while that for benzonitrile as $\lambda_{max}^{C_2H_5OH}$ 225 mμ (ε 12,000)[42] and $\lambda_{max}^{alcohol}$ 225 mμ (ε 12,600).[44] Again the role of the amino group is clear in producing a large (53 mμ) bathochromic shift as well as an appreciable hyperchromic effect.

TABLE VII

NITRILE FREQUENCIES FOR SUBSTITUTED CYANAMIDES

Compound	C≡N (cm.⁻¹) Pure Liquid	CHCl₃ Soln.
Dimethylcyanamide	2200,[a] 2212[b]	2218[c]
Diethylcyanamide	2202,[a] 2210[d]	2209[c]
Diallylcyanamide		2215[c]
p-Aminobenzonitrile	2221[e]	
Benzonitrile	2230[e]	

[a] Private communication from Dr. G. H. Dorion, American Cyanamid Co., Stamford, Conn. [b] M. Davies and W. J. Jones, *Trans. Faraday Soc.*, **54**, 1454 (1958). [c] J. P. Jesson and H. W. Thompson, *Spectrochim. Acta*, **13**, 217 (1958). [d] Ref. 39. [e] Ref. 11.

EXPERIMENTAL[45]

4-Aminospiro[Δ³-cyclohexene-1,9′-fluorene]-3-carbonitrile (I). This compound was prepared as described previously.[1b]

4-Amino-1′-oxo-3′,4′-dihydrospiro[Δ³-cyclohexene-1,2′(1′H)-naphthalene]-3-carbonitrile (II) *and 1′-oxo-3′,4′-dihydrospiro[cyclohexane-1,2′(1′H)-naphthalene]*(XI). The preparation of these compounds will be fully described in a subsequent communication.

3-Cyanospiro[cyclohexane-1,9′-fluoren]-4-one (VII). This compound was prepared by the published procedure.[46] It was found that dilute solutions of VII in chloroform or methanol decomposed within 2–3 days to produce a yellowish brown color with an unmistakable cyanide odor. Refrigeration and/or exclusion of air and moisture retarded this decomposition only for a day longer than before. These decomposition products were not investigated further. $\tilde{\nu}_{max}^{CHCl_3}$: 2252 (unconjd. C≡N), 2198 (conjd. C≡N), 1736 (C=O in six-membered ring with C≡N substitution on α-carbon)[8], and 1639 cm.⁻¹ (conjd. C=C). It appears that this compound is essentially in the enolized form VII for the following reasons: The absorption band at 2198 cm.⁻¹ is much more intense than that at 2252 cm.⁻¹. The appearance of a well-defined band at 1639 cm.⁻¹ indicates a conjugated C=C group while the intensity of the C=O band at 1736 cm.⁻¹ is relatively weak for this group.

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(44) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

(45) All melting points were taken on a Fisher-Johns apparatus with a calibrated thermometer. Infrared spectra were determined on a Perkin-Elmer Model 21 Spectrophotometer. Ultraviolet spectra were determined on a Cary Model 11MS Spectrophotometer in 95% ethanol (distilled) solutions *ca.* 5 × 10⁻⁵*M*.

(46) D. A. Stauffer and O. E. Fancher, U. S. Pat. **2,647,896** (1953); *cf. Chem. Abstr.*, **48**, 9405 (1954) and *J. Org. Chem.*, **25**, 935 (1960).

[JOINT CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BRUNEL COLLEGE OF TECHNOLOGY, LONDON, AND THE UNIVERSITY OF PUERTO RICO AT MAYAGUEZ]

Absorption Spectra of Aromatic Azo and Related Compounds. III. Substituted Azobenzenes[1]

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The ultraviolet and visible spectra of a number of mono- and dihalogeno azobenzenes are reported. The changes in wave length and intensity produced by the substituents are correlated with their electronic and steric effects, and are compared with analogous results previously obtained for azoxybenzenes.

