629. *Molecular Polarisation and Molecular Interaction. Part VI.** *The Apparent Dipole Moments of* m- *and* p-*Nitroaniline,* m- *and* p-*Bromoaniline, and* p-*Toluidine in Benzene and Dioxan Solutions.*

By J. W. Smith and (Miss) S. M. Walshaw.

The apparent dipole moments of the amines have been determined from dielectric constant, specific volume, and refractive-index measurements on dilute solutions in benzene and dioxan at 25°. The results for benzene solutions have been used to derive vectorial values of the "interaction moments," *i.e.*, the additional components to the moments arising through the simultaneous presence of the two substituents. These are interpreted as modifications in the inductive and mesomeric effects of the substituents. On the assumption that the higher apparent moments in dioxan solution arise principally from an increased mesomeric effect of the amino-group, vectorial values for these extra contributions to the moment are derived. It has been found that for amines so far studied, and in which no steric inhibition of the mesomerism of the amino-group or of its dioxan addition product is probable, this additional component to the moment in dioxan solution increases linearly with the interaction moment.

In Parts I, II, and V [1,2,3] it was shown that the apparent dipole moments of aniline and of some nuclear-substituted anilines are appreciably higher in dioxan solutions than in

---

* Part V, *J.*, 1953, 109.

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

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

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

benzene solutions. The differences are smaller for methylaniline and its derivatives, and the apparent dipole moments of dimethylaniline and its derivatives are almost the same in dioxan as in benzene. These results supported the view that the higher moments in dioxan solutions arise through hydrogen bonding between an amino-hydrogen atom and an oxygen atom of the dioxan molecule. From the data available it was inferred [3] that an appreciable increase in molecular polarisation, and consequently in apparent dipole moment, accompanies the hydrogen bonding only when an increase in the mesomeric effect can occur, *i.e.*, when it results in an increased donation of electron density from the amino-nitrogen atom to the ring. It was suggested, therefore, that comparative polarisation measurements on benzene and dioxan solutions might be used to test for the existence of a mesomeric effect in amines and phenols which are too complex to permit the satisfactory interpretation of their dipole moments in benzene only.

Further, it seemed probable that the extent to which hydrogen bonding occurs with different amines may also increase progressively with increase in the electron-shift accompanying the bonding. In confirmation of this view, Hulett, Pegg, and Sutton [4] have observed that for various systems in which hydrogen bonding can occur there is a fairly linear relation between the association constant for hydrogen-bond complex formation and the increase in the dipole moment of the complex above the value expected from vector addition. This gives the possibility that the apparent increase in dipole moment in dioxan as compared with benzene solutions might give a quantitative as well as a qualitative indication of the mesomeric effect of the amino-group.

To test this hypothesis the dipole moments of some other monosubstituted anilines in benzene and dioxan solutions 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 remaining symbols have their usual significance. The dipole moment values given under μ are calculated on the assumption that $P_{E+A} = [R_D]_2$, and those under μ' on the assumption that $P_{E+A} = 1{\cdot}05[R_D]_2$. In the following discussion the first series of values is used, but, particularly in view of the fact that the $\Delta\mu$ ($\mu_{\text{dioxan}} - \mu_{\text{benzene}}$) values are almost independent of the method of calculation used, the same conclusions would be reached on the basis of the μ' values.

TABLE 1. *Summary of polarisation data at 25°.*

	Solvent	100α	$10^3\beta$	$10^3\gamma$	$P_{2\infty}$ (c.c.)	$[R_D]_2$ (c.c.)	μ (D)	μ' (D)	Previous values (D)
p-Toluidine	Benzene	191	−133	166	70·8	35·1	1·32	1·30	1·31,[5]* 1·27[6]
p-Toluidine	Dioxan	290	29	458	82·1	36·0	1·50	1·47	
p-Bromoaniline	Benzene	591	−524	217	223·2	38·4	3·01	2·99	2·99,[5]* 2·87,[7] 2·85[8]
p-Bromoaniline	Dioxan	854	−357	413	270·3	39·7	3·36	3·34	
m-Bromoaniline	Benzene	472	−525	223	184·6	38·6	2·68	2·66	2·65[5]*
m-Bromoaniline	Dioxan	681	−355	375	223·8	38·6	3·01	2·99	
p-Nitroaniline	Benzene	3062	−405	277	826·0	37·3	6·22	6·20	6·4,[5] 6·32,[8] 6·17[9]
p-Nitroaniline	Dioxan	4235	−241	686	991·6	41·4	6·82	6·80	6·68,[10] 6·81[9]
m-Nitroaniline	Benzene	1920	−403	280	528·1	37·2	4·91	4·89	4·94,[5]* 5·00[11]
m-Nitroaniline	Dioxan	2507	−219	501	599·5	38·7	5·24	5·22	5·22[11]

* Recalculated from original data using modern values of the universal constants.

