1021. *Dipole Moments and Absorption Spectra of 4-Arylazo-1-naphthylamines.*

By D. A. IBBITSON, P. C. JAMES, and R. A. KNAUST.

Apparent dipole moments in benzene and dioxan, and ultraviolet absorption spectra of a series of 4-(*para*-substituted arylazo)-1-naphthylamines have been determined. The effect of the phenylazo-group is shown by comparing the moments with those of corresponding substituted anilines. The dipole moments determined in dioxan are all greater than those in benzene, indicating hydrogen bonding through the hydrogen atoms of the amino-group and the oxygen atom of the dioxan molecule. Interaction moments (μ_{int}) along the C(ring)–N(amino) axis necessary to explain the observed moments have been evaluated, and show a trend parallel with the frequency of maximum absorption in the Z-band, half-wave potential, light fastness, and the Hammett σ-function for each of the substituents. It is suggested that these trends are all a measure of the effect of the *para*-substituent on the degree of conjugation between the azo-group and the aromatic ring system.

INVESTIGATIONS of the polarographic behaviour [1] of a series of 4-(*para*-substituted arylazo)-1-naphthylamines indicate a linear relation between the half-wave potential, $E_{\frac{1}{2}}$, and the Hammett σ-function [2] for each of the substituents. The substituent groups cause electron displacements at the azo-linkage with resulting changes in the electron affinity of the molecule, the slope of the linear plot indicating that electron-attracting groups favour reduction.

Atherton and Seltzer,[3] and Atherton and Peters,[3] measured the rate of fading of the

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[1] Catchpole and Knaust, *J.*, 1960, 4241.

[2] Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.

arylazo-1-naphthylamines, in terms of a quantity k, the destruction efficiency, a low value of which corresponds to a high light-fastness. These authors claimed that their results were in accord with a reaction mechanism in which the dye molecule, excited by light absorption, was oxidised by the air, the nitrogen atoms of the azo-group acting as electron donors.

Dipole moments and ultraviolet absorptions are now reported, and found to be consistent with polarography and light-fastness data, and with the Hammett substituent constant.

Dipole moments determined in benzene and dioxan, and calculated as described previously,[4] are summarised in Table 1, where α and ν are the limiting values of $d\varepsilon/dw$ and dn^2/dw, respectively, and the other symbols have their usual significance.

TABLE 1.

Polarisation data for solutions of 4-(*para*-substituted arylazo)-1-naphthylamines at 25°.

Subst.	Solv.*	$10^3\alpha$	$10^2\nu$	$P_{2\infty}$ (c.c.)	μ (D)
MeO ...	B	2450	98	75·9	1·93
MeO ...	D	5325	134	175·5	2·93
Me	B	2033	104	47·9	1·53
Me	D	3925	131	106·9	2·29
H	B	3429	93	115·7	2·38
H	D	5775	120	181·3	2·97
Cl	B	6367	122	271·9	3·65
Cl	D	10,550	143	416·2	4·51
Br	B	6033	114	299·3	3·83
Br	D	8975	111	416·9	4·52
MeO_2C	B	5700	104	266·4	3·61
MeO_2C	D	10,400	132	449·5	4·69
Ac	B	11,750	101	583·4	5·34
Ac	D	17,050	163	725·9	5·96

* B = Benzene; D = dioxan.

In agreement with other workers,[5] it is found that, since these amino-compounds are capable of hydrogen bonding through the hydrogen atoms of the amino-group and the oxygen atom of the dioxan molecule, the dipole moments determined in dioxan are all greater than those in benzene. The greater differences between the apparent moments in dioxan and benzene of the arylazo-1-naphthylamines than those, in parentheses, for the corresponding substituted anilines [5d] may be due to enhancement of the $+M$ effect of the amino-group by the increased length of the conjugated system in the former compounds; H 0·59 (0·24), Me 0·76 (0·18), Cl 0·86 (0·38), Br 0·69 (0·35). Also, in this connection, it is noteworthy that the apparent moments in benzene of the arylazo-1-naphthylamines are all greater than those of the corresponding substituted anilines (Table 2).

