{\text{vect}}$) acting along the same axis as the interaction moment, it is found that, within experimental error ($\pm 0{\cdot}02$ D), this is given by $\Delta\mu_{\text{vect}} = 0{\cdot}33 + 0{\cdot}255\mu_{\text{int}}$.[5]

This observation gives strong support to the view that in the complexes with dioxan an appreciable increase in molecular polarisation, and consequently in apparent dipole moment, accompanies the hydrogen bonding only when it results in an increased mesomeric effect of the amino-group. It gives a particular interest, therefore, to the study of other substituted anilines, especially those in which steric inhibition of the mesomerism is possible either for the amine itself or for its complex with dioxan. Hence, the apparent dipole moments of 2 : 4- and 3 : 5-dibromoaniline, 2 : 4- and 3 : 5-dinitroaniline, 2 : 4 : 6-trinitroaniline, and 2-methyl-4-nitroaniline in benzene and dioxan have been measured. The results are summarised in Table 1, where α, β, and γ indicate the limiting values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, at zero concentration, and the other symbols have their usual significance. The dipole moment values given under μ are calculated on the assumption that $P_{E+A} = [R_D]$, and those under μ' on the assumption that $P_{E+A} = 1{\cdot}05[R_D]$. The first series of values is used in the following discussion. Whenever possible the values of $[R_D]$ used are derived from refractive-index measurements on the solutions, but in certain instances the results obtained with the highly coloured solutions appeared to be vitiated by anomalous dispersion, and hence values computed from the refractivities of related compounds together with the appropriate bond refractivities were used. These are shown in square brackets in Table 1.

TABLE 1. *Summary of polarisation data.*

Aniline deriv.	Solv.*	100α	$-10^3\beta$	$10^3\gamma$	$P_{2\infty}$ (c.c.)	$[R_D]_2$ (c.c.)	μ (D)	μ' (D)	Prev. values † (D)
2 : 4-Br_2 …………	B	325	653	204	189·9	45·8	2·65	2·63	
2 : 4-Br_2 …………	D	476	487	327	230·4	45·8	3·00	2·98	
3 : 5-Br_2 …………	B	419	655	204	234·4	45·8	3·04	3·02	
3 : 5-Br_2 …………	D	620	484	327	288·8	45·9	3·44	3·42	
2 : 4-$(NO_2)_2$ ……	B	2062	495	—	745·8	[43·6]	5·87	5·85	
2 : 4-$(NO_2)_2$ ……	D	2926	347	525	914·2	45·8	6·53	6·51	6·48
3 : 5-$(NO_2)_2$ ……	B	1800	504	—	654·9	[43·6]	5·47	5·45	
3 : 5-$(NO_2)_2$ ……	D	2434	325	346	758·7	43·6	5·90	5·88	5·91
2 : 4 : 6-$(NO_2)_3$ …	B	428	578	—	222·0	[50·1]	2·90	2·87	
2 : 4 : 6-$(NO_2)_3$ …	D	639	403	450	273·5	51·2	3·30	3·27	3·25
2-Me: 4-(NO_2)……	B	2960	389	288	881·4	42·0	6·42	6·40	
2-Me: 4-(NO_2) …	D	4053	210	671	1046·7	47·8	7·00	6·98	

* B = benzene; D = dioxan.

† Vasiliev and Syrkin, *Acta Physicochim U.R.S.S.*, 1941, **14**, 414; *J. Phys. Chem. U.R.S.S.*, 1941, **15**, 254.

The " theoretical " moments of the compounds have been calculated from the contributory group moments. For this purpose it has been assumed that the axis of the

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[4] Few and Smith, *J.*, 1949, 2781.

