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Long Wavelength Absorbing Azo Dyes Derived from 2-Amino-4-Chloro-5-Formylthiazole as Diazo Component

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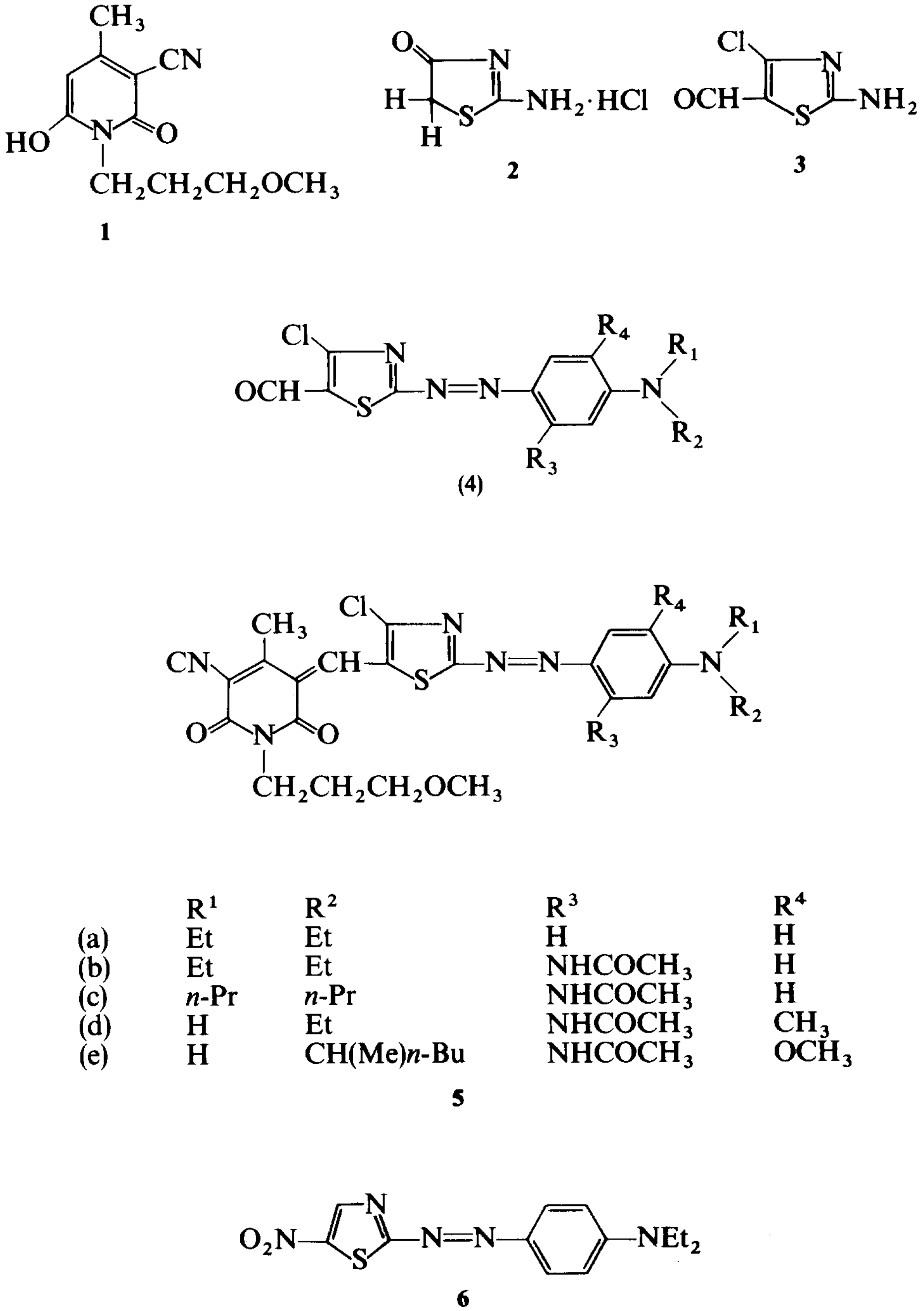
ABSTRACT

