379. *The Dipole Moments of Some Aromatic Diazoamino-compounds.*

By R. J. W. Le Fèvre and H. Vine.

The dielectric constants, densities, and refractive indices of solutions in benzene of diazoaminobenzene and some derivatives are recorded, and the dipole moments calculated from them.

It is concluded that in these compounds the two aryl groups are mutually inclined at *ca.* 140°. The change with concentration of the polarisation of the parent substance is considered in relation to the nature of the association which it undergoes (Hunter, this vol., p. 320); this does not appear to consist entirely of the formation of non-polar dimeric molecules.

The following dipole moments (in Debye units) have been obtained by measurements carried out on benzene solutions :

Diazoaminobenzene derivative.	μ.	Diazoaminobenzene derivative.	μ.
(Unsubstituted)	$0{\cdot}9_0$	4-Bromo-	$2{\cdot}0_0$
4 : 4′-Dichloro-	$1{\cdot}9_0$	4-Nitro-	$4{\cdot}7_7$
4 : 4′-Dibromo-	$1{\cdot}8_8$	*N*-Methyl-	$1{\cdot}4_9$
4 : 4′-Dimethyl-	$0{\cdot}9_3$	4 : 4′-Dibromo-*N*-methyl-	$2{\cdot}5_2$

The polarisation of diazoaminobenzene has also been measured in solutions of concentration up to 8%. Two points concerning which these data give some information are discussed below.

(1) *Structure of the Diazoamino-compounds.*—The system R·N:N·NHR′ or R·N:N·NMeR′ is complicated by the possibility of *cis-trans*-isomerism about the N:N bond and of rotation about the N–N single link. It may well be assumed, however, that, whether the azo-group has a *cis*- or a *trans*-configuration in the parent substance, it has the same configuration in the derivatives, and further that, if rotation occurs in the former about the N–N bond, it does so to the same extent in the latter. Hence the effective angle made by the N–R and the N–R′ direction should be approximately constant throughout the whole series. Moreover, the not unlikely occurrence of mesomeric effects within such molecules (producing real states in which the three central nitrogen atoms are united by links having a partial double-bond character) may be expected to confer a greater stiffness and resistance to rotation about the N–N link than the above unperturbed formulæ indicate.

In this discussion the phenyl groups have been regarded as symmetrical, and the C→Hal and C→NO$_2$ vectors taken as acting along the N–R and N–R′ directions and meeting at an angle θ. If it is assumed in the first instance that the resultant moments of diazoaminobenzene and its 4 : 4′-disubstituted derivatives are parallel to the bisector of θ, it is possible to estimate this angle by vector methods. The accuracy of the values obtained in such cases is reduced chiefly by interaction between the substituents and the molecule containing them (see Glasstone, *Ann. Reports*, 1935, **32**, 129). To some extent these effects may be allowed for in the dihalogeno-derivatives by taking as the C–Hal link moments the values obtained by Bergmann, Engel, and Sandor (*Ber.*, 1930, **63**, 2572) for *p*-chloro- and -bromo-azobenzenes in benzene solution.

Since the effect of replacing two hydrogen by two chlorine atoms in the 4 : 4′-positions is to increase the moment from 0·90 to 1·94, it is evident that, subject to the above approximations, the two C–Cl moments (1·55) themselves produce a component of *either* (1·94 + 0·90) or (1·94 — 0·90).

Then

$$1{\cdot}94 + 0{\cdot}90 = 2 \times 1{\cdot}55 \cos \theta/2, \text{ whence } \theta = 47\tfrac{1}{2}°,$$

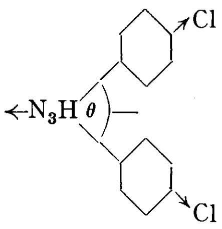
or

$$1{\cdot}94 - 0{\cdot}90 = 2 \times 1{\cdot}55 \cos \theta/2, \text{ whence } \theta = 141°.$$

These two solutions are illustrated in (I) and (II). If the former figure were the true one, the moment of 4 : 4′-dimethyldiazoaminobenzene would be measurably different from that of its parent, *i.e.*, approximately $0{\cdot}9 + 2 \times 0{\cdot}3 = 1{\cdot}5$. Actually its moment is 0·9, which is in better agreement with the second result. An angle of 47½° also appears, on general grounds, to be improbable.

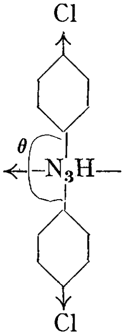
The occurrence of the interaction mentioned above does not disturb the calculation very seriously, for the value of θ is not greatly affected if a different value is taken for the C–Cl moment; for example, if in the above calculation this were $1{\cdot}55 \pm 0{\cdot}1$, θ would be 140° 45′ ± 2° 30′.

