passed in for 90 minutes until the solid had liquefied and no further change in color occurred. A small amount of hydrogen chloride was liberated during this period. On distilling the liquid product (60 g.) much hydrogen chloride was liberated and 30 g. of product boiling 75–87° (17 mm.) was obtained. On redistillation, 7 g. of product was obtained boiling 82–84° (15 mm.) and having n^{20}_D 1.5410, d^{20}_4 1.190. The molar refractivity and chlorine content of this fraction corresponded to methyl 2-chlorovinyl sulfide, $CH_3SCH{=}CHCl$. The yield of purified product, based on methyl disulfide, was only 10%.

Anal. Calcd. for C_3H_5SCl: Cl, 32.65; *MR*D, 28.2.[6] Found: Cl, 32.91; *MR*D, 28.4.

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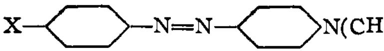
[6] Atomic and group refractivities are taken from Vogel, *J. Chem. Soc.*, 1833 (1948).

ORONO, MAINE RECEIVED JUNE 15, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Azo Dyes

BY TOD W. CAMPBELL, D. A. YOUNG AND MAX T. ROGERS

The electric dipole moments of a series of azo dyes  (with X = H, CH_3, t-C_4H_9, $-OCH_3$, Cl, I, $-SCN$, $-SeCN$, NO_2) have been measured in benzene solution at 25°. The observed moments have been compared with values calculated from bond moments; it is found that when the group X is a strong electron acceptor ($-NO_2$, $-SCN$ or $-SeCN$) or a halogen (Cl, I) the observed moment is larger than the expected value. The results have been interpreted in terms of resonance theory.

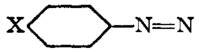
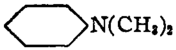
The electric moments of azobenzene and a number of para-substituted derivatives have been reported.[1-3] The moment of azobenzene is zero[4] and the moments of para-substituted compounds are close to those of the corresponding benzene derivatives (within experimental error in most cases); hence, it has been concluded that these compounds as ordinarily prepared have the *trans* configuration.

The observed[2] dipole moments of *p*-aminoazobenzene (2.71) and *p*-dimethylaminoazobenzene (3.68) are exceptions since they are much larger than aniline (1.53) and dimethylaniline (1.58). The value reported[3] for *p*-nitro-*p'*-dimethylaminoazobenzene (8.1) is larger than the sum of the moments of *p*-dimethylaminoazobenzene and nitrobenzene indicating an enhancement of resonance similar to that observed[5] with *p*-nitrodimethylaniline and, to a lesser extent, with other para-substituted dimethylanilines measured.

Enhancement of resonance[6] has so far only been demonstrated with a few aromatic nitro compounds but might be expected to be more general, especially when an electron-donating and an electron-receiving group are para to one another in a conjugated system. Such an effect should be magnified in *p,p'*-disubstituted azobenzenes, since the expected charge separation would be through nearly three times the distance in corresponding disubstituted benzenes. We have, therefore, measured the dipole moments of *p*-dimethylaminoazobenzene and eight *p'*-substituted derivatives of it in order to obtain information concerning the effects of substituents on resonance in azo dyes.

Experimental Part

Materials. Benzene.—Baker C.P. benzene was purified by freezing out about three-fourths of the liquid and collecting the crystals. This is repeated and the product of the second purification is distilled and dried over sodium: d^{25}_4 0.87355, n^{25}_D 1.4980.

Azo Dyes.—The dyes of the type   employed were made by conventional methods from a sodium acetate-buffered solution of the appropriate diazonium salt and an acetic acid solution of dimethylaniline. The crude product was recrystallized several times from *n*-propanol (boiling toluene when X was the nitro group). The following uncorrected melting points, in general slightly higher than those recorded in the literature, were observed: X = H,[7] m.p. 117.5–118°; $-CH_3$,[7] m.p. 171°; $-C(CH_3)_3$,[8] m.p. 142°; $-Cl$,[9] m.p. 159°; $-I$,[10] m.p. 163.5–164°; $-OCH_3$,[7] m.p. 163.5–164°; $-NO_2$,[7] m.p. 229–230°; $-SCN$, m.p. 154°; $-SeCN$, m.p. 180°.

Apparatus and Method.—The electric moments were determined in benzene at 25° by the dilute solution method. Dielectric constants were measured using a heterodyne-beat apparatus similar to that described by Chien.[11] Densities were determined with a modified Ostwald pycnometer.

