976. *Ultraviolet Absorption of Some Substituted Azobenzene and Symmetric 1,1′- and 2,2′-Azonaphthalene Derivatives*

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5,5′-Dinitro-, 6,6′-dinitro, 8,8′-dinitro, and 3,3′-dibromo-2,2′-azonaphthalenes, and 2,2′-dibromo-1,1′-azonaphthalene have been prepared from the corresponding bromo- and nitro-naphthylamines. Shifts of the region-II band in the ultraviolet spectra of substituted azonaphthalenes and azobenzenes are related to the positions of substitution.

Nitration of 2,2′-azonaphthalene gives 1,1′-dinitro-2,2′-azonaphthalene and other derivatives. Bromination and nitration of 1,1′-azonaphthalene gives the 4,4′-dibromo- and 4,4′-dinitro-derivatives.

THE region-II band[1] (*K*-band[2] or α-band[3]) in the spectrum of naphthalene at 312 mμ is due to ${}^1L_b \longleftarrow {}^1A$ transition and is longitudinally polarised.[4] The region-II band in the spectra of azo-compounds has been ascribed to conjugation between the aromatic nucleus and the azo-group.[1] Grammaticakis[5] demonstrated that *ortho*- and *para*-substituents in azobenzene produce bathochromic spectral shifts and *meta*-substituents very small bathochromic or hypsochromic shifts. The magnitude of the shifts were in the order $p > o > m$ for nitro-, carboxy-, methoxy-, methyl, and amino-substituents.

Badger and Buttery,[1] studying azo- and azoxy-naphthalenes, found that steric factors preventing coplanarity of the rings, and thus reducing conjugation between the rings as in 1,1′-azoxynaphthalene and 2,2′-dimethylazoxybenzene, caused hypsochromic shifts of the II band.

A number of substituted azobenzenes and azonaphthalenes have been examimed to attempt a correlation between their ultraviolet absorption spectra and the position of substitution. Table 1 gives values of the II band of the eleven known mono- and di-substituted azobenzenes with nitro- or bromo-groups as the only substituent. The position of the band is little affected by change in solvent from ethanol to chloroform. In the five cases where corresponding mono- and di-substituted azobenzenes were available, the shifts in the II band were not additive; additivity has been shown in a series of bromobenzo[*c*]-cinnolines.[6]

TABLE 1

Values of $\lambda_{max.}$ (mμ) of region-II band for substituted azobenzene

Solvent	Ethanol		Chloroform	
Substituent	$\lambda_{max.}$	$\delta\lambda$	$\lambda_{max.}$	$\delta\lambda$
None	318 *		319	
2-NO_2	318 †	0		
2,2′-$(NO_2)_2$	321	3	323	4
2-Br	325·5	7·5	326	7
3-NO_2	315 †	−3		
3,3′-$(NO_2)_2$	309·5	−8·5	311	−8
3-Br	321	3	323	4
3,3′-Br_2	320 *	2		
4-NO_2	333 †	15		
4,4′-$(NO_2)_2$	332	14	335	16
4-Br	328 *	10		
4,4′-Br_2	326 *	8		

* Values from Gore and Wheeler, *J. Org. Chem.*, 1961, **26**, 3295. † Grammaticakis, ref. 5.

In 4-bromoazobenzene the substituent is conjugated with the system; Brode, Seldin, Spoerri, and Wyman,[7] for example, used the resonance form (I) to explain the effect of hydration of the azo-group on the ultraviolet spectra of some 4-substituted azobenzenes. Conforming with this structure there is a bathochromic shift of 10 mμ in the II band.

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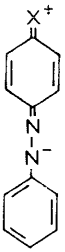
[1] G. M. Badger and R. G. Buttery, *J.*, 1953, 2156.
[2] A. Burawoy, *J.*, 1937, 1865.
[3] E. Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952.
[4] J. R. Platt, *J. Chem. Phys.*, 1949, **18**, 1168.
[5] P. Grammaticakis, *Compt. rend.*, 1957, **245**, 1145.
[6] J. F. Corbett, P. F. Holt, A. N. Hughes, and M. L Vickery, *J* , 1962, 1812.
[7] W R Brode, I. L. Seldin, P. E. Spoerri, and G. M. Wyman, *J. Amer. Chem. Soc.*, 1955, **77**, 2762.

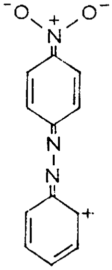
However, a second bromine atom in the 4-position of the other ring cannot be simultaneously conjugated in the same way and it does not shift the band further.

The nitro-group of 4-nitroazobenzene is conjugated through the ring with the azo-group, *e.g.*, structure (II), and a large bathochromic shift is observed. Introduction of a second nitro-group in the 4′-position of the other ring gives no further shift.