(I.)



2(C–Cl) resultant $= 1{\cdot}94 + 0{\cdot}90$; $\theta = 47\tfrac{1}{2}°$.

(II.)



2(C–Cl) resultant $= 1{\cdot}94 - 0{\cdot}90$; $\theta = 141°$.

If the resultant moment of 4 : 4′-dichlorodiazoaminobenzene is not parallel to the bisector of θ, but is at an angle A to this line, θ being approximately 140°, it can be shown that a more accurate value is given by the equation

$$\cos \theta/2 = (1{\cdot}94 \sec A - 0{\cdot}90)/2 \times 1{\cdot}55$$

Then if A is as great as 12°, θ becomes 139° 20′. The correction is small, and is of opposite sign to, and of the same order of magnitude as, that for interaction.

Similarly, Bergmann, Engel, and Sandor's value (*loc. cit.*) of 1·42 for *p*-bromoazobenzene being taken as the appropriate C–Br link moment,

$$1{\cdot}88 - 0{\cdot}90 = 2 \times 1{\cdot}42 \cos \theta/2, \text{ whence } \theta = 140°.$$

A reliable confirmatory value could not be obtained from the moment of 4 : 4′-dinitrodiazoaminobenzene, as this substance was too sparingly soluble in benzene.

The difference between the moments of *N*-methyl- and 4 : 4′-dibromo-*N*-methyldiazoaminobenzene corresponds to a similar angle :

$$2{\cdot}52 - 1{\cdot}49 = 2 \times 1{\cdot}42 \cos \theta/2, \text{ and } \theta = 137\tfrac{1}{2}°.$$

The value of θ in both the methylated and the unmethylated compounds may thus be given as 140°, with a probable error of less than 5°.

The moments of 4-bromo- and 4-nitro-diazoaminobenzene are found to be of no service in calculating θ, for the answers obtained depend very largely on the values taken for the C–Br and C–NO_2 link moments; *e.g.*, if the moment of the 4-bromo-derivative were the resultant of a group moment of 0·90 along the bisector of θ and a C–Br link moment of 1·37 or 1·47 at an angle $\theta/2$ to it, θ should satisfy the equation

$$(2{\cdot}00)^2 = (1{\cdot}37)^2 + (0{\cdot}90)^2 + 2 \times 1{\cdot}37 \times 0{\cdot}90 \cos \theta/2, \text{ whence } \theta = 116°;$$

or

$$(2{\cdot}00)^2 = (1{\cdot}47)^2 + (0{\cdot}90)^2 + 2 \times 1{\cdot}47 \times 0{\cdot}90 \cos \theta/2, \text{ whence } \theta = 134°.$$

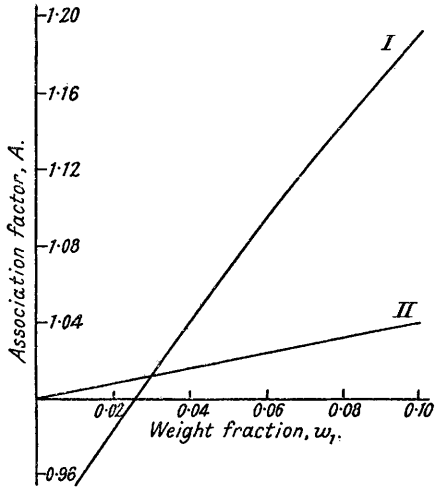
Similarly, if 4·0 or 4·1 is taken for the C–NO_2 link in 4-nitrodiazoaminobenzene,

$$(4{\cdot}77)^2 = (4{\cdot}0)^2 + (0{\cdot}90)^2 + 2 \times 4{\cdot}0 \times 0{\cdot}90 \cos \theta/2, \text{ whence } \theta = 67°;$$

or

$$(4{\cdot}77)^2 = (4{\cdot}1)^2 + (0{\cdot}90)^2 + 2 \times 4{\cdot}1 \times 0{\cdot}90 \cos \theta/2, \text{ whence } \theta = 91°.$$

(2) *Association of Diazoaminobenzene in Benzene Solution.*—The slight decrease in the polarisation of diazoaminobenzene with concentration is qualitatively in agreement with Hunter's observations (this vol., p. 320) of the molecular weights of diazoamino-compounds in benzene solution. He finds that association occurs as the solutions become more concentrated, and suggests the formation of a double molecule by resonance. He puts forward two possible forms, the first of which would be highly polar, and its formation would correspond to an increase in the polarisation, whilst the second form, which he regards as the more probable, would apparently have zero moment. His results, expressed as the association factor A, the ratio of the apparent to the true molecular weight, are shown in curve I. The dimeric form being assumed to have zero moment, the same factor has been calculated from the polarisation measurements (curve II): I is clearly much steeper than II. The divergence may be attributed to the incorrectness of the assumption that association consists entirely of the formation of non-polar double molecules.