The experimental data and molar polarizations are shown in Table I, and the derived values of P_2^∞ (the molar polarization of the solute at infinite dilution), *MR*D (calculated value of molar refraction), and μ (the dipole moment) for each compound are shown in Table II. The molar polarizations were obtained using the method of calculation suggested by Halverstadt and Kumler,[12] as well as by the conventional method.[13]

Table II also includes predicted values of the moments of the dyes calculated from the group moments and angles.[13] The group moments used, except for $-N(CH_3)_2$, are those derived from benzene derivatives[6b]; the $-N(CH_3)_2$ group moment and angle are derived from the measured dipole moments of dimethylaminoazobenzene and *p,p'*-didimethyl-

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[1] E. Bergmann, L. Engel and S. Sandor, *Ber.*, **63**, 2572 (1930).

[2] E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936).

[3] A. Weizmann, *ibid.*, **36**, 978 (1940).

[4] G. S. Hartley and R. J. W. LeFevre, *J. Chem. Soc.*, 531 (1939); the relatively unstable *cis* modification has a dipole moment of 3.0. It has been shown that the *cis* forms of some of these azo compounds are formed under certain conditions.

[5] R. J. W. LeFevre and J. W. Smith, *J. Chem. Soc.*, 2239 (1932).

[6] (a) For a discussion, see Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944; (b) T. W. Campbell and M. T. Rogers, THIS JOURNAL, **70**, 1029 (1948).

[7] *Cf.* Beilstein's "Handbuch," **16**, 321, *et seq.*

[8] *Anal.* carbon found 76.71, theory 76.83; hydrogen found 8.35, theory 8.24.

[9] *Anal.* carbon found 64.57, theory 64.74; hydrogen found 5.51, theory 5.43.

[10] *Anal.* carbon found 47.74, theory 47.88; hydrogen found 4.13, theory 4.02.

[11] J. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

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

[13] See, for example, C. P. Smyth, in Weissberger, "Physical Methods of Organic Chemistry," Volume I, Part II, Second edition, Chapter XXIV, Interscience Publishers, Inc., New York, N. Y., 1949.

Table I

Dielectric Constants, Densities, Refractive Indices and Molar Polarizations in Benzene Solutions at 25°

f_2	E	d^{25}_4	P_2
p-Dimethylaminoazobenzene			
0.000639	2.2815	0.87371	277.3
.001030	2.2884	.87391	293.3
.001147	2.2903	.87403	292.5
.001474	2.2953	.87404	294.0
p-Methoxy-*p*′-dimethylaminoazobenzene			
0.000428	2.2778	0.87392	244.8
.000727	2.2819	.87145	252.9
.000894	2.2832	.8723	240.6
.001199	2.2869	.87446	240.9
.001572	2.2912	.8774	239.0
p-*t*-Butyl-*p*′-dimethylaminoazobenzene			
0.000421	2.2772	0.87385	240.4
.000756	2.2810	.87390	241.0
.000936	2.2826	.87414	236.3
.001224	2.2855	.87414	233.5
.001343	2.2874	.87435	240.8
p-Methyl-*p*′-dimethylaminoazobenzene			
0.000597	2.2789	0.87389	223.2
.000740	2.2802	.87396	218.8
.001248	2.2873	.87426	238.9
.001341	2.2866	.87428	220.0
.001739	2.2932	.87452	239.6
.002300	2.2984	.87487	229.5
p-Chloro-*p*′-dimethylaminoazobenzene			
0.000436	2.2874	0.87392	565.6
.000552	2.2923	.87401	590.0
.000882	2.3035	.87430	576.8
.001356	2.3198	.87470	571.4
.001820	2.3348	.87503	561.3
p-Iodo-*p*′-dimethylaminoazobenzene			
0.000251	2.2808	0.87404	549.8
.000489	2.2888	.87446	553.5
.000748	2.2975	.87488	555.2
.001023	2.3064	.87537	550.0
.001257	2.3140	.87580	547.0
p-Selenocyano-*p*′-dimethylaminoazobenzene			
0.000290	2.2917	0.87409	1029
.000505	2.3063	.87430	1045
.000757	2.3222	.87465	1024
.001011	2.3390	.87499	1023
.001383	2.3629	.87554	1022
p-Thiocyano-*p*′-dimethylaminoazobenzene			
0.000438	2.2999	0.87382	981.2
.000639	2.3152	.87403	1040
.000760	2.3207	.87373	1006
p-Nitro-*p*′-dimethylaminoazobenzene			
0.000296	2.3010	0.87385	1453
.000334	2.3037	.87378	1421
.000389	2.3089	.87389	1433
.000436	2.3136	.87353	1456
.000872	2.3545	.87423	1457

aminoazobenzene.[14] All the azo derivatives are considered to be *trans*. The final column of Table II lists the differences between the observed moments and the values predicted by the above calculation.