The low solubilities of the nitroanilines in benzene restricted the concentration ranges which could be studied, but the results are in good agreement with previous measurements. For each of the amines studied the apparent moment in dioxan is appreciably higher than

---

[4] Hulett, Pegg, and Sutton, *J.*, 1955, 3901.
[5] Tiganik, *Z. phys. Chem.*, 1931, **14**, *B*, 135.
[6] Donle and Gehrckens, *ibid.*, 1932, **18**, *B*, 316.
[7] Bergmann and Tschudnovsky, *ibid.*, 1932, **17**, *B*, 116.
[8] Le Fèvre and Le Fèvre, *J.*, 1936, 1130.
[9] Vasiliev and Syrkin, *Acta Physicochim. U.R.S.S.*, 1941, **14**, 414.
[10] Kumler and Porter, *J. Amer. Chem. Soc.*, 1934, **56**, 2549.
[11] Davis, Bridge, and Svirbely, *ibid.*, 1943, **65**, 857.

in benzene, the greatest difference (0·60 D) being observed for *p*-nitroaniline, the compound in which the mesomeric effect of the amino-group would be expected to be greatest. As was noted for the amines studied previously, the molecular refractions in dioxan solution are usually slightly higher than those in benzene solution.

To calculate the " theoretical " moments of these compounds, *i.e.*, the moments which would be expected if all groups had group moments equal to the dipole moments of the corresponding monosubstituted benzenes, it is necessary to make some assumption regarding the angle of inclination of the dipole axis in aniline to the N–C bond. If the dipole moments of aniline and *p*-phenylenediamine in benzene solution are taken as 1·53 D [1] and 1·57 D,[5] respectively, and the amino-groups are assumed to have free and independent rotation about the N–C bonds, vector summation indicates that the dipole axis in aniline is inclined at either 46½° or 133½° to the N–C bond. This calculation is not vitiated by preferred orientations of the amino-groups with respect to the plane of the ring provided that these are independent, *i.e.*, " *cis* "- and " *trans* "-configurations have equal probability. Alternatively, from the values of 1·32 and 0·37 D for the moments of *p*-toluidine and toluene, respectively, it follows that if the mesomeric effect of the amino-group is the same in *p*-toluidine as in aniline the angle of inclination of dipole in the latter is 49°. Similar calculation from the dipole moment of *m*-toluidine (1·45 D [5]), assuming free rotation of the amino-group, leads to an inclination of 48½°. Considering the assumptions made the three results are in very satisfactory agreement, and indicate that no great error can be introduced if the angle is taken as 48½°, the positive end of the dipole being away from the aromatic ring.

On combining this result with the dipole moment in benzene solution of appropriate mono-substituted benzenes (PhX), the " theoretical " moments for the substituted anilines are given by:

$$\mu_{calc}^2\,(para) = \mu_{\mathrm{PhNH_2}}^2 + \mu_{\mathrm{PhX}}^2 + 2\mu_{\mathrm{PhNH_2}}\mu_{\mathrm{PhX}}\cos 48\tfrac{1}{2}^\circ \quad . \quad . \quad . \quad (1)$$

$$\mu_{calc}^2\,(meta) = \mu_{\mathrm{PhNH_2}}^2 + \mu_{\mathrm{PhX}}^2 + \mu_{\mathrm{PhNH_2}}\mu_{\mathrm{PhX}}\cos 48\tfrac{1}{2}^\circ \quad . \quad . \quad . \quad (2)$$

In calculating the values shown in Table 2, which includes not only the compounds the moments of which have been measured in this work but also other amines for which the pertinent data are available, the following values have been taken for the moments of the parent mono-substituted benzenes: nitrobenzene 4·01, chlorobenzene 1·58, bromobenzene 1·56, and benzonitrile 4·03 D.