Although the spectra of individual substituted azobenzenes can be found in the literature, there have been few attempts at a systematic study of the effects of substituents on the light absorption of the azobenzene system.[3] In this paper results have been obtained for a series of mono- and dihaloazobenzenes (see Table I) and the spectra are discussed and compared with our previous data on substituted azoxybenzenes.[4] Our measurements were determined in absolute ethanol solutions [in which solvent the photochemical (*trans* → *cis*) isomerization is most suppressed[5a]] after standing overnight in the dark, and there is little doubt that the data refer to solutions containing negligible amounts of the *cis*-isomers.[5b]

The azobenzenes showed three distinct regions of absorption in the ultraviolet and visible parts of the spectrum, with bands at 220–240 mμ, 320–360 mμ, and 430–460 mμ. The first two bands were relatively intense (A_M 10,000–20,000), whereas the visible band was considerably weaker (A_M 400–1000). This low intensity band has been assigned by Burawoy[3a] to a radical transition in the azo

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(1) Part II, *J. Am. Chem. Soc.*, **78**, 3363 (1956).

(2) (a) Brunel College of Technology, London, W. 3; (b) University of Puerto Rico at Mayaguez.

(3)(a) A. Burawoy, *J. Chem. Soc.*, 1865 (1937); (b) A. H. Cook, D. G. Jones, and J. B. Polya, *J. Chem. Soc.*, 1315 (1939).

(4) P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956).

(5)(a) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **75**, 1856 (1953); (b) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **74**, 4641 (1952).

TABLE I

Absorption Spectra of Azobenzenes[a]

	Bands		
Substituent	*E*	*K*	*R*
—	227 (12,600)	320 (17,300)	437 (510)
4 Fluoro	227 (15,400)	321 (19,600)	432 (500)
4-Chloro	228 (12,600)	325 (23,800)	450 (610)
4-Bromo	228 (13,600)	328 (19,800)	440 (780)
4-Iodo	232 (14,100)	331 (25,000)	443 (820)
4-Methyl	230.5 (12,700)	323 (21,000)	440 (590) 442 (590)
4-Methoxy	227 (12,600)	345 (14,400)	430 (1480)
4,4′-Difluoro	227 (13,100)	325 (16,800)	432 (545)
4,4′-Dichloro	235.5 (13,800)	331 (26,600)	Submerged[b]
4,4′-Dibromo	—	326 (24,800)	440 (850)
4,4′-Dimethyl	235 (11,300)	330 (19,300)	435 (840)
4,4′-Dimethoxy	228,244 (6,500)	354 (13,100)	427 (1,500)[c]
3,3′-Difluoro	227 (12,200)	320 (20,300)	435 (520)
3,3′-Dichloro	227 (11,800)	320 (14,100)	435 (450)
3,3′-Dibromo	227 (9,900)	320 (13,300)	435 (340)
3,3′-Diiodo	227 (26,700)	318 (19,400)	415–422 (850)[d] 428 (840)
2,2′-Dichloro	227 (11,800)	320 (14,100)	435 (450)
2,2′-Diiodo	221 (20,700) 250 (10,100)	327.5 (12,400)	482.5 (270)
2,2′-Dimethyl	227 (13,000)[c]	315 (14,100)[c] 330 (16,400)	442 (590)
2,2′-Dimethoxy	227,237 (8,500)	315 (8,500) 366 (11,900)	Submerged[e]
2,4,6,2′,4′,6′-Hexabromo	272 (11,600)	302 (11,900)	474 (1,020)

[a] Spectra determined in absolute ethanol. Wave lengths (λ) in mμ; molar extinction coefficients (ϵ) in parenthesis. [b] 440 mμ = 1,020. [c] Inflection. [d] Five structure. [e] 400 mμ = 2500.

linkage (an R-band), since similar maxima are found in aliphatic compounds. Thus, azomethane ($CH_3N{=}NCH_3$) had λ_{max} 347 mμ($A_m < 10$),[6] and *N*-methylazobenzene ($C_6H_5{=}NCH_3$) had λ_{max} 403.5 mμ(A_m 87) [as well as λ_{max} 259.5 mμ(A_m 7800)].[3a] More recently Birnbaum, Linford, and Style[7] have suggested that the transition is of an $n \rightarrow V_0$ type, an unpaired electron on the azo group being transferred to a π-electron orbital. The band of high intensity in the region of 320–360 mμ has been attributed[3a] to an electronic transition throughout the whole conjugate system, involving both aromatic rings and the azo group (an n-π or $N \rightarrow V$ transition[8]), thus constituting a *K*-(conjugation)-band. The maximum at 220–240 mμ was not recorded in many of the earlier measurements,[3] but it seems probable that this band arises from an electronic excitation of the benzene rings alone[7] (an *E*-band), since very similar bands are found in azoxybenzenes[4] and stilbenes.[7] The maximum will be that of the *B*-band ($\lambda_{max.}$ 205 mμ, A_m 6300[9]) of benzene displaced to longer wave lengths by substitution.