A range of azo dyes was prepared by coupling diazotised 2-amino-4-chloro-5-formylthiazole with various substituted arylamines. The formyl group of the dyes was then condensed with 3-cyano-4-methyl-6-hydroxy-1-(3'-methoxypropyl)-2-pyridone in refluxing ethanol to obtain a further series of dyes. The dyes obtained were highly bathochromic, absorbing in the range c. *690–740 nm; their photochemical stability was found to be moderate on cellulose acetate film, but the thermal stability was not good.*

INTRODUCTION

It has been previously shown that bathochromic aminoazo dyes can be obtained using 4-amino-3-nitrobenzaldehyde as diazo component;[1] these dyes did not absorb in the NIR, their λ_{max} being in the 570–660 nm region. Dyes derived from the use of 2-amino-4-chloro-5-formylthiazole however, do absorb in the NIR regions.[2]

We report here a further series of bathochromic dyes derived by condensation of the formyl group in derivatives of 2-amino-4-chloro-5-formylthiazole with the pyridone derivative **1**. Although pyridones of this type have been used extensively as coupling components for bright yellow dyes, there appear to be no references to their use as active methylene compounds in the synthesis of methine dyes. The synthesis of azo dyes of type **4** was therefore undertaken, and for this purpose five arylamine coupling components were used, viz. *N*,*N*-diethylaniline, 3-acetamido-*N*,*N*-diethylaniline, 3-acetamido-*N*,*N*-di-*n*-propylaniline, 5-acetamido-2-methyl-



1

2

3

(4)

	R^1	R^2	R^3	R^4
(a)	Et	Et	H	H
(b)	Et	Et	$NHCOCH_3$	H
(c)	*n*-Pr	*n*-Pr	$NHCOCH_3$	H
(d)	H	Et	$NHCOCH_3$	CH_3
(e)	H	CH(Me)*n*-Bu	$NHCOCH_3$	OCH_3

5

6

Scheme 1

N-ethylaniline and 5-acetamido-2-methoxy-*N*-2'-hexylaniline. The resultant dyes **4** were then condensed with 3-cyano-4-methyl-6-hydroxy-1-(3'-methoxypropyl)-2-pyridone **1** as an active methylene compound to give dyes **5a**–**5e**, respectively. The dyes were applied to cellulose acetate and their thermal and photochemical stability properties assessed. The structure of the dyes is shown in Scheme 1.

RESULTS AND DISCUSSION

Synthesis of intermediates and dyes

3-Cyano-4-methyl-6-hydroxy-1-(3'-methoxypropyl)-2-pyridone **1** was prepared by stirring a mixture of ethylcyanoacetate and 3-methoxy propylamine until a clear solution was obtained, and then adding ethylacetoacetate and heating the mixture in an autoclave at 120°C for 6 h. Dilution and acidification of the solution gave **1** in good yield as a white powder.

2-Amino-4-chloro-5-formylthiazole **3**[3] was prepared by Villsmeier formylation of 2-aminothiazolinone hydrochloride salt **2**, which was in turn prepared by refluxing thiourea and ethylchloroacetate in ethanol for 3 h. The aldehyde **3** was obtained by adding the hydrochloride salt **2** to a cooled mixture of dimethylformamide and phosphorous oxychloride and heating at 70°C for 24 h. After adding to water and hydrolysing with dilute sodium hydroxide, the product **3** precipitated as a yellow solid in good yield.

The amine **3** was then diazotised using nitrosylsulphuric acid diluted with propionic and acetic acids (1 : 4 by volume). The diazo solution was then used for coupling to various substituted anilines to obtain dyes **4a**–**4e**. Dyes **4** were then reacted with the pyridone **1** by refluxing in absolute ethanol to obtain dyes **5a**–**5e** in good purity, after one recrystallisation from toluene. Yield, melting point and microanalytical data for the dyes are shown in Table 1.