EXPERIMENTAL.

Preparation of Materials.—*N*-Methyldiazoaminobenzene was made from methylaniline and diazotised aniline; being an unstable liquid, it was purified by dissolving it in alcohol and cooling the solution in solid carbon dioxide–alcohol, whereupon it separated as a pale yellow sticky material. The most likely impurity was then methylaniline; to test the effect of this, the polarisation of a sample containing 10% was measured and found to be practically unchanged. 4 : 4′-Dibromo-*N*-methyldiazoaminobenzene, previously obtained only by direct methylation, was readily prepared from *p*-bromomethylaniline and diazotised aniline.

Diazoaminobenzene and its 4 : 4′-dimethyl-derivative were obtained in a pure state in one operation by a slight modification of Meunier's method (*Comp. rend.*, 1903, **137**, 1264; cf. Earl, *Proc. Roy. Soc. N.S.W.*, 1929, **53**, 89; 1930, **54**, 96). The base (0·1 g.-mol.), sodium nitrite (0·2 g.-mol.), water (40 c.c.), and alcohol (40 c.c.) were treated with carbon dioxide for about 4 hours. Filtration gave the diazoamino-compounds as pure yellow needles, m. p. 99° and 117·5—118° respectively. The latter m. p. is 1—1·5° greater than the highest previously recorded (Witt, *Ber.*, 1877, **10**, 1309).

Measurements, and Calculation of Results.—The dielectric constant and density of solutions of many substances vary linearly with concentration and can be expressed by the equations $\varepsilon = \varepsilon_2(1 + \alpha f_1)$ and $d = d_2(1 + \beta f_1)$, where the suffixes 1 and 2 denote the solute and solvent respectively and f is the mol.-fraction. Hedestrand (*Z. physikal. Chem.*, 1929, *B*, **2**, 428) has shown that the molecular polarisation at infinite dilution can be calculated from α and β thus,

$$P_{1_\infty} = A(M_1 - \beta M_2) + B\alpha\varepsilon_2$$

where A and B are constant. Fairly concentrated solutions can be used, and α and β determined accurately, whereas graphical extrapolation requires very dilute solutions from which P_1 cannot be found accurately.

A similar expression is obtained if the weight fraction w_1 and the specific polarisations p_1 and p_2 are used, and this involves less work in the calculation. Let $\varepsilon = \varepsilon_2(1 + \alpha w_1)$ and $d = d_2(1 + \beta w_1)$; then

$$\begin{aligned} p_1 &= (p_{12} - p_2 w_2)/w_1 \\ &= \frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{1}{d} + \frac{w_2}{w_1}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{1}{d} - \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2}\cdot\frac{1}{d_2}\right) \\ &= \frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{1}{d} + \frac{w_2}{d}\cdot\frac{3\alpha\varepsilon_2 - \beta(\varepsilon_2 - 1)[\varepsilon_2(1 + \alpha w_1) + 2]}{[\varepsilon_2(1 + \alpha w_1) + 2][\varepsilon_2 + 2]} \end{aligned}$$