In interpreting the difference between the observed and the calculated moment of a substituted aniline in terms of an " interaction moment " arising from the simultaneous presence of the two substituents, a definite direction must be assumed for the axis of the additional component to the moment. For the *p*-substituted anilines it has been assumed to lie along the axis of the N–C bond, when it is given by:

$$\mu_{\mathrm{int}}\,(para) = \{(\mu_{\mathrm{PhNH_2}}\cos 48\tfrac{1}{2}^\circ + \mu_{\mathrm{PhX}})^2 + \mu_{\mathrm{obs}}^2 - \mu_{\mathrm{calc}}^2\}^{\frac{1}{2}} - (\mu_{\mathrm{PhNH_2}}\cos 48\tfrac{1}{2}^\circ + \mu_{\mathrm{PhX}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the *m*-substituted anilines, however, the effect can be regarded as being located partly in the substituent as well as in the amino-group. If it is assumed that the contributions from the two sources are equal, and directed along the bonds linking the groups to the ring, the resultant contribution will act along an axis parallel to the line joining the ring carbon atoms carrying the substituents, and will have a magnitude given by:

$$\mu_{\mathrm{int}}\,(meta) = \{\tfrac{3}{4}(\mu_{\mathrm{PhNH_2}}\cos 48\tfrac{1}{2}^\circ + \mu_{\mathrm{PhX}})^2 + \mu_{\mathrm{obs}}^2 - \mu_{\mathrm{calc}}^2\}^{\frac{1}{2}} - \sqrt{3}/2(\mu_{\mathrm{PhNH_2}}\cos 48\tfrac{1}{2}^\circ + \mu_{\mathrm{PhX}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

None of the equations (1)—(4) is invalidated by the existence of any preferred orientations of the amino-group with respect to the ring, provided that either (*a*) in these preferred configurations the hydrogen atoms are on the same side of, and equidistant from, the plane of the ring, or (*b*) there are four preferred configurations with mirror-image symmetry with respect to one another.

The differences, $\Delta\mu$, between the apparent moments in dioxan and in benzene show a fairly systematic variation with the interaction moments, but the relation becomes clearer when the differences are evaluated vectorially. If $\Delta\mu$ is assumed to arise exclusively from electron-shifts in the amine molecule, it must involve increases in both the mesomeric moment of the amino-group and the interaction moment. For aniline, therefore, it can be interpreted in terms of an additional component to the moment, $\Delta\mu_{PhNH_2}$, directed along the axis of the N–C bond. For other amines, however, there will be an additional component, $\Delta\mu'$, directed along the axis of the interaction moment and superimposed upon the component $\Delta\mu_{PhNH_2}$ already present when aniline is studied in dioxan solution.

TABLE 2.

	μ_{calc} (D)	$\mu_{benzene}$ (D)	μ_{int} (D)	μ_{dioxan} (D)	$\Delta\mu$ (D)	$\Delta\mu_{vect}$ (D)
Aniline	1·53	1·53	—	1·77	0·24	0·33
p-Toluidine	1·32	1·32	—	1·50	0·18	0·31
p-Bromoaniline	2·82	3·01	0·20	3·36	0·35	0·38
m-Bromoaniline	2·52	2·68	0·19	3·01	0·33	0·38
p-Nitroaniline	5·16	6·22	1·08	6·82	0·60	0·61
m-Nitroaniline	4·75	4·91	0·18	5·24	0·33	0·39
p-Chloroaniline	2·84	3·01 [2]	0·19	3·39 [2]	0·38	0·40
4-Diphenylylamine	1·53	1·74 [12]	0·29	2·02 [12]	0·28	0·36
p-Aminobenzonitrile	5·18	5·96 [13]	0·80	6·46 [13]	0·50	0·51
β-Naphthylamine	1·53	1·77 [9]	0·33	2·10 [9]	0·33	0·41

For *p*-substituted anilines both these components act along the same axis. Hence equation (3) can be used to calculate the total interaction moment from the apparent moment in dioxan and the calculated moment for benzene solutions. Subtraction of the interaction moment in benzene solution then gives the vectorial value, $\Delta\mu_{vect}$, of the additional moment in dioxan solution.

For *m*-substituted anilines $\Delta\mu'$ and $\Delta\mu_{PhNH_2}$ act along axes inclined at 30° to one another. The sum of the former and the normal interaction moment is given by :

$$\begin{aligned}\mu_{int} + \Delta\mu'\ (\textit{meta}) = \{\tfrac{3}{4}(\mu_{PhNH_2}\cos 48\tfrac{1}{2}^\circ + \mu_{PhX} + \Delta\mu_{PhNH_2})^2 + \mu_{obs}{}^2 \\ - \mu_{calc}{}^2 - \Delta\mu_{PhNH_2}(2\mu_{PhNH_2}\cos 48\tfrac{1}{2}^\circ + \mu_{PhX} + \Delta\mu_{PhNH_2})\}^{\frac{1}{2}} \\ - \sqrt{3}/2(\mu_{PhNH_2}\cos 48\tfrac{1}{2}^\circ + \mu_{PhX} + \Delta\mu_{PhNH_2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)\end{aligned}$$