Table II

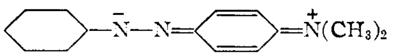
Molar Refractions, Molar Polarizations and Dipole Moments (Observed and Calculated) of *p*-Substituted-*p*′-Dimethylaminoazobenzenes

(1) Probable error in P_2^∞ is estimated to be about ±0.03 P and probable error in μ is therefore about ±0.10 D. (2) Molecular refractions are calculated from the observed value for azobenzene (62.0 cc./mole) along with the additive group constants.

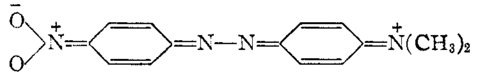
p-Substituent	MR_D[2] Calcd.	P_2^∞	μ Obsd.	μ Calcd.	Δ
–H	79.0	291	3.22D	..	....
$-OCH_3$	85.7	243	2.77	3.15	−0.38
$-C(CH_3)_3$	98.5	239	2.62	2.55	+ .07
$-CH_3$	84.0	239	2.75	2.89	− .14
–Cl	84.3	574	4.89	4.68	+ .21
–I	92.6	557	4.76	4.40	+ .36
–SeCN	96.9	1038	6.78	6.54	+ .24
–SCN	93.8	1000	6.65	5.98	+ .67
$-NO_2$	84.9	1447	8.16	7.01	+1.15

Discussion of Results

The dipole moment of *p*-dimethylaminoazobenzene (3.22) found here is somewhat lower than that reported previously,[2] but is nearly double that of dimethylaniline (1.58); this indicates that structures of type I contribute to the ground state of the



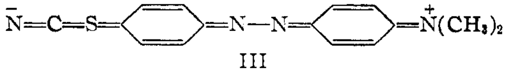
I



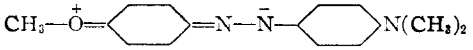
II

molecule in addition to those which are of importance in dimethylaniline[6a] and supports the observation that the phenylazo group is a good electron acceptor.[15] The value (8.16) found for the moment of *p*-nitro-*p*′-dimethylaminoazobenzene is in excellent agreement with that reported by Weizmann[2] and is 1.15 D larger than the calculated value, presumably as a result of the additional resonance with highly polar structures of type II in the disubstituted compound ("enhancement of resonance").

When the *p*-substituent is a strong electron acceptor such as –SCN or –SeCN enhancement of resonance is again observed, probably as a result of a small contribution to the ground state of the molecule from structures of type III possible only in the disubstituted derivative. The enhancement is larger (+0.67) in the *p*-SCN derivative than in the *p*SeCN derivative (+0.24) reflecting the small tendency of selenium to form multiple bonds.



III



IV

When the *p*-substituent is an electron-donor group such as CH_3–, *t*-$C(CH_3)_3$–, or $-OCH_3$ the moment is equal to (within experimental error),

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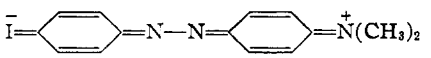
[14] M. T. Rogers, W. McAllister and T. W. Campbell, unpublished results.

[15] See, for example, L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

or slightly lower than, the value predicted. The large decrement (−0.38) observed in the *p*-OCH$_3$ compound may be the result of the contribution of structures of type IV which would in effect raise the -OCH$_3$ group moment above that derived from substituted anisoles; in agreement with this the moment of *p*-methoxyazobenzene (1.48) is larger than that of anisole (1.23).

Both *p*-chloro and *p*-iodo-*p*′-dimethylaminoazobenzene show a slight enhancement of resonance, increments of +0.21 and +0.39, respectively, being observed. Since a decrease might be anticipated due to the contribution, in the azobenzene series, of structures of type IV not possible in the halobenzenes, the observed increments may be significant. It is possible that by expanding their octets the halogens can act as electron-receiving groups; in the presence of a good electron-donating group resonance forms of type V may then be important enough to give rise to the observed increments.[16] A similar increment has been observed with the *p*-halogen substituted dimethylanilines[17] and is, as above, largest with the iodo compound



V

as would be expected since iodine has the greatest tendency to expand its octet.

[16] "Iodine-bond resonance" was suggested first by Pauling to account for interatomic distances in *p*-diiodobenzene; see H. P. Klug, *J. Chem. Phys.*, **3**, 747 (1935).