[5] Smith and Walshaw, *J.*, 1957, 3217.

dipole in aniline is inclined at 48½° to the N–C bond.[5] For the dibromo- and dinitro-anilines the contributions to the moments arising from the two bromine atoms and the two nitro-groups have been taken as 1·47 and 3·83 D, the dipole moments of *m*-dibromobenzene and *m*-dinitrobenzene, respectively, in benzene solution. The moments of the methyl and nitro-groups in 2-methyl-4-nitroaniline have been taken as equal to the dipole moments of toluene (0·37 D) and nitrobenzene (4·01 D), respectively. By combining the theoretical moments so obtained with the observed moments in benzene solution the interaction moments for the compounds have been derived. In these calculations it has been assumed that the interaction moments in the 3 : 5-disubstituted and 2 : 4 : 6-trisubstituted anilines act along the axis of the N–C bond, whilst in the 2 : 4-disubstituted anilines they act along an axis parallel to the line joining the $C_{(1)}$ and $C_{(3)}$ carbon atoms. The results are shown in Table 2, which includes, in addition to the compounds studied in the present work, data for 2 : 4 : 6-tribromoaniline, mesidine, and aminodurene. Similarly, by combining the values of the apparent moments in dioxan solution with the calculated values of the theoretical moments and of the interaction moments the values of $\Delta\mu_{\text{vect}}$ have been deduced, the assumption being made in all cases that $\Delta\mu_{\text{vect}}$ acts along the same axis as μ_{int}.

TABLE 2.

	$\mu_{\text{calc.}}$ (D)	$\mu_{\text{benz.}}$ (D)	μ_{int} (D)	$\mu_{\text{diox.}}$ (D)	$\Delta\mu$ (D)	$\Delta\mu_{\text{vect}}$ (D)
2 : 4-Dibromoaniline	2·45	2·65	0·23	3·00	0·35	0·38
3 : 5-Dibromoaniline	2·74	3·04	0·33	3·44	0·40	0·43
2 : 4 : 6-Tribromoaniline ...	1·53	1·73[2]	0·28	2·00[2]	0·27	0·33
2 : 4-Dinitroaniline	4·57	5·87	1·39	6·53	0·66	0·71
3 : 5-Dinitroaniline	4·98	5·47	0·53	5·90	0·43	0·46
2 : 4 : 6-Trinitroaniline	1·53	2·90	1·65	3·30	0·40	0·43
2-Methyl-4-nitroaniline......	5·36	6·42	1·08	7·00	0·58	0·59
Mesidine	1·53	1·45[3]	−0·13	1·57[3]	0·12	0·19
Aminodurene	1·53	1·45[3]	−0·13	1·57[3]	0·12	0·19

The results for the dibromo- and dinitro-anilines follow a similar pattern to that shown by the monosubstituted anilines, and emphasise the importance of the positions of the substituents in determining the values not only of μ_{int} but also of $\Delta\mu_{\text{vect}}$. For these compounds the results all lie within ±0·02 D of the straight line, $\Delta\mu_{\text{vect}} = 0{\cdot}33 + 0{\cdot}255\mu_{\text{int}}$, suggested by the measurements on monosubstituted anilines. The interaction moments of the dibromoanilines, like those of *m*- and *p*-bromoaniline, can be interpreted as arising because the strong inductive effects of the bromine atoms increase the mesomeric effect of the amino-group. The interaction moment of 3 : 5-dinitroaniline can be similarly explained, but the high values of both μ_{int} and $\Delta\mu_{\text{vect}}$ for 2 : 4-dinitroaniline indicate that the mesomeric effects of the amino- and nitro-groups act in conjunction, as in *p*-nitroaniline. This suggests that there is little or no steric inhibition of the mesomerism of the amino-group either in the amine itself or in its complex with dioxan. The surprising feature is that, in spite of the fact that some hydrogen bonding between the amino-group and the *ortho*-nitro-group must occur, the relative values of μ_{int} and $\Delta\mu_{\text{vect}}$ fall in line with those for compounds in which no such intramolecular hydrogen bonding is possible.