From this the value of $\Delta\mu'$ is obtained by subtracting the μ_{int} value for benzene solutions, and by vector summation of $\Delta\mu'$ and $\Delta\mu_{PhNH_2}$ the total $\Delta\mu_{vect}$ value for the *m*-substituted amine is obtained. For *m*-nitroaniline and *m*-bromoaniline the alternative and simpler method of assuming the whole of the additional component to the moment arising in dioxan solution to be directed along the axis of the interaction moment leads to $\Delta\mu_{vect}$ values 0·03 D less than those shown in Table 2 and derived by using equation (5).

There is a marked parallelism between the μ_{int} and $\Delta\mu_{vect}$ values shown in Table 2 : when these are plotted against one another all points excepting that for 4-diphenylylamine lie within experimental error (±0·02 D) of the straight line $\Delta\mu_{vect} = 0{\cdot}33 + 0{\cdot}255\,\mu_{int}$. It may be noted that this would lead to a value of $\Delta\mu_{vect} = 0$ when $\mu_{int} = -1{\cdot}29$ D. It may be fortuitous, but this is of the same order of magnitude as the mesomeric moment of aniline calculated from the moment of *n*-butylamine or *cyclo*hexylamine. If the moment of an aliphatic amine is taken as 1·32 D, the value obtained for the mesomeric moment of aniline varies between 1·2 and 1·4 D according to the assumption made regarding the direction of the axis of the dipole in the aliphatic compound.

---

[12] Halverstadt and Kumler, *ibid.*, 1942, **64**, 2988.
[13] Curran and Estok, *ibid.*, 1950, **72**, 4575.

The high values of both μ_{int} and $\Delta\mu_{vect}$ for *p*-nitroaniline and *p*-aminobenzonitrile are accounted for by the fact that the mesomeric effects of the two polar groups act in conjunction, and hence mutually enhance one another. In *m*-nitroaniline, on the other hand, such conjugation between the mesomeric effects of the two substituents cannot occur. The only interaction possible is that between the inductive effect of the nitro-group and the mesomeric effect of the amino-group, which will lead to a slight increase in each. The fact that the interaction moments in *p*- and *m*-bromoaniline are almost equal suggests that in each case the strong inductive effect of the bromine atom increases the mesomeric effect of the amino-group, thus resulting in a diminution in the mesomeric effect of the bromine atom and a slight increase in its inductive effect relative to that in bromobenzene. The greater values of both μ_{int} and $\Delta\mu_{vect}$ for *p*-diphenylylamine and β-naphthylamine as compared with aniline are attributable to transmission of the mesomeric effect into the additional conjugated system, such as is observed also for the corresponding nitro-compounds.