[17] R. J. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

EAST LANSING, MICHIGAN RECEIVED JUNE 28, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Catalytic Activity of Metals Produced by the Reduction of Salts in Liquid Ammonia. II. Nickel[1]

BY GEORGE W. WATT, WILBUR F. ROPER[2] AND SIDNEY G. PARKER[2]

Studies on the preparation and properties of nickel hydrogenation catalysts formed by the reduction of nickel(II) bromide with potassium in liquid ammonia show that the ammonia-insoluble reduction products include (in addition to elemental nickel and nickel amide) a potassium-containing substance that reacts with ethanol (the hydrogenation reaction medium) and with allyl alcohol (one of the hydrogen acceptors employed) and influences both the rate and mechanism of the hydrogenation of the latter.

It was reported earlier[3] that nickel from the reduction of nickel(II) bromide with potassium in liquid ammonia exhibits appreciable activity as a catalyst for the hydrogenation of allyl alcohol. More detailed studies are described in the present paper. Catalysts prepared in liquid ammonia, W-6 Raney nickel, and nickel from the reduction of nickel(II) oxide with hydrogen are compared in terms of surface areas, adsorbed hydrogen and hydrogenation rate measurements.

Experimental

Materials.—Nickel(II) bromide 6-ammonate was prepared as described by Watt.[4] Allyl alcohol was generously supplied by the Shell Chemical Corporation. Physical constants found (literature[5] values in parentheses): b.p. 96.7–96.9° cor. (96.90–96.98°); n^{25}D 1.4108 (1.4111). Hexene-1 (research grade, purity 99.22 ± 0.10%) obtained from the Phillips Petroleum Co. was used without further purification.

Preparation of Nickel Catalysts.—W-6 Raney nickel was prepared as described by Adkins and Billica,[6,7] stored under absolute ethanol at 0°, and at all times protected from the atmosphere.

Nickel was prepared from nickel(II) oxide by reduction with predried hydrogen[8] at known temperatures within the range 265–310°, cooled to room temperature in an atmosphere of dry hydrogen, and thereafter protected from exposure to the atmosphere. The nickel content of these products ranged from 96.0 to 97.5%.

The preparation of nickel catalysts by the reduction of nickel(II) bromide (used in the form of the 6-ammonate) with solutions of potassium in liquid ammonia was carried out using equipment and procedures described elsewhere.[9,10] Variables in addition to those investigated previously[3] were studied in an effort to produce catalysts having a nickel content comparable to those from the reduction of nickel(II) oxide with hydrogen. From runs employing from 1.5 to 3.0 g. of nickel(II) bromide 6-ammonate dissolved and suspended in from 12 to 65 ml. of liquid ammonia, and reduction with 2 to 4 gram atoms of potassium/mole of bromide, ammonia-insoluble products having a wide range of composition were obtained, *i.e.*, Ni, 47–90%; N, 2–13% and K, 10–28%. In 10 runs for which complete analytical data are available, analyses for these three elements account for an average of 94% of the gross ammonia-insoluble product. In addition to the range of variables indicated above, frequency of agitation and repetition of addition of potassium were also studied. In the latter experiments, the initial solid reduction products were washed with liquid ammonia, resuspended in ammonia and treated with excess potassium in an unsuccessful effort to reduce the by-product nickel(II) amide to elemental nickel.[11] The product of highest nickel content (90%) was obtained by reducing 2.0 g. of the bromide in 12 ml. of ammonia with 0.75 g. of potassium; the solid product was washed seventeen times with 20-ml. portions of ammonia. All transfers of solid catalyst samples were made in an inert oxygen-free atmosphere in a dry-box.

Surface Area Measurements.—Surface areas were measured by a modification[12] of the method of Brunauer, Emmett and Teller. Values found for nickel prepared in liquid ammonia ranged from 5 m.^{2}/g. for a product containing 67% Ni to 8 m.^{2}/g. for one containing 84% Ni. Simi-

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[1] This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

[2] Field Research Laboratories, Magnolia Petroleum Co., Dallas, Texas.

[3] G. W. Watt and D. D. Davies, THIS JOURNAL, **70**, 3753 (1948).

[4] G. W. Watt, *Inorganic Syntheses*, **3**, 194 (1950).

[5] Shell Chemical Corporation, "Allyl Alcohol," Tech. Publication 46-22, Knight-Counihan Co., San Francisco, p. 42, 1946.

[6] H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 695 (1948).

[7] Data on the composition of W-6 Raney nickel catalysts will be published elsewhere.

[8] V. Ipatieff, *J. prakt. Chem.*, **77**, 513 (1908).

[9] G. W. Watt and T. E. Moore, THIS JOURNAL, **70**, 1197 (1948).

[10] G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

[11] W. M. Burgess and J. W. Eastes, *ibid.*, **63**, 2674 (1941).

[12] H. E. Ries, R. A. Van Nordstrand and W. E. Kreger, *ibid.*, **69**, 35 (1947).