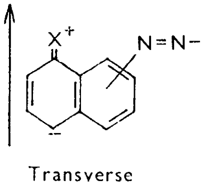
Only 2-nitro-, 2,2′-dinitro-, and 2-bromo-azobenzene had substituents in the 2-position. Nitro- and bromo-groups in the 2-position conjugate with the system but molecular models show that there is a slight restriction on the rotation of the aromatic rings in the 2,2′-dinitro-compound although not in the 2-bromo compound. A bathochromic shift of 7 mμ is observed in the II band of 2-bromoazobenzene but of only 4 mμ in that of the di-nitro-compound, while the 2-nitro-derivative gave no shift.



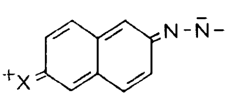
(I)



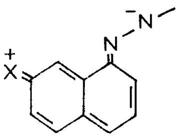
(II)



(III)



(IV)



(V)

Nitro- and bromo-groups in the 3-positions cannot take part in structures of the type (III). Hypsochromic shifts in the II band are characteristic of the spectra of 3-nitro- and 3,3′-dinitro-azobenzene, and the spectra of 3-bromo- and 3,3′-dibromo-azobenzenes show negligible shifts.

Fifteen bromo- and nitro-derivatives of 1,1′- and 2,2′-azonaphthalenes were prepared and the positions of the region-II bands were determined (Tables 2 and 3). The effects of bromo- and nitro-substituents in the inner rings of the azonaphthalenes are in the same directions as in azobenzene, except in the case of 2,2′-dibromo-1,1′-azonaphthalene where there is steric hindrance to coplanarity. As with 2,2′-dimethylazoxybenzene, the II band then suffers a large (—47 mμ) hypsochromic shift, and among these derivatives of 1,1′-azo-naphthalene it is the only case where substitution results in a decrease in the intensity of the II band. Structures similar to (I) and (II) can be drawn for 1,1′-azonaphthalene

TABLE 2

Values of $\lambda_{max.}$ (mμ) in region II of some 2,2′-azonaphthalenes in chloroform

Substituent	Region II	δλ	Substituent	Region II	δλ
None	342	0	6,6′-Br_2	355	+13
1,1′-Br_2	350	+8	1,1′-$(NO_2)_2$	353	+11
3,3′-Br_2	367	+25	5,5′-$(NO_2)_2$	333	−9
4,4′-Br_2	336	−6	6,6′-$(NO_2)_2$	354	+12
5,5′-Br_2	338	−4	8,8′-$(NO_2)_2$	322	−20

TABLE 3

Values of $\lambda_{max.}$ (mμ) and ε(× 10^{-4}) for some 1,1′-azonaphthalene derivatives in chloroform

Substituent	Region I	δλ	Region II	δλ
None	271 (1·7)	0	403 (1·2)	0
2,2′-$(NO_2)_2$	273 (2·0)	2	418 (1·3)	15
4,4′-$(NO_2)_2$	276 (1·6)	5	430·5 (1·1)	27·5
5,5′-$(NO_2)_2$	255 (1·7)	−16	398 (1·0)	−5
7,7′-$(NO_2)_2$	307 (2·0)	36	410 (1·8)	7
2,2′-Br_2	279 (1·5)	8	356 (0·7)	−47
4,4′-Br_2	274 (2·1)	3	415 (1·8)	12
5,5′-Br_2	274 (1·8)	3	405 (1·3)	2

with substituents in the 2- and 4- but not the 3-position and for 2,2′-azonaphthalene with substituents in the 1- and 3- but not the 4-position.

Bromo- and nitro-groups in 5,5′-disubstituted 1,1′-azonaphthalenes and in 8,8′-dinitro-2,2′-azonaphthalenes might be regarded as extending the conjugation and on that basis would be expected to produce bathochromic shifts. The shifts, however, are negligible or hypsochromic.

The effects of substituents in the outer rings can be predicted if these rings are considered to be substituents of the aromatic rings of azobenzene. Clar[3] has used this concept to explain the properties of naphthalene and other polycyclic aromatic systems. The polarisation of the outer rings then affects the polarisation of the II band. With substituents in the 5- and 8-positions of 1,1′- and 2,2′-azonaphthalene there is transverse polarisation, *e.g.*, structure (III). Substituents in the 6- and 7-positions produce longitudinal polarisation, *e.g.*, structures (IV) and (V). All the compounds with substituents in the 5- and 8-positions exhibit a negligible bathochromic or a hypsochromic shift in their II band (between +2 and −20 mμ) and those with substituents in the 5- and 7-positions give bathochromic shifts (between +7 and +13 mμ).

Nitration of 1,1′- *and* 2,2′-*Azonaphthalene.*—Both 1,1′- and 2,2′-azonaphthalene were nitrated in concentrated nitric acid to give dinitro-derivatives. 1,1′-Azonaphthalene gave 4,4′-dinitro-1,1′-azonaphthalene and 2,2′-azonaphthalene yielded mainly 1,1′-dinitro-2,2′-azonaphthalene and other products.

Bromination of 1,1′-*Azonaphthalene.*—1,1′-Azonaphthalene, brominated in chloroform, gave 4,4′-dibromo-1,1′-azonaphthalene exclusively.