Visible absorption properties of the dyes

The visible absorption spectra of the dyes were measured in dichloromethane (quantitatively) and in toluene (qualitatively); the results are summarised in Table 2.

The data in Table 2 show that the bathochromic effect of the 4-chlorothiazole residue is very pronounced; thus one can compare the parent formylthiazole dye **4a** (λ_{max} CH_2Cl_2 574 nm), with 4-formyl-4'-

TABLE 1
Yields and Characterisation Data for Dyes **4** and **5**

Dye	Yield (%)	M.p.[a] (°C)	Formula	Found (%)			Required (%)		
				C	H	N	C	H	N
4a	74	198–201	$C_{14}H_{15}ClN_4OS$	52·65	4·80	17·65	52·17	4·65	17·39
4b	83	176–180	$C_{16}H_{18}ClN_5O_2S$	50·70	4·60	18·30	50·65	4·74	18·46
4c	71	172–175	$C_{18}H_{22}ClN_5O_2S$	53·40	5·50	17·00	53·07	5·40	17·19
4d	70	242–245	$C_{15}H_{16}ClN_5O_2S$	48·95	4·15	18·90	49·31	4·38	19·18
4e	64	246	$C_{19}H_{24}ClN_5O_3S$	51·90	5·65	15·75	52·17	5·49	16·01
5a	60	184	$C_{25}H_{27}ClN_6O_3S$	57·00	5·05	15·30	57·03	5·13	15·96
5b	74	213	$C_{27}H_{30}ClN_7O_4S$	55·35	5·20	16·25	55·57	5·14	16·80
5c	79	180	$C_{29}H_{34}ClN_7O_4S$	56·35	5·60	15·95	56·86	5·72	16·01
5d	56·6	241	$C_{26}H_{28}ClN_7O_4S$	54·90	4·90	17·15	54·83	4·92	17·22
5e	65	195–198	$C_{30}H_{38}ClN_7O_5S$	55·90	5·55	15·19	56·07	5·76	15·26

[a] By differential scanning calorimetry.

diethyl-aminoazobenzene (λ_{max} 472 nm in CH_2Cl_2)[4] and 4-formyl-2-nitro-4'-diethylamino-azobenzene (λ_{max} 515 nm in CH_2Cl_2).[1] The chlorothiazole system is thus shown to exert a bathochromic effect of approximately 100 nm relative to a phenyl ring. The molar absorption coefficients of the dyes derived from the 4-chlorothiazole residue are also very high and are generally between 50 000 and 80 000 l mol^{-1} cm^{-1} (e.g. 51 600 l mol^{-1} cm^{-1} for the aldehyde dye **4a**) compared with values of 30 000–50 000 for the 2-nitrophenyl analogues.[1]

TABLE 2
Visible Absorption Data for Dyes **4** and **5**

Dye	λ_{max} (CH_2Cl_2) (nm)	$\varepsilon_{max} \times 10^{-4}$ (l mol^{-1} cm^{-1})	λ_{max} (toluene) (nm)	$\Delta\lambda$[a] (nm)
4a	574	5·16	550	+24
4b	582	5·22	566	+16
4c	584	6·06	570	+14
4d	570	5·00	556	+14
4e	610	5·92	596	+14
5a	688	6·61	650	+24
5b	690	7·45	672	+18
5c	696	7·36	672	+24
5d	680	5·07	660	+20
5e	736	7·95	700	+36

[a] λ_{max} (CH_2Cl_2) − λ_{max} (toluene).

One cause of the increased intensity might be attributed to the greater planarity of the thiazole dyes, because of the lower steric interaction of a five-membered ring in comparison with a six-membered ring.