Introduction of a *p*-methoxy-group in aniline causes an increase in the apparent moment from 1·53 to 1·80 D, whereas a decrease in moment from 2·38 to 1·93 D occurs when this group is substituted in phenylazo-1-naphthylamine. The same effect is observed with the following compounds: *NN*-dimethylaniline (1·55 D),[6] *p*-methoxy-*NN*-dimethylaniline (1·70 D),[6] 4-amino-*NN*-dimethylazobenzene (3·22 D),[7] 4-amino-4′-methoxy-*NN*-dimethylazobenzene (2·77 D).[7] Campbell, Young, and Rogers [7] suggest that the difference in moment of the last two compounds arises from contributions, to the resonance state of the 4′-methoxy-compound, of structures of the type $\mathrm{Me{\cdot}O^{+}{:}C_6H_4{:}N{\cdot}N^{-}{\cdot}C_6H_4{\cdot}NMe_2}$. A similar explanation is possible for the effect of the methoxy-group when substituted in phenylazo-1-naphthylamine. In addition to the methoxy-group, the methyl group is electron-releasing and on substituting this group in phenylazo-1-naphthylamine a decrease in moment from 2·38 to 1·53 D is observed. The same effect occurs on substituting the methyl group in the 4′-position in 4-amino-*NN*-dimethylazobenzene, the decrease in

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[3] Atherton and Seltzer, *J. Soc. Dyers and Colourists*, 1949, **65**, 629; Atherton and Peters, *ibid.*, 1952, **68**, 64.

[4] Erić, Goode, and Ibbitson, *J.*, 1960, 55.

[5] (*a*) Vassiliev and Syrkin, *Acta Physicochim. U.R.S.S.*, 1941, **14**, 414; (*b*) Few and Smith, *J.*, 1949, 753; 1949, 2663; (*c*) Smith, *J.*, 1950, 3532; 1953, 109; (*d*) Smith and Walshaw, *J.*, 1957, 3217

[6] Hertel and Dumont, *Z. phys. Chem.*, 1935, *B*, **30**, 139.

[7] Campbell, Young, and Rogers, *J. Amer. Chem. Soc.*, 1951, **73**, 5789.

TABLE 2.

Substituent	H	*p*-Cl	*p*-Br	*p*-Me	*p*-MeO$_2$C	*p*-Ac	*p*-MeO
μ (D) (arylazo-1-naphthylamine deriv.)	2·38	3·65	3·83	1·53	3·61	5·34	1·93
μ (D) (aniline deriv.)	1·53 [a]	3·01 [a]	3·01 [a]	1·32 [a]	—	4·48 [b]	1·80 [c]

[a] Ref. 5*d*. [b] Curran and Estok, *J. Amer. Chem. Soc.*, 1950, **72**, 4575. [c] Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1930, **52**, 1356.

TABLE 3.

Subst.	μ_{int}	σ †	$E_{\frac{1}{2}}$ (V) at pH = 5·1	k * (mean values)	$10^{-3}\tilde{\nu}_1$ (cm.$^{-1}$)	$10^{-3}\tilde{\nu}_2$ (cm.$^{-1}$)	Previous values [15] $10^{-3}\tilde{\nu}_2$ (cm.$^{-1}$)
OMe	1·40	−0·268	−0·455	0·25	34·7	23·0	22·99
Me	1·04	−0·170	−0·429	0·13	34·6	22·9	22·73
H	1·44	0·000	−0·410	0·00	34·7	22·7	22·83
Cl	1·49	0·227	−0·389	−0·37	34·5	21·8	21·83
Br	1·52	0·232	−0·381	−0·33	34·4	21·5	
CO$_2$Me	2·05	0·636	−0·366	−0·66	34·1	20·5	
Ac	2·09	0·874	−0·308	−0·38	33·9	20·3	

* k = log of the ratio of the destruction efficiencies of the substituted and unsubstituted compound.

† σ = Hammett's substituent constant.

moment being from 3·22 to 2·75 D. Again, contributions from structures similar to that suggested for the methoxy-substituted compounds may occur, due to hyperconjugation of the methyl group with the azo-linkage.

Apparent dipole moments in benzene and dioxan of aniline,[5b] 1-naphthylamine,[8] 4-aminoazobenzene,[9] and 4-phenylazo-1-naphthylamine are 1·51 (1·75), 1·49, 2·43 (3·04), and 2·38 D (2·97 D), respectively, values in dioxan being given in parentheses. These moments suggest that replacement of a benzene by a naphthalene residue only slightly affects the polarity of the molecule. Therefore, a C(ring)–NH$_2$ group moment in dioxan of 1·75 D and moments of 1·50 D [5d] and 0·37 D for *p*-toluidine and toluene, respectively, were assumed, and the angle which the C(ring)–NH$_2$ group moment in aniline makes with the C(ring)–N(amino) axis was calculated vectorially by Marsden and Sutton's method [10] to be 42° 49′. By assuming also that this angle remains unchanged in 4-phenylazo-1-naphthylamine, additional moments (μ_{int}) along the C(ring)–N(amino) axis, necessary to explain the observed moments in dioxan of the arylazo-1-naphthylamines have been calculated from equation 1:

$$\mu_{\text{obs}}^2 = 1{\cdot}75^2 + (\mu_{\text{int}} + \mu_{\text{PhX}})^2 + 2(1{\cdot}75)(\mu_{\text{int}} + \mu_{\text{PhX}}) \cos 42^\circ\, 49' \qquad (1)$$

The following values have been taken for the moments of the parent monosubstituted benzenes (μ_{PhX}): chlorobenzene 1·58, bromobenzene 1·56, toluene −0·37.

In the case of those arylazo-1-naphthylamines with angular substituents, the angles (α) which the substituent group moments make with a direction parallel to the C(ring)–N(amino) bond have been calculated vectorially from the following dipole moments: anisole [5d] 1·23, *p*-methylanisole [5d] 1·20, toluene 0·37 (α = 76° 40′); acetophenone [11] 2·96, 4-methylacetophenone [11] 3·23, toluene 0·37 (α = 134° 22′); methyl benzoate [8] 1·83, methyl *p*-toluate [8] 2·04, toluene 0·37 D (α = 119° 58′). The values of μ_{int} have been computed from the vector diagram (Fig. 1), free rotation of the two vectors about the direction of the C(ring)–N(amino) axis being assumed. Results are recorded in Table 3.

The absorption spectrum of azobenzene shows an intense band at 31450 cm.$^{-1}$ which has been ascribed to conjugation between the azo-group and the aromatic ring system.[12] *para*-Substituted azobenzenes exhibit a bathochromic shift in the absorption spectra,

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[8] Wesson, " Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

[9] Ibbitson, Jackson, McCarthy, and Stone, *J.*, 1960, 5127.

[10] Marsden and Sutton, *J.*, 1936, 599.

[11] Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957.

[12] Burawoy, *J.*, 1939, 1177.

and Sawicki,[13] from a study of a series of substituted *NN*-dialkylaminoazobenzenes, concluded that conjugation of the *p*′-substituent with the substituted amino-group is important in bringing about this bathochromic shift. This type of band structure involving zwitterionic resonance structures is called the *Z* band.[14] Examination of the absorption spectra of the arylazo-1-naphthylamines, determined within the range 40,000—15,000 cm.$^{-1}$, reveals two pronounced absorption maxima at frequencies $\bar{\nu}_1$ and $\bar{\nu}_2$ (Table 3). We attribute frequencies $\bar{\nu}_2$ to the *Z* band, an absorption maxima for phenylazo-1-naphthylamine at 22,700 cm.$^{-1}$ corresponding to Turner's value [15] of 22,830 cm.$^{-1}$. As in the case of azobenzene derivatives, substitution of electron-acceptor groups in a position of conjugation in the benzene ring decreases the energy of the zwitterionic structures. The energy change involved in the transition from ground to excited state is decreased, and the wavelength maximum of the band system shows the expected bathochromic shift. Although the value for the methoxyl group is anomalous, $\Delta\mu_{\rm int}(\mu_{\rm sub} - \mu_{\rm unsub})$ may be regarded as a measure of the tendency of the *p*′-substituent to withdraw electrons from the azo-group. The greater this tendency, the more readily will reduction occur, and the more difficult it will be for oxidation to occur at the azo-group. Again, the frequency shift $\Delta\bar{\nu}_2$ is greater the more powerful the electron-accepting property of the substituent group. From the results in Table 3, therefore, it appears that, in general, the trends in $\mu_{\rm int}$, $\bar{\nu}_2$, $E_{\frac{1}{2}}$, and k are all a measure of the effect of the *p*′-substituent groups on the degree of conjugation between the azo-group and the aromatic ring system.

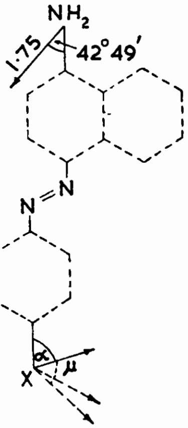

FIG. 1. Calculation of $\mu_{\rm int}$ for 4-*p*-methoxyphenylazo-1-naphthylamine, 4-*p*-acetylphenylazo-1-naphthylamine, and 4-*p*-methoxycarbonylphenylazo-1-naphthylamine.