w_1.	$\epsilon^{1200}_{25°}$.	$d^{25°}_{4°}$.	p_{12}.	P_1.	$\alpha\epsilon_2$.	β.	$n^{25°}_D$.	r_{12}.	$[R_L]_D$.
0	2·2725	0·87378	0·34086	—	—	—	1·49724	0·33503	—
Diazoaminobenzene.									
0·00351	2·2759	0·87451	0·34121	86·9	0·97	0·238	1·49795	0·33494	72·7
0·01188	2·2837	0·87624	0·34200	86·1	0·94	0·237	1·49948	0·33536	71·5
0·02589	2·2970	0·87923	0·34330	85·7	0·95	0·241	1·50203	0·33566	70·7
0·02900	2·3001	0·87992	0·34360	85·7	0·95	0·243	1·50263	0·33574	70·7
0·03587	2·3057	0·88126	0·34411	85·1	0·926	0·239	1·50388	0·33594	70·9
0·04187	2·3117	0·88257	0·34470	85·3	0·936	0·240	1·50492	0·33602	70·7
0·07100	2·3398	0·88880	0·34735	85·1	0·948	0·243	1·51012	0·33657	70·3
0·08486	2·3514	0·89182	0·34824	84·3	0·930	0·243	1·51273	0·33687	70·3
4 : 4′-*Dimethyldiazoaminobenzene.*									
0·00774	2·2788	0·87518	0·34149	95	0·81	0·207	—	—	—
0·00826	2·2797	0·87523	0·34164	98	0·87	0·201	1·49859	0·33524	81·0
0·00929	2·2806	0·87543	0·34173	98	0·87	0·203	—	—	—
0·01663	2·2872	0·87677	0·34244	98	0·88	0·206	1·49996	0·33543	80·8
0·02000	2·2906	0·87729	0·34287	99	0·90	0·201	—	—	—
0·03009	2·2993	0·87902	0·34381	99	0·89	0·199	1·50228	0·33589	81·7
4 : 4′-*Dichlorodiazoaminobenzene.*									
0·00460	2·2829	0·87518	0·34226	172	2·26	0·348	1·49803	0·33494	83·9
0·00739	2·2884	0·87608	0·34294	165	2·15	0·353	1·49843	0·33483	81·9
0·00995	2·2935	0·87687	0·34357	163	2·11	0·352	1·49891	0·33480	83·0
0·01518	2·3020	0·87849	0·34451	151	1·95	0·351	1·49967	0·33461	81·7
0·02148	2·3146	—	—	—	1·96	—	—	—	—
0·02470	2·3200	—	—	—	2·00	—	—	—	—
4 : 4′-*Dibromodiazoaminobenzene.*									
0·00261	2·2757	0·87490	0·34102	143	1·23	0·491	1·49762	0·33482	90·4
0·00430	2·2794	0·87566	0·34142	167	1·60	0·500	1·49787	0·33467	89·1
0·00779	2·2838	0·87722	0·34163	156	1·45	0·505	1·49841	0·33438	89·1
0·01042	2·2888	—	—	—	1·56	—	—	—	—
0·01487	2·2949	0·88035	0·34247	159	1·51	0·505	1·49939	0·33375	88·4
0·02139	2·3042	—	—	—	1·48	—	—	—	—
4-*Bromodiazoaminobenzene.*									
0·00857	2·2892	0·87694	0·34275	155	1·95	0·422	1·49865	0·33462	79·2
0·01588	2·3050	0·87941	0·34470	161	2·05	0·406	1·49978	0·33432	80·0
0·03571	2·3468	0·88681	0·34938	160	2·08	0·418	1·50291	0·33329	78·9
0·04634	2·3700	0·89053	0·35093	154	2·10	0·413	1·50474	0·33292	79·9
0·05360	2·3850	0·89335	0·35356	160	2·10	0·418	1·50582	0·33247	79·3
4-*Nitrodiazoaminobenzene.*									
0·00265	2·3030	0·87455	0·34625	574	11·5	0·332	1·49776	0·33503	92
0·00414	2·3191	0·87501	0·34904	564	11·3	0·340	1·49808	0·33504	93
0·00462	2·3240	0·87515	0·34988	555	11·1	0·339	1·49818	0·33504	93
0·00566	2·3358	0·87541	0·35193	556	11·2	0·331	1·49846	0·33510	96
0·00583	2·3362	0·87548	0·35198	544	10·9	0·334	1·49842	0·33505	93
N-*Methyldiazoaminobenzene.*									
0·00789	2·2859	0·87528	0·34278	123	1·70	0·217	1·49856	0·33521	75·5
0·01525	2·2970	0·87672	0·34428	119	1·61	0·221	1·49970	0·33530	74·5
0·02245	2·3097	0·87815	0·34606	121	1·657	0·223	1·50089	0·33543	74·5
0·03281	2·3260	0·88022	0·34823	119	1·631	0·224	1·50264	0·33563	74·7
0·04623	2·3463	0·88285	0·35086	118	1·596	0·224	—	—	—
4 : 4′-*Dibromo*-N-*methyldiazoaminobenzene.*									
0·00571	2·2858	0·87619	0·34241	226	2·33	0·483	—	—	—
0·00745	2·2899	0·87692	0·34289	227	2·34	0·482	1·49825	0·33440	92·3
0·01443	2·3048	0·87990	0·34446	218	2·24	0·485	1·49919	0·33380	92·3
0·02133	2·3205	0·88282	0·34620	218	2·25	0·485	1·50021	0·33328	93·4