Condensation of the aldehyde dye **4a** with 3-cyano-4-methyl-6-hydroxy-1-(3'-methoxylpropyl)-2-pyridone gave dye **5a**, which absorbed at 688 nm in dichloromethane, showed a large bathochromic shift (114 nm), and confirmed that the pyridone residue was a useful and powerful electron acceptor moiety.

As can be seen from the data in Table 2, additional bathochromic shifts can also be obtained by enhancing the electron donor properties of the arylamine ring, e.g. by introducing an acetamido group *ortho* to the azo group, as in dye **4b**. This, however, gave only a small shift of 8 nm relative to dye **4a**, an effect also reflected in the derivative obtained by condensing the formyl group of dye **4b** with the pyridone.[1] The acetylamino group is a weak electron donor, but more importantly, it can take part in hydrogen bonding with the azo group. This enhances the planarity of the dye and helps to explain the higher intensities of dyes containing the acetamido group compared with *N*,*N*-diethylaniline analogues.

An additional bathochromic shift of 2 nm also resulted from increasing the alkyl chain length of dye **4b**; for example, when replacing the ethyl group by the *n*-propyl group, the resulting dye **4c** absorbed at 584 nm. A similar effect was obtained when the dye was condensed with the pyridone.[1]

It is interesting to note that use of 5-acetamido-2-methyl-*N*-ethylaniline as coupling component gives dye **4d**, which absorbs at slightly shorter wavelengths than the dye derived from *N*,*N*-diethylaniline; the hypsochromic shift is due to a decrease in the donor strength of the arylamine ring resulting from loss of one *N*-ethyl group, which is not completely compensated for by the 5-methyl group.

The results summarised in Table 2 for dyes derived from 3-anisidine demonstrate more clearly how increasing the number of electron donating groups in the arylamine ring results in general bathochromic shifts. Thus dye **4e** is blue-green, with absorption maximum at 610 nm in dichloromethane, i.e. a 36 nm longer wavelength than that of the *N*,*N*-diethylaniline analogue **4a**. The 5-methoxy group exerts a pronounced effect, as can be seen by comparing dyes **4e** and **4d**, and this has been exploited in some commercial azo dyes.[5] The angular nature of the ether group, together with the presence of only one alkyl group attached to the nitrogen atom, means that reasonable overlap between the lone pair of electrons of the nitrogen and oxygen atoms with the rest of the dye chromophore can be maintained. The ability of such dyes to maintain planarity and good orbital overlap is reflected in the high intensities of dyes **4e** and **5e**.

Condensation of 3-cyano-4-methyl-6-hydroxy-1-(3'-methoxylpropyl)-2-pyridone with **4e** also resulted in a dye with NIR absorption, i.e. **5e** with λ_{max} at 736 nm in dichloromethane. This is the first example of a dye containing the pyridone acceptor unit absorbing beyond 700 nm; the molar extinction coefficient of this dye was also exceptionally high (ε_{max} 79 500 l mol^{-1} cm^{-1}) for an azo dye.

Spectroscopic results for the various azo dyes described based on the 4-chlorothiazole system indicate the importance of the strength of the electron donor system in determining long wavelength absorption, as shown by the progressive shift to longer wavelength as the electron donating properties of the arylamine ring are increased. The largest shift observed was between the *N*,*N*-diethylaniline substituted dyes and dyes derived from the 5-methoxy substituted coupler, and was roughly the same for all corresponding pairs of dyes (*c*. 30–50 nm).

The effects of solvent polarity on the λ_{max} of the dyes are shown in Table 2. It is apparent that there is a consistent and significant bathochromic shift when the solvent polarity is increased from toluene to dichloromethane (positive solvatochromism). More significantly, the λ_{max} values are displaced to longer wavelengths by around 14–36 nm in dichloromethane relative to the less polar toluene. For example, in the former solvent, dye **5e** absorbs at 736 nm.

