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## The Electric Moments of Some Derivatives of Azobenzene

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The electric moments of *p*-aminoazobenzene, *p*-nitroazobenzene, *p,p'*-tetramethyldiaminoazobenzene, *p,p'*-dinitroazobenzene and three derivatives of *p*-benzalaminoazobenzene have been measured in benzene solution at 25°. A redetermination of the electric moment of tetramethyl-*p*-phenylenediamine also has been made and the magnitude and direction of the dimethylamino group moment in benzene and in azobenzene compounds calculated and compared. The effects of resonance on the electric moments of azobenzene derivatives is discussed; it is shown that both azobenzene and *p*-benzalaminoazobenzene are good electron acceptors, the effect increasing with length of the conjugated system.

During the course of an investigation of the properties of some azo dyes<sup>1,2</sup> it became desirable to have experimental values for the electric moments of some simple derivatives of azobenzene. Values reported in the literature<sup>3</sup> for the dipole moments of *p*-chloro-, *p*-bromo-, *p*-amino- and *p*-dimethylaminoazobenzene are 1.55, 1.42, 2.71 and 3.22<sup>1</sup> Debye units, respectively. The first two are close to the moments of chlorobenzene (1.57) and bromobenzene (1.48), whereas the latter are much larger than the moments of aniline (1.54) and dimethylaniline (1.58). This suggests that azobenzene is a better electron acceptor than benzene, but not a better electron donor; to study this question further the electric moment of *p*-nitroazobenzene has been measured, and that of *p*-aminoazobenzene has been redetermined. The large moment of dimethylaminoazobenzene might be the result of coplanarity of the dimethylamino group with the azobenzene ring; we have measured the electric moment of *p,p'*-tetramethyldiaminoazobenzene to test this possibility and have also redetermined the moment of tetramethyl-*p*-phenylenediamine so that the magnitudes and directions of the dimethylamino group moment could be compared in the benzene and azobenzene series. The electric moment of *p,p'*-dinitroazobenzene was measured to provide evidence that the azobenzene derivatives have the *trans* configuration, and to provide a value for the magnitude of the atomic polarization in azobenzene derivatives.

The properties of molecules containing several conjugated groups are of interest; we have measured the electric moments of *p*-benzalaminoazobenzene and two of its derivatives so a comparison could be made between the electron accepting power of the azobenzene and *p*-benzalaminoazobenzene rings.

Values reported in the literature for tetramethyl-*p*-phenylenediamine are 1.23<sup>3</sup> and 1.12<sup>4</sup> *D*, and for *p*-aminoazobenzene<sup>3</sup> 2.71 *D*; the other compounds have not been reported previously.

### Experimental

**Materials.** *p*-Nitroazobenzene.—This was prepared by

(1) T. W. Campbell, D. A. Young and M. T. Rogers, *THIS JOURNAL*, **73**, 5789 (1951).

(2) M. T. Rogers, T. W. Campbell and R. W. Maatman, *ibid.*, **73**, 5122 (1951).

(3) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

(4) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, 2807 (1951).

the condensation of *p*-nitroaniline with nitrosobenzene<sup>5,6</sup> in concentrated alcoholic solution containing a drop of acetic acid. The product was recrystallized several times from alcohol, m.p. 134°.

*p,p'*-Dinitroazobenzene.—This was prepared by the method of Antener<sup>7</sup> and recrystallized several times from alcohol, m.p. 223–224°.

*p,p'*-Tetramethyldiaminoazobenzene.—Methods described in the literature<sup>8</sup> proved unfruitful for the preparation of this compound. It was prepared by treating *p*-nitrodimethylaniline with an ether solution of lithium aluminum hydride; the product was extracted with hydrochloric acid and recovered by neutralizing with ammonia. The crude material was extracted with dioxane and reprecipitated with water; copper colored needles from alcohol, m.p. 260–261°.

*p*-Benzalaminoazobenzene and *p*-(*p*-Tolualamino)-azobenzene.—These were prepared from *p*-aminoazobenzene and the appropriate aromatic aldehyde,<sup>9,10</sup> m.p. 128 and 117°, respectively.