Diazoaminobenzene derivative.	M.	Mean values of $\alpha\epsilon_2$.	Mean values of β.	P_∞.	$[R_L]_D$.	μ.
(Unsubstituted)	197	0·940	0·241	85·8	70·6	0·90 ± 0·02
4 : 4′-Dimethyl-	225	0·87	0·203	98·1	81·2	0·90 ± 0·04
4 : 4′-Dichloro-	266	2·04	0·351	161	83	1·94 ± 0·04
4 : 4′-Dibromo-	355	1·52	0·503	162	89	1·88 ± 0·04
4-Bromo-	276	2·06	0·415	162	79·5	2·00 ± 0·04
4-Nitro-	242	11·2	0·335	565	93	4·77 ± 0·06
N-Methyl-	211	1·64	0·223	120·9	74·8	1·49 ± 0·03
4 : 4′-Dibromo-*N*-methyl-	369	2·29	0·484	224	93	2·52 ± 0·04

Taking the limit, as $w_1 \rightarrow 0$,

$$p_\infty = \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} \cdot \frac{1}{d_2} + \frac{3\alpha\varepsilon_2 - \beta(\varepsilon_2 - 1)(\varepsilon_2 + 2)}{d_2(\varepsilon_2 + 2)^2}$$

$$= \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} \cdot \frac{1}{d_2}(1 - \beta) + \frac{3\alpha\varepsilon_2}{d_2(\varepsilon_2 + 2)^2}$$

$$= p_2(1 - \beta) + c\alpha\varepsilon_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p_2 and c are constants for the solvent and were equal to 0·34086 and 0·18809 respectively for the benzene used.

Density and dielectric constant were plotted against w_1 for the solutions of each substance and found to give good straight lines; $\alpha\varepsilon_2$ and β were, therefore, obtained and p_∞ calculated by means of the equation (1). The data are tabulated on page 1808.

Association of Diazoaminobenzene.—If a substance 'a' is partly associated in solution, let w_a, w_{a_1}, and w_{a_2} be the weight fractions and ${}_0p_a$, ${}_0p_{a_1}$, and ${}_0p_{a_2}$ the specific orientation polarisations of the mixture and of the mono- and the di-meric form respectively, and let $\gamma w_a = w_{a_2}$.

Then $${}_0p_a w_a = {}_0p_{a_1} w_{a_1} + {}_0p_{a_2} w_{a_2}$$

Therefore $${}_0p_a = {}_0p_{a_1}(1 - \gamma) + {}_0p_{a_2}\gamma$$

and $$\gamma = ({}_0p_{a_1} - {}_0p_a)/({}_0p_{a_1} - {}_0p_{a_2})$$

If ${}_0p_{a_2} = 0$ and if r_a is the specific refraction of a,

$$\gamma = (p_{a_1} - p_a)/(p_{a_1} - r_a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is easily seen that the association factor A is equal to $2/(2 - \gamma)$.

The measurements show that the specific refraction of diazoaminobenzene is 0·3585. By assuming $\alpha\varepsilon_2 = 0{\cdot}940$ and $\beta = 0{\cdot}241$, values of d and ε have been calculated at various concentrations, from which the specific polarisation has been obtained. Formula (2) has been used to find A in each case, p_∞ being taken as 0·4355, as calculated from equation (1). The results are expressed by curve II in the diagram.

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Note (*added September* 27*th*, 1937).—Since the preceding results were obtained, it has been shown (Hartley, *Nature*, 1937, **140**, 281) that azobenzene is partly converted in solution into the *cis*-form when exposed to daylight. Measurements of the dipole moments of the pure *cis*-, pure *trans*-, and equilibrated azobenzenes have been carried out by one of us and reported briefly in the above reference. Illumination causes a considerable increase in the dielectric constants of solutions of the stable *trans*-form. It was, therefore, considered important to discover whether errors have been introduced into the measurement of the dielectric constant of solutions of the diazoamino-compounds owing to their being allowed to stand in ordinary white glass vessels. The dielectric constants (ε_{I}) of solutions of diazoaminobenzene and 4 : 4′-dibromo-*N*-methyldiazoaminobenzene which have been kept in brown bottles have been compared with those ($\varepsilon_{\mathrm{II}}$) of solutions which have been exposed to bright sunlight for about 3 hours. As the differences (see below) are small, the results tabulated above are considered to be satisfactory.

Diazoaminobenzene.			*4 : 4′-Dibromo-N-methyldiazoaminobenzene.*		
w_1.	ϵ_{I}.	ϵ_{II}.	w_1.	ϵ_{I}.	ϵ_{II}.
0·01888	2·2887	2·2891	0·01614	2·3083	2·3079
0·04912	2·3190	2·3198	0·02256	2·3228	2·3230