The effect of substituents on the *E*-band of azobenzenes was found to be very small (Table I), as the wave lengths remained constant and there were only small differences in the intensities; the situation with the corresponding band in azoxybenzenes was similar.[4] The *K*-band, however, was greatly affected in both wave length and intensity by substitution. In the 4-monohalo series there was a regular increase in both wave length and intensity for fluoro (+ 1 mμ), to chloro (+5 mμ), to bromo (+8 mμ) and the iodo compound (+11 mμ). The sequence F< Cl < Br < I is the one generally observed[10] and is the order of the increasing mesomeric effect of these atoms. The large displacements of the *p*-methoxy compound (+25 mμ) reflects the large mesomeric effect of the methoxy group, while the small displacement for *p*-methylazobenzene (in which no mesomeric effect can operate) is in agreement with small hyperconjugative contribution of the methyl group. The 4,4′-dihalo series showed the expected order of substituent effects (F < Cl < Br). The displacements, however, are larger (F +5, Cl +10, Br +16 mμ) than for the mono derivatives, and both halo atoms must contribute nearly equally to the polarization of the molecule. For the corresponding azoxybenzenes,[4] the displacements were somewhat smaller (F +2, Cl +7, Br +10 mμ). The 4,4′-dimethylazobenzene exhibited a small shift of 10 mμ, which was twice that for monosubstitution, while the 4,4′-dimethoxy compound showed a displacement (+34 mμ) which was less than double that of the monomethoxy derivative (+25 mμ).

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(6) A. Hantzch and J. Lifschitz, *Ber.*, **45**, 3011 (1912).

(7) P. P. Birnbaum, J. H. Linford, and D. W. G. Style, *Trans. Farad. Soc.*, **49**, 735 (1953).

(8) H. McConnel, *J. Chem. Phys.*, **20**, 700 (1952).

(9) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(10) *Cf.* 4,4′-dihalodiphenyls, B. Williamson and W. H. Rodebush, *J. Am. Chem. Soc.*, **63**, 3018 (1941).

The 3,3′-dihaloazobenzenes, in which the halogen atoms are in positions *meta* to the azo linkage, exhibited no displacement of wave length (except for a small hypsochromic shift in the diiodo compound). This is to be expected since the mesomeric effect of these atoms cannot be operative.

In the case of the 2,2′-dihalo derivatives there were small bathochromic shifts together with a decrease in intensity which was more pronounced for the iodo substituent than for the less bulky chloro atom. Moreover, 2,2′-dimethyl- and 2,2′-dimethoxyazobenzene exhibited a splitting of the *K*-band into two peaks, which was probably due to steric hindrance to coplanarity. Similar splitting has been observed in the spectra of azobenzenes.[4] 2,4,6,2′,4′,6′-Hexabromoazobenzene, having four large bromine atoms in all four *ortho*- positions, showed the expected large hypsochromic shift (−18 mμ), as well as a considerable decrease in intensity.[11] A decrease of the molar absorbancy of an *ortho*- substituted compound with respect to that of the *para*- isomer can be used to calculate the angle of distortion (θ) from coplanarity, by assuming that the intensity in the absence of steric effects is the same as that of the *para*-isomer. Values of θ, calculated from the formula $\cos^2 \theta = A^o{}_m/A^p{}_m$[12] (where $A^o{}_m$ and $A^p{}_m$ are the molar absorbancy coefficients of the *ortho*- and *para*-isomers, respectively) for a number of azobenzenes are given in Table II, together with previously determined data for substituted azoxybenzenes.[4] While noncoplanarity increased in the sequenced $CH_3O < CH_3 < Cl$ for substituted azobenzenes, the corresponding values for azoxybenzenes were with $CH_3 < Cl < CH_3O$ It is probable that in 2,2′-dimethoxyazobenzene, the two substituents can be accommodated on either side of the central nitrogen linkage with only small out-of-plane twisting (18°), whereas introduction of the azoxy oxygen atom encroaches upon the available space and substantial rotation (72°) of the aryl groups results.