*p*-(*p*-Dimethylaminobenzalamino)-azobenzene.—Concentrated alcoholic solutions of *p*-aminoazobenzene and *p*-dimethylaminobenzaldehyde, plus a drop of acetic acid, were mixed. The product was recrystallized from alcohol, m.p. 176°.

Tetramethyl-*p*-phenylenediamine and *p*-Aminoazobenzene.—Eastman Kodak Co. materials were purified by several recrystallizations, m.p.s. are 49 and 124°, respectively.

**Apparatus and Method.**—The electric moments were determined in benzene solution at 25° by use of apparatus and technique described previously.<sup>1</sup> Measurements of dielectric constant and density were made, in each case, on six solutions ranging in mole fraction of solute from 0.0001 to 0.002. The molar polarizations and dipole moments were calculated from observed dielectric constants and densities by the method of Halverstadt and Kumler.<sup>11</sup> The empirical constants  $\alpha^1$ ,  $\beta^1$ ,  $\epsilon_{10}$  and  $V_{10}$  of their equation, are shown in Table I along with the calculated molar polarizations, molecular refractions and dipole moments. The molar refractions were calculated from empirical constants using the value 62.0 cc. for azobenzene. The probable error in molar polarization is estimated to be about  $\pm 0.03 P$  and the probable error in dipole moments about  $\pm 0.10 D$ .

### Discussion

The electric moments of *p*-nitroazobenzene (4.45) and *p*-aminoazobenzene (2.48) are larger than the corresponding values<sup>3</sup> for nitrobenzene (3.95) and aniline (1.58), showing that azobenzene is a much better electron acceptor, and a somewhat better

(5) E. Bamberger and R. Hubner, *Ber.*, **36**, 3811 (1903).

(6) A. Pongratz, G. Markgraf and E. Mayer-Pitsch, *ibid.*, **71B**, 1287 (1938).

(7) I. Antener, *Helv. Chim. Acta*, **21**, 812 (1938).

(8) E. Lippman and R. Lange, *Ber.*, **13**, 2137 (1880); O. Fischer and L. Wacker, *ibid.*, **21**, 2612 (1888); E. Nolting, *ibid.*, **18**, 1144 (1885); E. Nolting and E. Fournieux, *ibid.*, **30**, 2946 (1897); A. Quilico and M. Freri, *Gazz. chim. ital.*, **59**, 273 (1929).

(9) G. Berju, *Ber.*, **17**, 1403 (1884).

(10) F. Pope and W. Willett, *J. Chem. Soc.*, **103**, 1259 (1913).

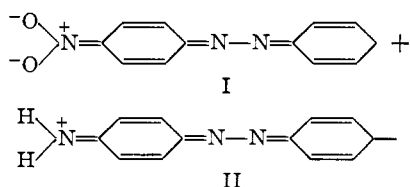
(11) I. F. Halverstadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

TABLE I  
DIELECTRIC CONSTANTS,<sup>a</sup> DENSITIES, MOLECULAR REFRACTIONS<sup>b</sup> AND DIPOLE MOMENTS IN BENZENE AT 25°

$\epsilon_{10}$	$\alpha^1$	$V_{10}$	$\beta^1$	$P_2$	$MR_D$	$\mu$
Tetramethyl- <i>p</i> -phenylenediamine						
2.2742	2.477	1.14494	-0.2406	86.8	52.57	1.29
<i>p</i> -Aminoazobenzene						
2.2735	9.65	1.14487	-0.755	191.5	65.42	2.48
<i>p</i> -Nitroazobenzene						
2.2721	28.35	1.14515	-0.952	472.4	67.54	4.45
<i>p-p'</i> -Tetramethyldiaminoazobenzene						
2.2746	6.48	1.14492	-0.9583	167.12	88.36	1.95
<i>p-p'</i> -Dinitroazobenzene						
2.2755	1.467	1.14491	-1.486	79.9	73.03	(0) <sup>b</sup>
<i>p</i> -Benzalaminoazobenzene						
2.2729	7.217	1.14484	-0.913	182.1	97.8	2.03
<i>p</i> -( <i>p</i> -Dimethylaminobenzalamino)-azobenzene						
2.2736	30.19	1.14497	-1.320	527.5	110.93	4.51
<i>p</i> -( <i>p</i> -Tolualamino)-azobenzene						
2.2725	9.74	1.14498	-1.111	208.9	102.42	2.47

