

Orientation Effects in the Benzene Chromophore Bearing One Donor and Two Acceptor Groups. Electronic Absorption Spectra of the Dicyanoanilines

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The light absorption properties of the benzene chromophore substituted with one donor (+M) and two acceptor (-M) groups have been investigated using the dicyanoanilines as model compounds. The absence of strong steric *ortho*-interactions and intramolecular hydrogen bonding enables the dependence of the wavelength of the first absorption band on substitution pattern to be determined. The syntheses of the two remaining members of this series, 2,4- and 2,6-dicyanoaniline, are described. The observed influence of the position of the cyano-groups on λ_{max} order was: 2,5 > 2,3 > 2,6 > 3,5 > 3,4 > 2,4, and cannot be explained in terms of resonance theory. However, the PPP SCF-CI molecular orbital method predicted this wavelength dependence accurately.

ALTHOUGH the electronic absorption spectra of simple substituted benzenes have been investigated in great detail, relatively little is known about orientation effects (*i.e.* the influence of positional isomerism) in derivatives containing three or more mesomerically interacting substituents. Attachment of one electron-donating (+M) and one electron-withdrawing (-M) group to the benzene ring gives rise to a long wavelength transition which possesses considerable charge-transfer character, *i.e.* there is a pronounced migration of electron density from the donor to the acceptor group in the excited state. Simple resonance theory predicts that the *ortho*- and *para*-orientations should be the most bathochromic, since low energy charge-separated structures can be drawn for these. In contrast, however, the *para*-isomer is almost always hypsochromic relative to the *ortho*- and *meta*-isomers (*e.g.* the nitroanilines and the cyanophenols).¹ Molecular orbital calculations have shown that simple resonance theory is totally inapplicable to the problem, and in fact charge transfer in the first excited singlet state is greater for the *meta*- than for the *para*-acceptor.¹

The attachment of two electron donors and one acceptor to the benzene chromophore is particularly interesting, as the additional donor produces a general bathochromic shift, and orientation effects are more pronounced. Again, resonance arguments lead to incorrect predictions for the influence of isomerism on the relative shifts, and in a classic series of empirical studies Kauffmann² developed his 'distribution of auxochromes' principle, which has been elaborated subsequently by Wizinger³ and examined theoretically by Grinter and Heilbronner.¹ Curiously, for benzene derivatives possessing two electron-donor groups (auxochromes) in the 2,4-, 3,4-, and 2,5-positions relative to the acceptor group, the wavelength order for the first absorption bands is 2,4- < 3,4- < 2,5-. The most hypsochromic substitution pattern (2,4-) is that which gives maximum resonance interaction between the donor and acceptor groups in the ground state. The distribution rule can be of considerable practical value in

predicting the optimum substitution pattern for producing deeply coloured dyes. For example, the alkylated 2,5-diaminonitrobenzenes provide useful red-to-violet hair dyes, whereas the other positional isomers are relatively hypsochromic (yellow-to-orange) and have no practical value.

Benzene derivatives substituted with one electron donor and two electron acceptors show a bathochromic shift due to the introduction of the second acceptor group. However, few systematic investigations of orientation effects in these compounds have been made. The only such series of compounds for which all positional isomers are known is that based on the dinitrophenol system. Thus Davis has reported the absorption maxima of the six dinitrophenols and their anions,⁴ but unfortunately, because of the steric crowding resulting from two adjacent nitro-groups, and the ability of the hydroxy-group to form a hydrogen bond with an *ortho*-nitro-group, the dependence of the wavelength order on substitution pattern is somewhat obscured. A better series, in which steric and hydrogen-bonding interactions are minimised, is the dicyanoanilines. The rod-like shape of the cyano-group ensures very little steric crowding when two groups are *ortho* to each other,⁵ and thus partial deconjugation with the ring is prevented. Similarly, geometrical considerations preclude the formation of a significant hydrogen bond between the cyano-group and an *ortho*-amino-group.⁶

Recently we have described the synthesis of four of the six isomeric dicyanoanilines.⁷ We have now prepared the remaining two isomers, and have measured the electronic absorption spectra of all the members of this series. The effects of positional isomerism have also been examined by application of the PPP MO method.

RESULTS AND DISCUSSION

Synthesis of Dicyanoanilines.—Syntheses of 2,3-, 2,5-, 3,4-, and 3,5-dicyanoaniline have been described previously.⁷ The 2,4-isomer was prepared by dehy-

¹ R. Grinter and E. Heilbronner, *Helv. Chim. Acta*, 1962, **45**, 2496.

² H. Kauffmann and W. Franck, *Ber.*, 1906, **39**, 2722; H. Kauffmann and W. Kugel, *ibid.*, 1911, **44**, 2386; H. Kauffmann and F. Kieser, *ibid.*, 1913, **46**, 3789; H. Kauffmann, *ibid.*, 1919, **52**, 1422.

³ R. Wizinger, *Chimia (Switz.)*, 1965, **19**, 339.