TABLE II

DEFORMATION ANGLES OF 2,2′-DISUBSTITUTED AZOBENZENES, AZOXYBENZENES, AND STILBENES

Substituent	ϵ_o[a]	ϵ_p[a]	θ Azo	θ Azoxy[b]	θ Stilbenes
Methyl	16,400[c]	19,300	23°	38°	28°[d]
Methoxy	11,900[c]	13,100	18°	72°	—
Chloro	14,100	20,800	35°	51°	—

[a] ϵ_o and ϵ_p denote molar absorption intensities of *ortho*- and *para*-azobenzenes. [b] Ref. 4. [c] Double maxima; higher wave-length value used. [d] Calculated from data of R. N. Beale and E. M. F. Roe, *J. Am. Chem. Soc.*, **74,** 2302 (1952).

Substitution by a polar group did not, in general, produce regular or predictable changes in the position and intensity of an *R*-band,[3a] and this was also found for the visible band of the azobenzenes.

X-ray diffraction measurements have shown[13] that the azobenzene molecule is planar with the two benzene rings *trans* to each other across the azo-bond and this is supported by dipole moment measurements.[14] *cis*-Azobenzenes have been prepared[15] and they have a weaker *K*-band than the corresponding *trans* isomers, although their *R*-bands are more intense.[3b] Hodgson,[16] has suggested that the reactions of *cis*-azobenzene[14a] and the difference in the dipole moments of *trans*- and *cis*-azobenzene[14a] can be explained if the compound were a mixture of azoxybenzene and hydrazobenzene. However, the infrared spectrum[17] was consistent with the *cis*-isomer being a pure substance. Hodgson cited as evidence against the *cis*-azobenzene structure the fact that it does not show a displacement of the visible band with respect to the *trans*-compound. However, his argument is valueless since this band is an *R*-band and systemic displacements such as those found in the *K*-band cannot be expected. Moreover, neither azoxybenzene nor hydrazobenzene display *R*-bands (see below). The *K*-bands of *cis*-azobenzenes showed the expected shift to shorter wave length, resulting from the decreased resonance energy in the nonplanar molecule.[13]

The absorption spectra of azobenzenes showed some important general differences to the spectra of azoxybenzenes.[4] Azobenzenes possess a characteristic visible band (near 440 mμ), while azoxybenzenes have no maximum above 370 mμ. In addition, some azobenzenes have an E_2-band near 260 mμ, while no azobenzene examined had a maximum in this region. The bathochromic effect of substituents was very similar but was more pronounced with substituted azobenzenes, suggesting that conjugation is easier in the azobenzene system. No experimental data, however, relating to this have been published.

EXPERIMENTAL

Compounds. The preparation of many of the azobenzenes has been previously described.[18] The monohalo compounds were prepared by Sandmeyer reactions[15a,19] on *p*-aminoazobenzene.

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[11] J. S. P. Blumberger [*Rec. trav. chim.*, **63,** 127 (1944)] predicted by means of model diagrams that steric interference was likely to occur between the azo linkage and *ortho*- substituents in azobenzene.

[12] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

[13] J. M. Robertson, *J. Chem. Soc.*, 409 (1941).

[14] (a) G. S. Hartley and R. J. W. LeFevre, *J. Chem. Soc.*, 531 (1939); (b) T. W. Cambell, W. A. McAllister, and M. T. Rogers, *J. Am. Chem. Soc.*, **75,** 864 (1953).

[15] (a) A. H. Cook, *J. Chem. Soc.*, 876 (1938); (b) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1309 (1939).

[16] H. H. Hodgson, *J. Chem. Soc.*, 1907 (1948).

[17] K. S. Tetlow, *Research*, **3,** 187 (1950).

[18] P. H. Gore and G. K. Hughes, *Austr. J. Sci. Res.*, **3A,** 136 (1950); **4A,** 185 (1951).

[19] D. A. Shirley, "Synthesis of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 184; E. Noelting and A. Werner, *Ber.*, **23,** 3252 (1890); C. Willgerodt and C. Smith, *Ber.*, **37,** 1311 (1904).