EXPERIMENTAL

Symmetric Disubstituted Azonaphthalenes.—The general method of Hodgson, Nicholson, and Turner[8] was applied to the preparation of 3,3′-dibromo-, 5,5′-dinitro-, 6,6′-dinitro- and 8,8′-dinitro-2,2′-azonaphthalene and of 4,4′-dinitro-, 5,5′-dinitro-, 2,2′-dibromo-, 4,4′-dibromo-, and 5,5′-dibromo-1,1′-azonaphthalene. The relevant amine was diazotised and treated with sodium acetate and sodium sulphite under the conditions given.[8] The product was purified by chromatography on alumina, eluting in each case the first band with chloroform.

3-Bromo-2-naphthylamine (0·94 g.) gave 3,3′-*dibromo*-2,2′-*azonaphthalene* (0·7 g.), as orange needles from chloroform, m. p. 266°, purple solution in sulphuric acid going to red then yellow on dilution (Found: C, 53·2; H, 2·55; Br, 36·0; N, 6·5. $C_{20}H_{12}Br_2N_2$ requires C, 54·5; H, 2·7; Br, 36·4; N, 6·3%). 5-Nitro-2-naphthylamine (2 g.) gave 5,5′-*dinitro*-2,2′-*azonaphthalene* (0·5 g.) as yellow needles from acetone–ethanol, m. p. 185°, dark red solution in sulphuric acid (Found: C, 64·0; H, 3·25; N, 12·7. $C_{20}H_{12}N_4O_4$ requires C, 64·5; H, 3·25; N, 15·1%). 6-Nitro-2-naphthylamine (1·9 g.) gave 6,6′-*dinitro*-2,2′-*azonaphthalene* (50 mg.) as orange-yellow plates from chloroform, m. p. 307°, magenta solution in sulphuric acid (Found: C, 62·3; H, 3·6; N, 15·0%). 8-Nitro-2-naphthylamine (1·9 g.) gave 8,8′-*dinitro*-2,2′-*azonaphthalene* (0·1 g.) as orange needles from chloroform, m. p. 287°, deep red solution in sulphuric acid (Found: C, 63·3; H, 3·35; N, 15·1%). 2-Bromo-1-naphthylamine (2·2 g.) gave 2,2′-*dibromo*-1,1′-*azonaphthalene* (0·4 g.) as deep red cubes from chloroform, m. p. 161°, blue solution in sulphuric acid (Found: C, 54·6; H, 2·65; Br, 36·5; N, 6·1%).

The preparation of the other dibromo-2,2′-azonaphthalene derivatives is described by Holt and Smith.[9]

2,2′-Dinitro-1,1′-azonaphthalene and 1,1′-dinitro-2,2′-azonaphthalene were prepared from their respective nitroamines by oxidation with phenyl iodosodiacetate.[10]

Nitration of 1,1′-*Azonaphthalene and* 2,2′-*Azonaphthalene.*—The finely ground azonaphthalene (1 g.) was suspended in concentrated nitric acid for 2 days. The mixture was filtered and the residue dried. The solid obtained was dissolved in chloroform and chromatographed on alumina, eluting with chloroform. The first broad coloured band was collected and the solution was allowed to crystallise. In the one case, 4,4′-dinitro-1,1′-azonaphthalene (1 g.) was isolated as

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[8] H. H. Hodgson, D. E. Nicholson, and H. G. Turner, *J.*, 1944, 15.

[9] P. F. Holt and A. E. Smith, *J.*, 1964, 6095.

[10] G. B. Barlin, K. H. Pausacker, and N. V. Riggs, *J.*, 1954, 3122.

red-brown needles, m.p. 310°, identical (m. p. and mixed m. p., and infrared and ultra violet spectra), with 4,4′-dinitro-1,1′-azonaphthalene prepared by the method of Hodgson *et al.*[8]

From nitrated 2,2′-azonaphthalene a mixture was collected which gave an analysis indicating dinitro-2,2′-azonaphthalene. Recrystallisation from ethanol yielded some 1,1′-dinitro-2,2′-azonaphthalene identical with that obtained from 1-nitro-2-naphthylamine using the method of Barlin, Pausacker, and Riggs.[10] Apparently one or more other dinitro-compounds were present in the mixture.

Bromination of 1,1′-*Azonaphthalene.*—1,1′-Azonaphthalene (2 g.) was dissolved in chloroform (50 ml.) and bromine (0·5 ml.) in chloroform (10 ml.) added slowly. Hydrogen bromide was evolved. The solution was allowed to evaporate to dryness. The residue was dissolved in chloroform and chromatographed on alumina, eluting in chloroform. The first orange band was collected and the solution was allowed to crystallise to give golden-brown needles of 4,4′-dibromo-1,1′-azonaphthalene (2 g.), m. p. 268°, identical (m. p. and infrared and ultraviolet spectra) with a specimen prepared from 4-bromo-1-naphthylamine by the method of Bogoslavskii and Kazokova.[11]

Spectra.—Ultraviolet spectra were determined with an Optica spectrophotometer, model C.F.4.

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[11] B. M. Bogoslavskii and Z. S. Kazokova, *Zhur. obshchei. Khim.*, 1952, **22**, 1183.