Stability properties of the dyes on cellulose acetate film

The results of photochemical and thermal stability studies of the dyes on cellulose acetate film are summarised in Table 3. From these results, we can see that the parent aldehyde dyes show good stability and are superior, in some cases both thermally and photochemically, relative to the standard azo dye. Replacement of the formyl group of dyes **4** by the pyridone acceptor unit has a detrimental effect on both the thermal and photochemical stabilities.

Introduction of an acetamido group *ortho* to the azo linkage results in a significant improvement in the thermal stability, and this is particularly noticeable in the case of the dye obtained from 3-acetamido-*N*,*N*-di-*n*-propylaniline. Differences in photochemical stability relative to the standard azo dye were not as pronounced as for thermal stability. Certain trends were, however, evident, e.g. the formyl dyes were always better than the standard dye, and, at the other extreme, dyes **5** derived from the pyridone **1** invariably displayed the lowest photochemical and thermal stability.

In terms of the influence of the coupling component on the photochemical stability, the 3-acetamido-*N*,*N*-di-*n*-propylaniline coupler gave

TABLE 3
Stability Properties of Dyes **4** and **5**

Dye	*Thermal stability (%)*	*Photochemical stability (%)*
Standard dye	10·1	5·3
4a	13·1	3·6
4b	5·0	4·2
4c	3·50	1·2
4d	—	—
4e	5·30	4·4
5a	65·1	13·3
5b	65·5	9·5
5c	51·6	15·1
5d	—	—
5e	45·9	17·9

dyes with significantly better lightfastness than those derived from *N*,*N*-diethylaniline; in both series of dyes the acetamido group exerted a useful stabilising effect, as can be seen in Table 3. This may be due to the intramolecular hydrogen bond formed between the acylamino group and the azo group.

CONCLUSION

Diazotised 2-amino-4-chloro-5-formylthiazole couples with substituted *N*,*N*-diarylanilines to give the corresponding formyl dyes which can then be condensed with a pyridone derivative to give green dyes. Within the range of dyes synthesised, the largest bathochromic shift was observed with dye **5e**, which was green with λ_{max} 736 nm in dichloromethane. The aldehyde-substituted dyes show good photochemical stability on cellulose acetate films, but replacement of the formyl group by the pyridone acceptor unit had a detrimental effect on both thermal and photochemical stability properties.

EXPERIMENTAL

3-Cyano-4-methyl-6-hydroxy-1-(3'-methoxypropyl)-2-pyridone (1)

A mixture of ethylcyanoacetate (28·2 cm^3) and 3-methoxypropylamine (72 cm^3) was stirred until a clear solution was obtained and ethylacetoacetate (39·3 cm^3) was then added. The mixture was refluxed at 110°C for

9 h and the solution diluted with water (400 cm^3) and acidified with hydrochloric acid to give **1** as a white solid. This was filtered and washed with water (44·2 g, 62%), m.p. 201°C. ν_{max}(KBr): >C=O 1660 cm^{-1}; —C≡N 2210 cm^{-1}.

2-Aminothiazoline hydrochloride salt (2)

Ethylchloroacetate (103·5 g) was added dropwise over 30 min to a refluxing solution of thiourea (63 g) in ethanol (400 cm^3). After refluxing for 3 h the liquor was cooled to room temperature and the white precipitate filtered and washed with ethanol (116 g, 92%). m.p. 195°C (dec.).

2-Amino-4-chloro-5-formylthiazole (3)

This was prepared by adding the hydrochloride salt **2** (30·4g) to a cooled mixture of dimethylformamide (154 cm^3) and phosphorus oxychloride (56 cm^3) and heating the mixture at 70°C for 24 h. After adding the liquor to ice-water (240 cm^3) and hydrolysing with dilute sodium hydroxide solution (24 g in 80 cm^3) the product **3** rapidly precipitated; it was purified by repasting the cake in water and adjusting the pH to 5 with sodium acetate. The product was obtained as a yellow solid (26 g, 80%), m.p. 167–170°C (lit.[3] 167°C).

