5-Acceptor-substituted 4-amino-2-arylazothiazoles. A unique black monoazo chromophoric system

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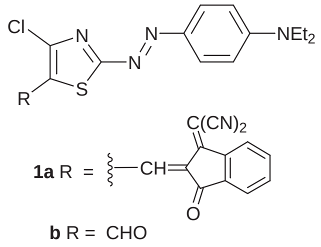
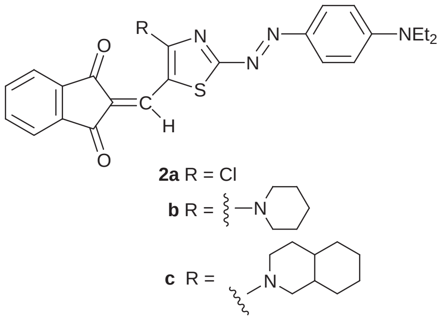
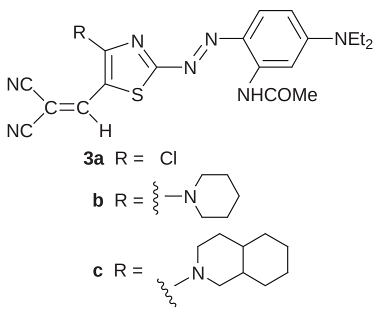
Replacement of the chlorine substituent in blue dyes of the 5-acceptor-4-chloro-2-(4-*N*,*N*-dialkylaminophenylazo)thiazole type by a tertiary amino group produces a black monoazo chromophoric system with three π → π* bands spanning the whole of the visible spectrum.







Black dyes, *i.e.* those with two or more absorption bands extending across the whole of the visible spectrum, are rare, and known examples invariably have a large molecular size in order to provide the requisite conjugation and number of chromophoric sub-units for multiple π → π* transitions in the visible range. The most commonly encountered examples are bis-azo or higher poly-azo dyes; their large size can lead to problems associated with aggregation or low solubility and this can limit their technical application. The traditional alternative is to use mixtures of dyes, even though these may introduce dye compatibility and shade reproducibility problems. Given the currently increasing importance of soluble black colorants in areas such as ink-jet and other digital printing systems, liquid crystal displays and optical filters, there is a growing need for the development of new, relatively low molecular weight black chromophores which can overcome these difficulties. We now describe the synthesis of a unique 2-arylazothiazole chromophoric system, whereby simple replacement of a chlorine substituent by an amino group causes a dramatic change in the light absorption properties of the molecule, and the single visible π → π* absorption band is replaced by three intense π → π* bands more or less equally spaced across the visible spectrum.

The 5-acceptor-4-chloro-2-(4-*N*,*N*-dialkylaminophenylazo)-thiazole dyes, as exemplified by **1** and **2a**,[1] are highly polarised molecules that show a single intense π → π* absorption band in the range *ca.* 550–800 nm,[2] which can be considered to involve electron density migration from the amino group into the azo group, thiazole ring and the 5-acceptor substituents on the latter ring. Whilst normally violet to blue–green in colour, the use of multiple donor groups in the donor ring and powerful acceptor groups R in **1** (*e.g.* **3a**) can displace the band into the near IR region, leading to useful near-IR dyes.[2] The 4-chloro substituent in molecules such as **1**, **2a** and **3a** should be capable of nucleophilic replacement, particularly if the 5-substituent is strongly electron withdrawing, and this was investigated in the case of the indane-1,3-dione derivative **2a**.

A solution of the blue dye **2a** and piperidine (2 equiv.) in THF was heated under reflux, when the colour of the solution became black, and after 6 h the reaction was judged to be complete by TLC analysis. After filtration to remove piperidine hydrochloride, the solution was evaporated and the product recrystallised from a mixture of CH_2Cl_2 and EtOH to afford **2b** as black crystals in 65% yield. The structure was confirmed by microanalysis, mass spectrometry and NMR spectroscopy. The dye was readily soluble in solvents such as toluene and CH_2Cl_2, giving black solutions which showed three absorption bands in the visible region. The absorption spectra of **2a** and **2b** in cyclohexane are compared in Fig. 1(*a*) and (*b*). The second band of **2b** shows vibrational structure, which is most evident in non-polar solvents such as cyclohexane [Fig. 1(*b*)]. In CH_2Cl_2 the absorption maxima occurred at 437, 528 (shoulder at 500 nm) and 665 nm (ε_{max} 19 900, 26 500 and 29 400 l mol^{-1} cm^{-1}, respectively). Thus, introduction of the piperidino group into the thiazole ring generates three visible π → π* absorption