X = MeO; $\alpha = 76° 40'$; $\mu = 1{\cdot}23$ D.
X = Ac; $\alpha = 134° 22'$; $\mu = 2{\cdot}96$ D.
X = MeO$_2$C; $\alpha = 119° 58'$; $\mu = 1{\cdot}83$ D.

EXPERIMENTAL

Materials.—The 4-arylazo-1-naphthylamines were prepared from the anilines by diazotisation and coupling with 1-naphthylamine, followed by recrystallisation to constant m. p. Dioxan and benzene were repeatedly refluxed with sodium and then fractionally distilled under anhydrous conditions.

Methods and Results.—Absorption spectra were determined on a Unicam S.P. 700 instrument with 10 mm. cells, the concentration of the solutions of the azo-compounds in absolute alcohol being 5×10^{-5}M.

Dielectric constants and refractive indices of solutions of graded concentration of each azo-compound in benzene and dioxan were determined at 25° by the same methods and in the same apparatus as in a previous investigation.[4] Dielectric constants were calculated

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[13] Sawicki, *J. Org. Chem.*, 1957, **22**, 915.
[14] Sawicki, *J. Org. Chem.*, 1956, **21**, 605.
[15] Turner, *J.*, 1949, 2282.

TABLE 4.

4-Phenylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2113	1·4198
0·226	2·2800	1·4988	0·049	2·2138	1·4200
0·451	2·2882	1·4995	0·094	2·2168	1·4202
0·677	2·2957	1·5002	0·290	2·2282	1·4211
0·899	2·3033	1·5009	0·387	2·2336	1·4214

4-*p*-Chlorophenylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2114	1·4198
0·118	2·2797	1·4986	0·047	2·2163	—
0·171	2·2833	1·4988	0·121	—	1·4204
0·227	2·2866	1·4990	0·195	2·2323	1·4208
0·284	2·2907	1·4992	0·291	—	1·4213
0·340	2·2942	1·4995	0·295	2·2427	—
			0·397	2·2530	1·4218

4-*p*-Bromophenylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2098	1·4198
0·111	2·2795	1·4985	0·047	2·2142	1·4200
0·166	2·2829	1·4987	0·095	2·2182	1·4202
0·227	2·2857	1·4990	0·202	2·2278	1·4206
0·284	2·2892	1·4992	0·282	2·2352	1·4209
0·340	2·2930	1·4994	0·401	2·2458	1·4214

4-*p*-Tolylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2135	1·4198
0·115	2·2747	1·4985	0·047	2·2153	1·4200
0·170	2·2760	1·4987	0·098	2·2175	1·4203
0·231	2·2773	1·4989	0·199	2·2214	1·4207
0·282	2·2782	1·4991	0·291	2·2250	1·4211
0·341	2·2793	1·4993	0·388	2·2284	1·4216

4-*p*-Acetylphenylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2117	1·4198
0·114	2·2857	1·4985	0·028	2·2165	1·4200
0·171	2·2927	1·4987	0·050	2·2205	—
0·227	2·2995	1·4989	0·074	—	1·4202
0·283	2·3052	1·4991	0·096	2·2282	—
			0·121	—	1·4205
			0·193	2·2444	—
			0·200	2·2462	1·4210

4-*p*-Methoxycarbonylphenylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2117	1·4198
0·110	2·2791	1·4985	0·098	2·2217	1·4202
0·169	2·2823	1·4987	0·192	2·2313	1·4207
0·226	2·2850	1·4989	0·295	2·2423	1·4212
0·282	2·2882	—	0·386	2·2520	1·4216
0·339	2·2920	1·4993	0·482	2·2619	1·4220

4-*p*-Methoxyphenylazo-1-naphthylamine

in benzene			in dioxan		
$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
0·000	2·2725	1·4981	0·000	2·2135	1·4198
0·104	2·2750	—	0·187	2·2235	1·4207
0·368	2·2814	1·4993	0·256	2·2270	—
0·553	2·2859	1·4999	0·376	2·2333	1·4216
0·785	2·2916	1·5007	0·462	2·2382	—
1·026	2·2975	—	0·553	2·2428	1·4224
			0·756	—	1·4233

relative to the value of 2·2725 at 25° for pure benzene. The results are recorded in Table 4, where the symbols have their usual significance.

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DERBY AND DISTRICT COLLEGE OF TECHNOLOGY.

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