Diazotisation of 2-amino-4-chloro-5-formylthiazole (3)

Sodium nitrite (2·8 g, 0·04 mole) was added to cold concentrated sulphuric acid (30 cm^3) at such a rate that brown fumes were not evolved. After addition, the mixture was warmed gradually on a water-bath to between 65 and 70°C, when all the sodium nitrite went into solution. The solution was then cooled externally to 5°C and diluted with a mixture of propionic and acetic acid (20 cm^3 1 : 4 by volume). The aminothiazole (0·04 mole) was added gradually to the nitrosylsulphuric acid paste at 0°C with vigorous stirring and the liquor then stirred for 30 min, maintaining a temperature of 10°C. The diazo solution was then used for coupling to the various substituted anilines, as exemplified below.

General procedure for coupling diazotised aminothiazole 3 to substituted *N*,*N*-dialkylarylanilines

The arylamine (0·04 mole) was dissolved in water (400 cm^3) and 77% sulphuric acid (10 cm^3) and the diazonium liquor was added at 0°C sufficiently slowly to prevent liberation of nitrous gases. Although the solution was not buffered, coupling occurred rapidly, and after 30 min the dye was filtered off and purified by recrystallisation from toluene. Microanalytical data are given in Table 1.

General procedure for condensing dyes 4 with the pyridone derivative 1

The aldehyde dye **4** (6 mmol) and the pyridone derivative **1** (6 mmol) were refluxed in absolute ethanol (150 cm^3) for 30 min. On cooling the product often crystallised and could be filtered. In some instances, the product had good solubility in ethanol and the solutions were therefore concentrated (*in vacuo*) after cooling. The crude product was recrystallised from toluene; relevant data are shown in Table 1.

Determination of thermal and photochemical stabilities

The method adopted for the assessment of the thermal and photochemical properties of the dyes on cellulose acetate film was to cast films of cellulose acetate containing the dye in a fully dissolved state. Such films were then subjected to heat, or to photochemical treatments, and the degradation of the dye assessed by visible absorption spectroscopy. For comparative purposes, a reference blue dye **6** which had reasonable but not exceptional stability as far as textile applications were concerned, and which was readily soluble in cellulose acetate, was employed.

For photochemical stability evaluation, each film was cut into suitable pieces and mounted in a slide frame. The films, together with the standard film made with dye **6**, were irradiated for 72 h using a Microsal Fadeometer. The optical densities of the films were measured before exposing the films to the source of irradiation, and after irradiation. The difference between the two measurements, expressed as a percentage of the original optical density, corresponds to the amount of dye decomposed during exposure.

In order to assess the thermal stability of the dyes, pieces of the coloured films were sandwiched between Melinex clear films, and heated between the plates of a transfer printing press at 190°C for 1 h. From the optical density of the films before and after heating, the percentage loss of dye was calculated. Measurement of the visible spectra of the Melinex films enabled detection of any loss from the acetate film through sublimation to be made. In the event, none of the samples showed any dye transfer under the conditions used; thus, the calculated percentage loss of dye in each case represents the thermal degradation of the chromophore only.

General procedure for preparing cellulose acetate film

Cellulose acetate (2·5 g) was added to a mixture of dichloromethane/methanol (25 cm^3, 9 : 1) containing the calculated amount of dye in a beaker covered with a watch glass. The mixture was thoroughly stirred for 1·5–2 h at room temperature until a uniform solution was obtained. The film was cast on a glass sheet using a TLC spreader adjusted to a thickness of 50 μm. After casting, a similarly sized glass sheet was immediately placed over the wet film a few millimetres from its surface to prevent 'clouding' caused by moisture condensation on the surface of film due to rapid evaporation of solvent. When the film was dry, it was carefully peeled off from the glass, and kept in a vacuum desiccator for at least 3 days. The film was cut into suitable pieces and mounted in a slide frame. The films were then subjected to heat or photochemical treatments and the degradation of the dye assessed by visible absorption spectroscopy.

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