The interaction moments for both 2 : 4 : 6-tribromoaniline (0·28 D) and 2 : 4 : 6-trinitroaniline (1·65 D) are such as would be expected from the values for *p*-bromoaniline [5] (0·20 D), 2 : 4-dibromoaniline (0·23 D), *p*-nitroaniline [5] (1·08 D), and 2 : 4-dinitroaniline (1·39 D). The evidence, therefore, is against any appreciable steric inhibition of mesomerism in these compounds. The interaction moments for mesidine and aminodurene, however, are −0·13 D, indicating that here the mesomeric moment of the amino-group is less than in aniline. For all the compounds with two substituents *ortho* to the amino-group the values of $\Delta\mu_{\text{vect}}$ are lower than would be expected from the linear relationship. With mesidine and aminodurene this may be due to a much greater steric opposition to the mesomerism in the dioxan complex than in the free amine, but in 2 : 4 : 6-trinitroaniline, and possibly also in 2 : 4 : 6-tribromoaniline, complications arise through a competition between intermolecular and intramolecular hydrogen bonding.

That *ortho*-methyl groups have only a slight effect on the mesomerism of an amino-group is illustrated by the fact that μ_{int} for 2-methyl-4-nitroaniline is identical with that for *p*-nitroaniline. Since the dioxan complex can attain the near-coplanar configuration with the dioxan molecule linked to the amino-hydrogen atom remote from the methyl group, the value of $\Delta\mu_{\text{vect}}$ is also within experimental error of the value expected from the linear relationship.

The results indicate, therefore, that, provided not more than one position *ortho* to the amino-group is occupied by a substituent, the difference between the apparent dipole moments of an amine in dioxan and benzene solutions serves as a reliable guide to the extent of the mesomeric effect of the amino-group in the free amine. When both such positions are occupied, however, the mesomeric effect in the free amine may be greater than would be inferred from the $\Delta\mu_{\text{vect}}$ value.

EXPERIMENTAL

Materials.—Benzene and dioxan were purified and dried as described previously.[5]

2 : 4-Dibromoaniline was prepared by bromination of *p*-bromoacetanilide by Chattaway and Clemo's method [6] and subsequent hydrolysis. Repeatedly recrystallised from aqueous alcohol it had m. p. 79·5° (lit., 78—79°).

3 : 5-Dibromoaniline was prepared by reducing 1 : 3-dibromo-5-nitrobenzene (obtained from *p*-nitroaniline by Meyer, Meyer, and Jaeger's method [7]) with iron filings and concentrated hydrochloric acid in methanol. After steam-distillation from alkaline solution and repeated recrystallisation from petroleum (b. p. 40—60°) it had m. p. 55·1° (lit., 47·5—57°).

2 : 4-Dinitroaniline was prepared from 1-chloro-2 : 4-dinitrobenzene and ammonium acetate by Wells and Allen's method [8] and recrystallised from aqueous alcohol; it had m. p. 180° (lit., 180—186°).

3 : 5-Dinitroaniline was prepared by a modification of Nicolet's method,[9] 1 : 3 : 5-trinitrobenzene (15 g.) being reduced with the solution obtained by passing hydrogen sulphide into 95% alcohol (150 c.c.) and ammonia solution (*d* 0·880; 75 c.c.) until the weight increased by 6·3 g. After recrystallisation from water it had m. p. 161° (lit., 155—162°).

Picryl chloride was prepared from picric acid and phosphorus pentachloride by Brady and Horton's method,[10] and was converted into 2 : 4 : 6-trinitroaniline by treatment with ammonia in boiling nitrobenzene [11]: after removal of ammonium chloride and recrystallisation from glacial acetic acid it had m. p. 189° (lit., 187—190°).

2-Methyl-4-nitroaniline was prepared by nitrating acet-*o*-toluidide with fuming nitric acid at −5°. The product was recrystallised from alcohol and, after hydrolysis, the 2-methyl-6-nitroaniline was removed by steam distillation from acid solution: after repeated recrystallisation from aqueous alcohol the 2-methyl-4-nitroaniline had m. p. 129° (lit., 129°).