TABLE 3. *Polarisation data.*

100*w*	ε	*v*	n_D
	p-*Toluidine in benzene*		
0·0000	2·2725	1·14460	1·4980
0·6381	2·2852	1·14371	1·4983
0·9689	2·2911	1·14331	1·4985
1·2649	2·2967	1·14290	1·4987
1·5544	2·3024	1·14253	1·4989
1·8586	2·3086	1·14211	1·4990
2·0379	2·3118	1·14142	1·4991
3·2662	2·3358	1·14027	1·4998
3·3365	2·3374	1·14017	1·4999
3·3638	2·3379	1·14011	1·4999
3·7640	2·3456	—	1·5001
6·1371	2·3928	1·13641	1·5013
	p-*Toluidine in dioxan*		
0·0000	2·2122	0·97309	1·4199
0·6111	2·2298	0·97325	1·4209
1·2117	2·2470	0·97344	1·4219
1·9778	2·2695	0·97364	1·4230
2·5478	2·2860	0·97381	1·4240
3·7677	2·3216	0·97419	1·4260
5·8703	2·3832	0·97479	1·4293
	p-*Nitroaniline in benzene*		
0·0000	2·2725	1·14460	1·4980
0·0622	2·2915	1·14437	—
0·1113	2·3068	1·14415	1·4981
0·1716	—	1·14389	—
0·2025	2·3354	1·14377	—
0·2612	2·3538	1·14357	1·4982
0·3336	2·3768	1·14322	—
0·3618	2·3854	1·14311	1·4984
	p-*Nitroaniline in dioxan*		
0·0000	2·2120	0·97304	1·4200
0·6259	2·4799	0·97152	1·4215
1·1971	2·7289	0·97015	1·4229
1·8488	3·0183	0·96857	1·4244
2·4947	3·3065	0·96701	1·4261
3·7102	3·8820	0·96418	1·4292
	m-*Bromoaniline in benzene*		
0·0000	2·2725	1·14462	1·4977
0·5453	2·2984	1·14178	1·4981
1·1485	2·3271	1·13860	1·4986
2·1855	2·3768	1·13312	1·4994
2·7200	2·4031	1·13035	1·4998
3·5843	2·4453	1·12581	1·5002
	m-*Nitroaniline in benzene*		
0·0000	2·2725	1·14459	1·4980
0·1481	2·3006	1·14403	—
0·2716	2·3247	1·14358	—
0·4154	2·3523	1·14303	1·4984
0·5324	2·3753	1·14256	—
0·6361	2·3957	1·14212	1·4986
0·7416	2·4158	1·14167	—
0·8656	2·4416	1·14111	1·4988
	m-*Nitroaniline in dioxan*		
0·0000	2·2169	0·97322	1·4200
0·5884	2·3647	0·97193	1·4209
1·1338	2·5076	0·97071	1·4219
1·7381	2·6620	0·96940	1·4230
2·3073	2·8126	0·96821	1·4240
2·8900	2·9684	0·96690	1·4250
5·5876	3·7173	0·96106	1·4298
	p-*Bromoaniline in benzene*		
0·0000	2·2725	1·14457	1·4978
0·4137	2·2971	1·14244	1·4980$_5$
0·8649	2·3236	1·14003	1·4983$_5$
1·2547	2·3474	1·13798	1·4988
1·6885	2·3735	1·13567	1·4990
2·3484	2·4135	1·13220	1·4995
3·3782	2·4771	1·12695	1·5003
	p-*Bromoaniline in dioxan*		
0·0000	2·2152	0·97368	1·4194
0·6200	2·2684	0·97148	1·4203
1·2231	2·3207	0·96929	1·4212
1·8509	2·3749	0·96707	1·4221
2·4778	2·4303	0·96482	1·4230
3·1159	2·4873	0·96258	1·4239
4·0471	2·5711	0·95925	1·4253
	m-*Bromoaniline in dioxan*		
0·0000	2·2081	0·97304	1·4201
0·4723	2·2404	0·97133	1·4207
1·0489	2·2801	0·96932	1·4215
1·5168	2·3152	0·96764	1·4221
1·9210	2·3408	0·96622	1·4227
2·4336	2·3768	0·96439	1·4232
3·0376	2·4198	0·96226	1·4242

EXPERIMENTAL

Materials.—Benzene was purified as described in Part I.[1] Dioxan was repeatedly refluxed with sodium and then fractionally distilled under anhydrous conditions.

Commercial pure *p*-toluidine was recrystallised from alcohol and then from benzene: it had m. p. 44·8°. Commercial pure *p*-nitroaniline, recrystallised from water, had m. p. 148·9°, whilst *m*-nitroaniline, prepared by reduction of *m*-dinitrobenzene with sodium polysulphide and recrystallised from water, had m. p. 112·4°. *p*-Bromoaniline, prepared by bromination of acetanilide and subsequent hydrolysis, and recrystallised from *cyclo*hexane, had m. p. 63·5°. *m*-Bromoaniline was prepared by bromination of nitrobenzene by Johnson and Gauerke's method,[14] followed by reduction of the *m*-bromonitrobenzene by Mathieson and Newbery's method.[15] It was redistilled several times under reduced pressure and had b. p. 120°/15 mm.

Methods and Results.—The dielectric constants, specific volumes, and refractivities of the solutions were determined at 25° by the methods used in the previous investigations. The results are recorded in Table 3. For some of the compounds the dielectric constants of the solutions were linear with w over the concentration range studied, and hence the slope of the best straight line through these points was taken as α, but where the relation 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.

Grateful thanks are tendered to the Department of Scientific and Industrial Research for a Maintenance Grant to S. M. W. and to Imperial Chemical Industries Limited for a grant and or the loan of a precision variable condenser.

BEDFORD COLLEGE, REGENT'S PARK, LONDON, N.W.1. [*Received, February 27th,* 1957.]

---

[14] Johnson and Gauerke, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 123.

[15] Mathieson and Newbery, *J.*, 1949, 1136.