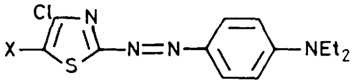
Azo Dyes with Absorption Bands in the Near Infrared

Kasali A. Bello and John Griffiths*
Department of Colour Chemistry and Dyeing, The University, Leeds LS2 9JT, U.K.

The first examples of monoazo dyes absorbing in the near infrared (up to 806 nm in dimethyl sulphoxide) have been prepared from 2-(4-amino-2-acetylaminophenylazo)-4-chloro-5-formylthiazoles by condensing the formyl group with suitably electronegative active methylene compounds under base catalysed conditions.

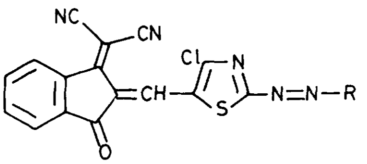
Interest in near infrared absorbing dyes (*i.e.* dyes with absorption maxima beyond *ca.* 700 nm) has been intense in recent years, principally because of their many applications in such areas as lasers and optical data storage technology. Although a small number of chromophoric systems have been modified to give light absorption at such long wavelengths, it is notable that no azo dyes appear to be known at present with such properties. This is remarkable in view of the synthetic versatility of the azo dyes, which has made them the most widely used and the single most commercially important dye class.

Substitution of the basic 4-aminoazobenzene system with



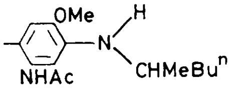
(1)

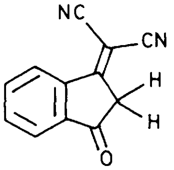
a; X = $-CHO$
b; X = $-CH{=}C(CN)_2$
c; X = $-C(CN){=}C(CN)_2$



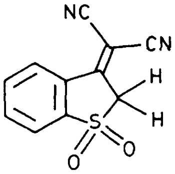
(2)

a; R = $4\text{-}Et_2NC_6H_4$
b; R = $4\text{-}Et_2N\text{-}2\text{-}AcNHC_6H_3$
c; R = $4\text{-}Pr^n{}_2N\text{-}2\text{-}AcNHC_6H_3$
d; R =

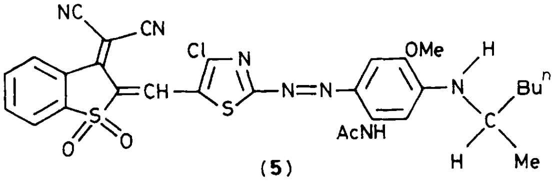




(3)



(4)



(5)

$+M$ groups in the aminophenyl ring and $-M$ groups in the second ring causes a progressive bathochromic shift of the absorption band, and heavily substituted examples are known which absorb up to *ca.* 650 nm. Although empirical additivity relationships suggest that further shifts, perhaps as far as 760 nm, could be achieved in this way,[1] synthetic problems are considerable. An alternative approach to systems absorbing beyond 700 nm is to make use of the known bathochromic effect of the thiazole ring in azo dyes,[2] and consequently we have examined dyes (**1**), which contain a 4-chlorothiazole residue.

2-Amino-4-chloro-5-formylthiazole[3] was diazotised in nitrosylsulphuric acid and coupled to *N,N*-diethylaniline to give the violet dye (**1a**) ($\lambda_{max.}$ 574 nm in dichloromethane). The pronounced bathochromic effect of the 4-chlorothiazole residue can be seen by comparing (**1a**) with 4′-formyl-4-diethylaminoazobenzene, the latter having $\lambda_{max.}$ 472 nm in the same solvent. Reaction of (**1a**) with malononitrile gave (**1b**), and conversion of the dicyanovinyl group into tricyanovinyl[4] gave the green dye (**1c**), which showed an intense absorption band ($\varepsilon_{max.}$ 75 100 l mol^{-1} cm^{-1}) at 725 nm in dichloromethane.

Near infrared absorbing dyes (**2**) could similarly be obtained by condensing 3-dicyanomethyleneindan-1-one (**3**)[5,6] with the appropriate formyl-substituted azo dyes, and these had the advantage of greater solvolytic stability than (**1c**). Thus for example, (**2a**) was obtained in 80% yield by heating equimolar amounts of (**1a**) and (**3**) in ethanol under reflux in the presence of a small amount of piperidine. The absorption maxima of (**2a**—**d**) (Table 1) show the expected progressive shift to longer wavelengths as the electron donating properties of the arylamine ring are increased.

Table 1. Light absorption properties of dyes (**1**), (**2**), and (**5**).[a]

Dye	$\lambda_{max.}$/nm (CH_2Cl_2)	$\varepsilon_{max.}$/l mol^{-1} cm^{-1} (CH_2Cl_2)	$\lambda_{max.}$/nm (Me_2SO)
(**1a**)	574	51 000	592
(**1b**)	645	61 000	668
(**1c**)	725	75 100	745
(**2a**)	700	67 800	720
(**2b**)	710	74 700	730
(**2c**)	716	74 000	740
(**2d**)	750	82 600	799
(**5**)	778	83 850	806

[a] All new compounds gave satisfactory microanalytical data.

An even more effective electron withdrawing group can be introduced by reaction of the formyl group with compound (**4**),[7] as in dye (**5**). This dye proved to be the most bathochromic in the present series ($\lambda_{max.}$ 778 nm, $\varepsilon_{max.}$ 83 850 l mol^{-1} cm^{-1} in dichloromethane).

Dyes (**1c**), (**2**), and (**5**) give green solutions in dichloromethane, and the long wavelength band is both broader and more intense (by almost 100% in some cases) than that of simpler aminoazobenzenes. The bands tail down to *ca.* 600 nm, with minimal absorption in the rest of the visible region down to *ca.* 450 nm. A weak secondary band near 420 nm is discernible. As expected for such highly polarised structures, the dyes show a positive solvatochromism, and, for example, the $\lambda_{max.}$ values are displaced to longer wavelengths by around 20—30 nm in dimethyl sulphoxide relative to the less polar dichloromethane (Table 1). In the former solvent, dye (**5**) shows a $\lambda_{max.}$ value of 806 nm.

The dyes also show the negative halochromism (*i.e.* reversible shift of the absorption band to shorter wavelengths on addition of acid) typical of azo dyes containing strong electron withdrawing groups,[8] an effect attributable to the formation of an azonium cation. In this series, the halochromic shifts are extremely large, and, for example, the displacement of the band of (**5**) from 782 to 586 nm in butan-2-one on addition of hydrochloric acid is unprecedented.

Received, 7th August 1986; Com. 1132

References

1 H. Mustroph and J. Epperlein, *J. Prakt. Chem.*, 1981, **323**, 755.
2 J. B. Dickey, E. B. Towne, M. S. Bloom, W. H. Moore, H. M. Hill, H. Heynemann, D. G. Hedberg, D. C. Sievers, and M. V. Otis, *J. Org. Chem.*, 1959, **24**, 187.
3 R. Egli, U.S. Pat. 4 395 544.
4 K. Y. Chu and J. Griffiths, *Tetrahedron Lett.*, 1976, 405.
5 H. Junek, *Monatsh. Chem.*, 1964, **95**, 1201.
6 G. Irick, *J. Chem. Eng. Data*, 1971, **16**, 118.
7 W. Baumann, U.K. Pat. 2 026 528.
8 L. M. Yagupol'ski and L. Z. Gandel'sman, *J. Gen. Chem. USSR.*, 1967, **37**, 1992.