Methods and Results.—The dielectric constants, specific volumes, and refractivities of the solutions were determined at 25° by the same methods as were used in the previous investigations. The results are recorded in Table 3. For most of the series of measurements the dielectric constants of the solutions were linear with w over the concentration range used, and hence the slope of the best straight line through these points was taken as α, but where the relationship was not linear the limiting value of $d\varepsilon/dw$ at low concentration was used. In all cases both v and n^2 were linear with w and the slopes of the best straight lines were taken as β and γ, respectively. The values of $P_{2\infty}$ and $[R_D]_2$ were calculated from these parameters in the

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[6] Chattaway and Clemo, *J.*, 1916, **109**, 90.
[7] Meyer, Meyer, and Jaeger, *Ber.*, 1920, **53**, 2041.
[8] Wells and Allen, *Org. Synth.*, Coll. Vol. II, p. 221.
[9] Nicolet, *J. Amer. Chem. Soc.*, 1927, **49**, 1813.
[10] Brady and Horton, *J.*, 1925, **127**, 2233.
[11] Le Fèvre, Moir, and Turner, *J.*, 1927, 2337.

usual way and checked by comparison with the values of P_2 and $[R_D]_2$ calculated from the measurements on each individual solution.

TABLE 3. *Polarisation data.*

10^6w	$10^4\Delta\varepsilon$	$10^5\Delta v$	$10^4\Delta n$	10^6w	$10^4\Delta\varepsilon$	$10^5\Delta v$	$10^4\Delta n$
2 : 4-*Dibromoaniline in benzene.*				2 : 4-*Dibromoaniline in dioxan.*			
4388	143	286	2·5	2412	115	119	2·5
8734	287	569	4·5	4653	224	228	4·5
12,675	419	827	8	7255	351	357	8
15,007	501	978	9	9416	458	459	9·5
23,899	805	1561	13·5	13,499	662	659	13·5
30,807	1037	2012	20	25,606	1265	1248	25·5
3 : 5-*Dibromoaniline in benzene.*				3 : 5-*Dibromoaniline in dioxan.*			
4847	203	316	3	3518	223	171	3
9687	408	632	6	7223	458	349	7
15,503	659	1003	10	10,220	628	495	11
21,582	916	1420	14	14,682	918	708	14
29,390	1257	1928	19	15,138	943	733	16
36,569	1568	2394	25	19,836	1246	962	22
2 : 4-*Dinitroaniline in benzene.*				2 : 4-*Dinitroaniline in dioxan.*			
165·3	36	7	—	1472	431	49	2
415·5	83	17	—	2472	725	86	3
631·2	133	32	—	3655	1071	128	7
833·5	173	39	—	5203	1523	183	10
991·0	203	49	—	6684	1953	232	12
1283·5	265	69	—	8055	2350	279	17
3 : 5-*Dinitroaniline in benzene.*				3 : 5-*Dinitroaniline in dioxan.*			
217·4	36	11	—	1172	289	37	1·5
399·2	68	20	—	2093	510	70	2·5
718·4	127	36	—	3692	907	121	4
1137	206	57	—	4781	1167	155	5
1776	323	90	—	6852	1673	217	9
2158	391	109	—	12,689	3076	409	16
2 : 4 : 6-*Trinitroaniline in benzene.*				2 : 4 : 6-*Trinitroaniline in dioxan.*			
1214	50	70	—	2377	155	95	3
2333	103	134	—	3496	224	143	5
2763	116	161	—	4536	291	181	7
3679	158	215	—	6613	425	268	12
4770	204	274	—				
5880	256	340	—				
2-*Methyl*-4-*nitroaniline in benzene.*				2-*Methyl*-4-*nitroaniline in dioxan.*			
706	209	27	0·5	6254	2510	131	15
1479	430	54	1	11,106	4375	231	25
2011	594	79	1·5	17,718	7278	378	42
3098	917	125	2·5	22,969	9347	487	56
5323	1593	205	6	35,261	14,573	741	83
6635	2024	260	7				

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