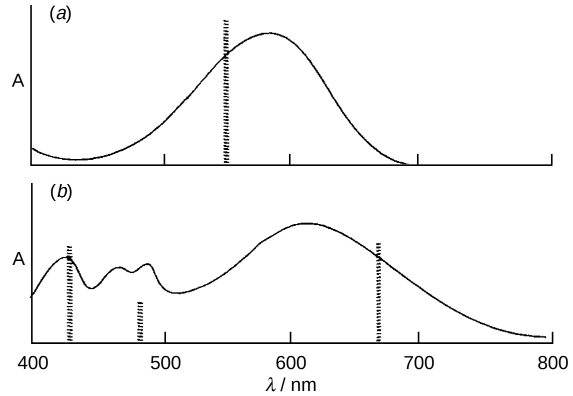


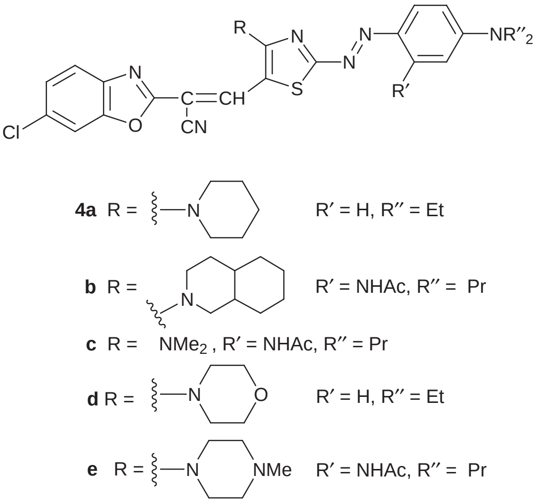
Fig. 1 Absorption spectra of (*a*) **2a**, and (*b*) **2b** in cyclohexane. Vertical broken lines represent the PPP-MO predicted absorption band λ_{max} values and relative intensities.

bands in place of the original single band. Such a dramatic change in the characteristics of a dye chromophore induced by a single substituent appears to be without precedent.

The electronic origin of the three bands was examined by application of PPP-MO theory to the π-chromophores of **2a** and **2b**.[3] Using standard parameters[3,4] the method predicted correctly that replacing the chlorine atom in **2a** by an amino group produces three visible absorption bands (Fig. 1).

The absorption bands, in order of increasing transition energy, approximate to the one electron excitation processes: HOMO → LUMO, HOMO → (LUMO + 1) and (HOMO-1) → (LUMO), although there is extensive configuration interaction between the three excited states. From the wavefunctions for these various orbitals one can deduce that the longest wavelength band involves the whole of the conjugated π system, the second band is associated predominantly with the 4-amino-5-acceptor-thiazole residue, and the shortest wavelength band is confined predominantly to the arylazo residue and the thiazole ring. All three bands show positive solvatochromism, shifting respectively from 608, 493 and 424 nm in cyclohexane to 677, 532 and 433 nm in DMF.

Replacement of the chlorine atom in the thiazole ring could also be effected with a variety of secondary amines, and with other 5-acceptor substituted analogues of **2a**. Thus the deeply coloured dyes **2c**, **3b**,**c** and **4**‡ were prepared in 50–95% yields by heating the appropriate chlorine-substituted dye and amine in solvents such as THF, EtOH and CH_2Cl_2. All showed the characteristic three visible absorption bands of this type of chromophore, their solutions ranging from dark blue, through greenish black to neutral black in colour. In general the rate of the replacement reaction and product yields were enhanced when the arylamine group had an acylamino substituent capable of hydrogen bonding to the azo group (*e.g.* **3**, **4b**,**c**,**e**).



The success of the chlorine replacement reaction is critically dependent on the nature of both the reacting amine and the thiazole 5-acceptor group. Weakly nucleophilic amines, *e.g.* primary and secondary arylamines, do not react, whereas primary alkylamines cause extensive decomposition of the chromophore, leading to (among other products) the parent aldehyde dye (*e.g.* formation of **1b** from **2a**). If the 5-acceptor group is particularly electron withdrawing then it undergoes preferential attack by the amine, leading to degradation of the chromophore and formation of red products. For example **1a** gave only decomposition products on reacting with a range of secondary amines. In the case of the aldehyde derivative **1b** reversible addition of the amine to the formyl group occurred, giving the unstable magenta aminohydroxy derivative.

The dyes **2b**,**c**, **3b**,**c** and **4** represent a new class of black chromophore that is capable of considerable structural diversity. Preliminary investigations have shown that hydrolytic, thermal and photochemical stability properties are typical for azo dyes of this general type and thus these systems offer considerable potential for the development of novel black colorants for many technical applications.

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Notes and References

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‡ Structures of new compounds were consistent with FAB-MS, 300 MHz NMR spectra and/or microanalytical data.

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