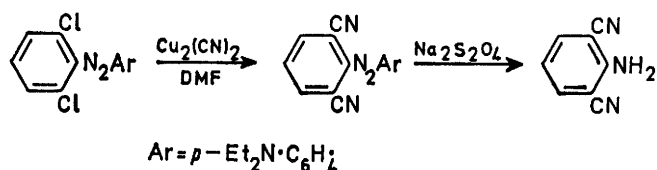
⁴ M. M. Davis, *J. Amer. Chem. Soc.*, 1962, **84**, 3623.

⁵ W. A. Sheppard, in 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, Interscience, London, 1970, p. 209; E. Hoyer, R. Schickfuss, and W. Steckelberg, *Angew. Chem. Internat. Edn.*, 1973, **12**, 926.

⁶ P. J. Krueger, *Canad. J. Chem.*, 1962, **40**, 2300.

⁷ J. Griffiths and B. Roozpeikar, *J.C.S. Perkin I*, 1976, 42.

dration of nitrobenzene-2,4-dicarboxamide with acetic anhydride, followed by reduction of the resultant dicyano-nitrobenzene with iron and hydrochloric acid. 2,6-Dicyanoaniline presented more difficulties; the most effective route involved reductive cleavage of a suitable 2,6-dicyanoazobenzene derivative. Compounds of the latter type are readily available by cyanodehalogenation of bromo- or chloro-azobenzenes with copper(I) cyanide in dimethylformamide. The procedure shown in the Scheme gave 2,6-dicyanoaniline in 23% yield.



SCHEME

Electronic Absorption Spectra and MO Calculations.—

The wavelengths and intensities of the first $\pi \rightarrow \pi^*$ bands of the dicyanoanilines, measured in 95% ethanol, are given in Table 1. The six dicyanoaniline isomers show the wavelength order: 2,5 > 2,3 > 2,6 > 3,5 > 3,4 > 2,4. Thus the 2,4-isomer is the most hypsochromic member of the series, absorbing at shorter wavelengths even than the 3,5- (*meta,meta*-) isomer. The wavelength order differs from that observed by Davis for the dinitrophenols, *i.e.* 2,5 > 2,3 ~ 2,6 > 2,4 ~ 3,5 > 3,4.⁴ The higher position of the 2,4-isomer in the latter wavelength series can be attributed to hydrogen bonding between the hydroxy-group and the 2-nitro-group, which should enhance the electron-donating strength of the hydroxylic oxygen and the acceptor strength of the nitro-group, thus giving a bathochromic shift. On the other hand, the close similarity between the 2,3- and 2,6-dinitrophenols can be attributed to steric interaction between the 2- and 3-nitro-groups, causing their partial deconjugation with the ring and a corresponding hypsochromic shift. Thus it is likely that the wavelength series for the dicyanoanilines gives a better representation of orientation effects, as steric crowding⁵ and hydrogen-bonding⁶ will be largely absent.

It was of interest to examine the dicyanoanilines by a suitable molecular orbital method, to see if the observed wavelength order could be predicted, and to evaluate the charge-transfer character of the first excited states of the various isomers. Two methods which specifically include electron repulsion effects are the PP SCF CI procedure, and the CNDO/S method of Del Bene and Jaffé.⁸ The latter has been used successfully with several carbocyclic and heterocyclic aromatic systems, and is particularly useful for examining $\sigma-\pi$ interactions and for predicting $n-\pi^*$ transition energies. However, as σ and π electrons are included in the calculations, the method makes heavy demands on computer time, and cannot yet be applied routinely to very large molecules. The PPP method considers π -electrons only, and is thus a simpler procedure for routine use. The inherent $\sigma-\pi$ separation

principle is a reasonable approximation in planar molecules, and thus the method should be applicable to the dicyanoanilines. Consequently the PPP method, with limited configuration interaction, was adopted for examination of the spectra of these compounds.

Bond lengths of 1.395 Å were assumed throughout, except for the cyano-group (1.15 Å), and the C-N bond for the amino group (1.38 Å). The cyano-group was assigned a resonance integral of 2.675 eV, VSIP values 11.19 (C) and 14.18 (N) eV, and electron affinities 0.1 (C) and 3.50 (N) eV. All other atoms and bonds were assigned the values given elsewhere.⁹ The computed wavelength values and oscillator strengths given in Table 1 were obtained after a configuration interaction treatment involving the first nine singly excited singlet states.

TABLE 1

Experimental and calculated data for the first absorption band of the dicyanoanilines

Position of cyano-group(s)	$\lambda_{\max.}/\text{nm}^a$ (obs.)	$\epsilon_{\max.}^a$ (obs.)	$\lambda_{\max.}^a$ (calc.)	f^b (calc.)
2,4	328	2 150	334	0.26
3,4	336	5 360	342	0.34
3,5	345	2 500	353	0.15
2,6	348	6 700	364	0.44
2,3	353	5 000	371	0.30
2,5	355	4 470	374	0.30

^a Measured in 95% ethanol. ^b Oscillator strength.