2,2'-Dimethoxybenzene. The 2,2'-dimethoxyazobenzene[18] (2.6 g.) in ether (50 ml.) and benzene (20 ml.) was treated at 0° with lithium aluminum hydride (0.6 g.) in ether (20 ml.). The color of the solution changed from red through yellow to apple green. After stirring at room temperature for 30 min., aqueous ammonium chloride was added at 0°. The organic layer was separated, washed with water, dried and the solvent removed. The residue was chromatographed on alumina from benzene giving a yellow fore-band, which afforded yellow crystals (0.32 g.) of the azo compound, m.p. 152–153°,[20] and a main band of unchanged azoxy compound.

2,2'-Diiodoazobenzene. The 2,2'-diiodoazoxybenzene[15b] was similarly reduced to the azo derivative, orange needles, m.p. 194°[21]

2,4,6,2',4',6'-Hexabromoazobenzene. This was obtained by a Wallach rearrangement of hexabromoazoybenzene[21] as dark purple crystals, m.p. 213°.[22]

Absorption spectra. The spectra were determined in absolute ethanol as solvent with an Unicam S.P. 5000 spectrophotometer, using 1-cm. quartz cells with the concentration of compound chosen to give optical densities between 0.4 and 0.8.

Acknowledgment. The authors are grateful to Professor J. Lichtenberg (Mulhouse) for samples of 4-fluoro- and 4,4'-difluoroazobenzenes, to Dr. R. W. Kiersted (New York) for a sample of 4-methylazobenzene and to Mrs. I. Boston, Spectroscopic Laboratory, Department of Chemistry, Imperial College of Science and Technology, London, for determining many of the spectra.

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[20] K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, 4003 (1954), give m.p. 153°.

[21] P. H. Gore and G. K. Hughes, unpublished results.

[22] J. T. Edwards, *J. Chem. Soc.*, 222 (1956), gives m.p. 212–3°.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF PUERTO RICO AT MAYAGUEZ AND BRUNEL COLLEGE OF TECHNOLOGY]

Absorption Spectra of Aromatic Azo and Related Compounds. IV. Benzanils[1]

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The ultraviolet absorption of a number of substituted benzanils has been measured in anhydrous methanol. Some previous measurements are incorrect, because of the ready hydrolysis of the compounds in aqueous solvents. The electronic and steric effects of various substituents are discussed and compared with previous data on substituted azobenzenes.

Although the ultraviolet spectrum of benzanil itself has been reported a number of times[3] the only detailed study of substituted benzanils is that of Smets and Delvaux[4] who measured the spectra of some twenty benzanils in neutral, acid, and alkaline solution. However, their data showed no systematic relationships of wavelength and intensity. Thus, *N*-4-methoxy- and α-4-methoxybenzanil[5] were reported to have λ_{max} 276 (ϵ 19,500) and 230 mμ (ϵ 26,000), respectively, and *N*-3-nitro- and α-3-nitrobenzanil to have λ_{max} 264 (ϵ 39,200) and 277 mμ (ϵ 17,000), respectively (all in neutral solution). In previous studies of the structurally related azobenzenes,[1] phenylnitrones,[6a] and azoxybenzenes[6b] differences in the spectra were observed to be systematic. Because of the apparent anomaly of the benzanils it was decided to prepare a new series of these compounds and to investigate their spectra.

Preliminary measurements gave variable values of both wavelength intensities with different samples of 95% ethanol, and the spectra changed further on standing. In 100% methanol, however, the spectra were completely reproducible and did not vary with time (Table I).[7] The reason for the variable results previously found using 95% ethanol can not be due to a photochemical reaction,[8a] as irradiation had little effect on the spectra of benzanil in methanol (Table I). However, in the presence of water (95% methanol) a slow, presumably hydrolytic change took place, and this was very greatly accelerated by traces of mineral acid (Table I).[8b] The final spectrum was that expected for a mixture of the hydrolysis products of benzanil; benzaldehyde λ_{max} 242 (ϵ 14,000), 248 mμ (ϵ 12,500)[9] and aniline λ_{max} 230 mμ (ϵ 8,000).[10] The data of Smets

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[4] G. Smets and A. Delvaux, *Bull. soc. chim. Belges*, **56**, 106 (1947).

[5] *N*-denoted substitution in the ring attached to the nitrogen atom and α- in the other ring.

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[7] Our own values agree best with the determination of Bohlmann, ref. 3d.

[8] (a) *Cf.* M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957); (b) M. J. Kamlet, personal communication.

[9] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

[10] E. A. Braude, *Ann. Rep. Chem. Soc. (London)*, **42**, 105 (1945).