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CYANOVINYL - SUBSTITUTED AZO DYES. AN UNUSUAL EXAMPLE OF NEGATIVE HALOCHROMISM IN A MONOSUBSTITUTED AMINOAZOBENZENE

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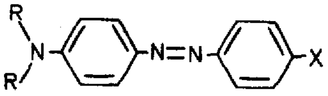
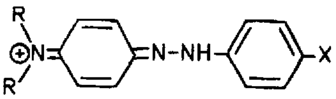
The well known colour change, or halochromism, of aminoazobenzenes e.g. (I) in acid solution is caused by protonation of the β-nitrogen atom of the azo group, giving the normally more bathochromic cation (II).[1] Whereas the visible absorption band of (I) moves to longer wavelengths as the electron withdrawing strength of X increases, the reverse is true for the cation, and this can be attributed to the opposite directions of charge migration accompanying electronic excitation. Thus it is found that the long wavelength bands of the neutral and protonated forms converge with increasing electron accepting strength of X.[2] If X is sufficiently powerful, the bands may cross, thus giving a negative halochromism, with the cation absorbing at shorter wavelengths than the neutral molecule. However, this is a rare phenomenon, and the only monosubstituted aminoazobenzene known to give a negative halochromism is (I; $R = Me$, $X = N_2^+$), where the substituent is positively charged.[3] In view of the known powerful electron acceptor properties of the di- and tri-cyanovinyl groups, we have prepared various aminoazobenzene dyes containing these substituents, and have noted an interesting example of negative halochromism in one of these derivatives.



(I)



(II)

a; $R = Et$, $X = CHO$
b; $R = Et$, $X = CH{=}C(CN)_2$
c; $R = Et$, $X = C(CN){=}C(CN)_2$
d; $R = Et$, $X = C(OEt){=}C(CN)_2$

The aldehyde (Ia), prepared by coupling diazotised p-aminobenzaldehyde to N,N-diethylaniline, condensed readily with malononitrile in ethanol to give deep violet crystals of the dicyanovinyl derivative (Ib), m.p. 215-217°, in 97% yield.[4] The effectiveness of the dicyanovinyl residue as an electron acceptor was indicated by the deeper colour of (Ib) (λ_{max}^{EtOH} 523 nm) when compared with 4'-nitro-4-N,N-diethylaminoazobenzene (λ_{max}^{EtOH} 488 nm). However, (Ib) showed a positive halochromism (+ 27 nm in acidified ethanol), although this was reduced in comparison with the nitro analogue (+ 38 nm) and the aldehyde (Ia) (+ 49 nm).

Conversion of (Ib) to the tricyanovinyl derivative (Ic) was effected in 94% yield by addition of potassium cyanide to the vinyl group, followed by oxidation of the product with lead tetracetate.[5] The product formed lustrous green crystals, m.p. 174-175°.[4] The additional cyano group in (Ic) resulted in a remarkable bathochromic shift of the visible absorption band, and solutions of the dye were blue (λ_{max}^{EtOH} 587 nm). No other neutral monosubstituted aminoazobenzene has been reported that shows an absorption band at such long wavelengths. The tricyano dye was rather unstable in ethanol, slowly fading to a red product identified as the ethoxy compound (Id), and thus its halochromism was examined in dry benzene. Complete protonation occurred in 5×10^{-4}N anhydrous HCl in benzene, the absorption band moving from 592 nm (log ε 4.60) to 586 nm (log ε 4.68). Thus the tricyanovinyl group is sufficiently electron withdrawing to cause negative halochromism. The reversibility of the colour change was established by neutralising the solution, when the original spectrum was completely restored.

The 1-ethoxy-2,2-dicyanovinyl group was less effective as an electron acceptor, as evidenced by the spectrum of (Id) (λ_{max}^{EtOH} 473 nm), which closely resembled that of the aldehyde (Ia) (λ_{max}^{EtOH} 472 nm). The spectra of the cations were also similar (λ_{max}^{EtOH} 520 and 521 nm respectively).

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