The predicted wavelength values for the dicyanoanilines are in reasonable agreement with experiment, although the transition energies tend to be underestimated by *ca.* 0.1 eV. The predicted wavelength order (2,5 > 2,3 > 2,6 > 3,5 > 3,4 > 2,4) is in exact agreement with that observed experimentally, and reasonable agreement is also found for the absorption intensities, (experimental: 2,6 > 3,4 > 2,3 > 2,5 > 3,5 > 2,4; predicted: 2,6 > 3,4 > 2,3 ~ 2,5 > 2,4 > 3,5). The molecular orbital method thus appears to be well suited to this series of compounds, and reasonable deductions concerning the general characteristics of the electronic transitions can be made.

The electron density changes at the donor (amino) group and cyano (acceptor) groups give a useful indication of the charge-transfer character of the first absorption band, and these values, calculated before configuration interaction and thus neglecting the small differences between the singlet and triplet states, are shown in Table 2. It is evident that the degree of charge transfer in the excited state is not related to the observed wavelength order, and, for example, the isomer showing the greatest electron-density migration is 3,5-dicyanoaniline, which lies fourth in the wavelength series. The most hypsochromic isomer (2,4-dicyanoaniline) does show the smallest degree of charge transfer, however. It is also

⁸ J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, 1968, **48**, 1807, 4050; 1968, **49**, 1221; R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, 1972, **26**, 131.

⁹ J. Griffiths and M. Lockwood, *J.C.S. Perkin I*, 1976, 48.

evident that a *meta*-cyano-group, if present, is always the more powerful acceptor, and an *ortho*-group is usually more effective than a *para*-substituent.

TABLE 2

π -Electron density changes (Δq) accompanying the first electronic transition of the dicyanoanilines

Position of cyano-groups	Δq^a			
	NH ₂	<i>o</i> -CN ^b	<i>m</i> -CN ^b	<i>p</i> -CN ^b
2,4	-0.265	0.337		-0.060
3,4	-0.319		0.332	0.124
3,5	-0.390		0.218	
2,6	-0.319	0.156	0.218	
		0.156		
2,3	-0.340	0.164	0.276	
2,5	-0.330	0.154	0.281	

^a Calculated before CI. A negative sign indicates a decrease in electron density. ^b Summation of Δq for the carbon and nitrogen atoms.

Thus the orientation dependence for benzene chromophores bearing one donor and two acceptor groups appears to parallel that found for the analogous two-donor, one-acceptor systems. The same wavelength order is found for 2,5-, 3,4-, and 2,4-diaminonitrobenzene as for 2,5-, 3,4-, and 2,4-dicyanoaniline, and in neither case can the order be reconciled with resonance theory. Unfortunately, insufficient spectroscopic data are available for the bis-donor systems to test this parallelism further for other substitution patterns.

We emphasise that resonance theory can predict orientation effects successfully in certain cases, particularly if the molecule is relatively complex, and if the acceptor-substituted ring is only partly involved in the electronic transition. This has been demonstrated in

the case of the cyano-substituted 4-diethylaminoazobenzenes.⁷

EXPERIMENTAL

2,4-Dicyanoaniline.— Nitrobenzene-2,4-dicarboxamide (2×10^{-2} mol) was added to a mixture of acetic anhydride (25 g) and chlorobenzene (6 g). The solution was heated under reflux for 20 h, then distilled to remove 20 ml of mixed solvent, and the residue was poured into hot water (100 ml). The crude 2,4-dicyanonitrobenzene was filtered off, and was used directly for reduction without further purification.

The product was added to a mixture of methanol (80 ml) and concentrated hydrochloric acid (18 ml) and the suspension heated to the boil. Iron powder (4.0 g) was added in small portions over 45 min. The mixture was poured into cold water and the precipitate filtered off. Recrystallisation from benzene gave 2,4-dicyanoaniline (0.140 g, 5%), m.p. $>240^\circ$ (decomp.) (Found: C, 67.1; H, 3.7; N, 29.55. C₈H₅N₃ requires C, 67.1; H, 3.5; N, 29.4%).

2,6-Dicyanoaniline.—A solution of 2,6-dicyano-4'-diethylaminoazobenzene⁷ (0.5 g) in acetone (50 ml) was added slowly to a solution of sodium dithionite (2.0 g) in water (200 ml) and acetone (50 ml). After 15 min the solution was boiled to remove acetone, and the aqueous solution extracted with methylene chloride. The dried extracts were concentrated and the residue purified by preparative t.l.c. (silica; benzene). The required band was identified by its intense fluorescence under u.v. light. Extraction gave 2,6-dicyanoaniline (0.030 g, 23%), m.p. 150–152° (Found: C, 67.0; H, 3.7; N, 29.45. C₈H₅N₃ requires C, 67.1; H, 3.5; N, 29.4%).

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