<sup>a</sup> The observed dielectric constants,  $\epsilon_{12}$ , and specific volumes,  $V_{12}$ , of the solutions were plotted graphically against mole fraction of solute. The points fall, within experimental error, on straight lines with slopes  $\alpha^1$  and  $\beta^1$ , respectively, and the intercepts at zero mole fraction are  $\epsilon_{10}$  and  $V_{10}$ , respectively. The molar polarizations at infinite dilution,  $P_2$ , and dipole moments,  $\mu$ , expressed in debye units, were calculated from these constants.<sup>1</sup> <sup>b</sup> See Discussion.

electron donor, than benzene. This would be expected since the charge can be distributed over both ring systems in azobenzene and the contribution of several structures such as I and II, in each case,



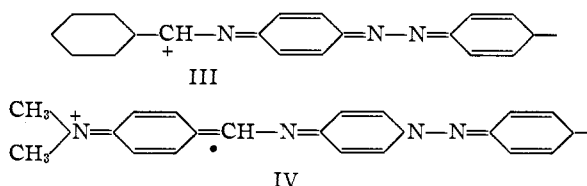
should give rise to a larger moment than the corresponding benzene derivative.

The small difference, 6.9 cc., between the observed molar polarization and the calculated molar refraction of *p,p*-dinitroazobenzene is quite close to the usual estimate for the atomic polarization of large molecules (about 10% of  $MR_D$ , or 7.3 cc. in this case). The orientation polarization and dipole moment of this molecule are therefore taken to be zero, and the molecule has the *trans* configuration. It is highly probable that the other azobenzene derivatives all have *trans* configurations, and this assumption is made in the calculations.

The moment of *p,p'*-tetramethyldiaminoazobenzene (1.95) may be combined with that of dimethyl-

aminoazobenzene<sup>1</sup> (3.22) to obtain the magnitude ( $m = 3.56D$ ) and direction ( $\theta = 22^\circ 45'$ ) of the dimethylamino group moment in azobenzene derivatives. The dimethylamino group moment ( $m = 1.92D$ ) and direction ( $\theta = 28^\circ 20'$ ) in the benzene series were similarly derived from the electric moments of tetramethyl-*p*-phenylenediamine (1.29) and dimethylaniline<sup>3</sup> (1.58). These group moments and directions should be comparable and are derived from pairs of compounds selected to eliminate errors due to enhancement of resonance which might arise in molecules containing different substituents. The azobenzene molecule is a much better electron acceptor than benzene but the direction of the group moment is not greatly different; in neither case is the group moment directed along the bond between nitrogen and the ring ( $\theta = 0^\circ$  when the negative end of the dipole is directed toward the ring), as would be expected if resonance made the group coplanar with the molecule.

The electric moments of benzalaniline (1.55), *p*-dimethylaminobenzalaniline (3.60), and other derivatives of benzalaniline have been studied.<sup>12-14</sup> Our results show that *p*-benzalaminoazobenzene has a larger moment (2.03) than benzalaniline itself (1.55), and *p*-(*p*-tolualamino)-azobenzene has a larger moment, 2.43, than calculated for *p*-tolualaniline (about 1.90); thus the phenylazo group acts as an electron acceptor in these molecules. The increase in electric moment may be attributed to a small contribution to the ground state of the molecule from highly polar structures such as III. The moment observed for



*p*-(*p*-dimethylaminobenzalamino)-azobenzene, (4.51), is 0.9  $D$  larger than that of *p*-dimethylaminobenzalaniline showing that the phenylazo group increases the already large ability of benzalaniline to act as an electron acceptor; resonance with structures, such as IV, in which there is a very large charge separation, would account for the large increment observed above. The negative charge can be distributed over both rings in structures III and IV and the combined contributions of all such structures is evidently appreciable.

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