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Methine and Azamethine Dyes Derived from 2-Pyridone

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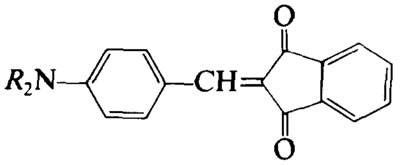
ABSTRACT

Condensation of 3-cyano-4-methyl-6-hydroxyl-1-[3'-methoxypropyl]-2-pyridone 2 with nitroso- and formyl-substituted N,N*-dialkylarylamines in ethanol at room temperature in the absence of catalyst afforded dyes giving from magenta to cyan colouration of cellulose acetate film. The visible absorption properties of the dyes were studied in different solvents and their thermal and photochemical stabilities assessed.*

INTRODUCTION

Dyes based on **1** are generally yellow to orange in colour with a high absorption intensity.[1] Replacement of one of the carbonyl groups in **1** by the more powerful electron acceptor dicyanovinyl groups results in dyes which absorb at some 70 nm to longer wavelength than **1**, but with reduced intensity.[2] Further modification of **1** by replacing the second carbonyl group by dicyanovinyl groups, and replacement of the carbon bridge by the more electronegative nitrogen, results in IR dyes absorbing up to 850 nm.[3] In this present investigation, it is shown that if the pyridone **2** is used as active methylene compound instead of 1,3-indandione and cyanovinyl analogues, violet to cyan dyes with a very broad visible absorption maxima are obtained. The dyes studied were synthesized by condensing 3-cyano-4-methyl-6-hydroxyl-1-[3'-methoxypropyl]-2-pyridone **2** in ethanol with 4-*N*,*N*-dimethylaminobenzaldehyde and 4-*N*,*N*-diethyl-3-hydroxyaminobenzaldehyde to give dyes **3** and **4**, respectively. Similarly, reactions of dimethylaminocinammaldehyde with **2** gave dye **5**. The reaction between the pyridone **2** and 4-nitroso-*N*-*N*-dialkylanilines



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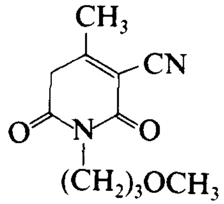

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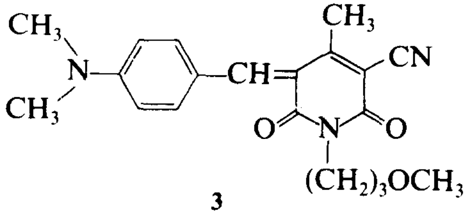

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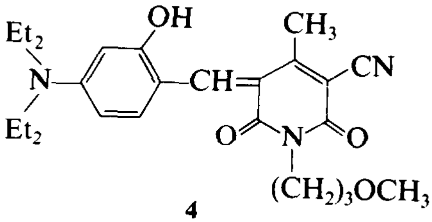

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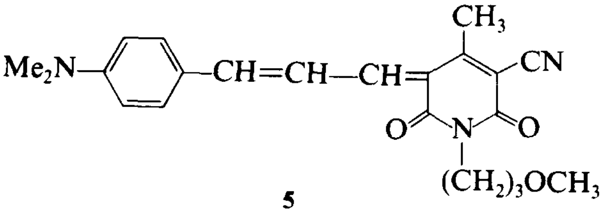

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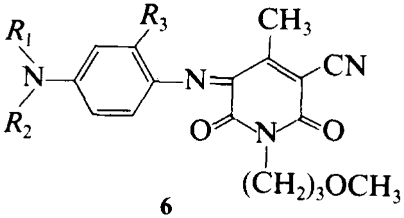

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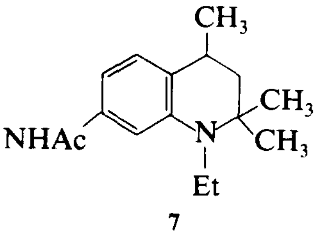
	R_1	R_2	R_3
a	Me	Me	H
b	Et	Et	H
c	Et	Et	NHAc
d	Me	Me	OH
e	Et	Et	OH
f	*n*-Pr	*n*-Pr	NHAc



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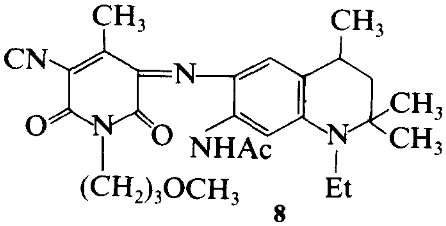

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was relatively facile and occurred in most cases within 5 min without catalyst, to give dyes **6** in quantitative yields. Similar condensation of **2** with the six-membered ring nitrosotetrahydroquinoline system **7** gave dye **8** in 60% yield.

RESULTS AND DISCUSSION

Synthesis of intermediates and dyes

3-Cyano-4-methyl-6-hydroxy-1-[3'-methoxypropyl]-2-pyridone **2** 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 **2** in good yield.

The *p*-nitroso-*N*,*N*-dialkylamines were prepared using the conventional methods found in the literature.[4,5] Thus, the amine was nitrosated with sodium nitrite in cold concentrated hydrochloric acid, and the hydrochloride salt of the product was converted to the free base by addition of sodium carbonate solution. This generally caused the nitroso compound to separate out as a dark green solid, which could be purified by recrystallization from petroleum ether.

Condensation of **2** with the appropriate 4-dialkylaminobenzaldehyde and 4-dialkylaminonitroso compounds afforded the corresponding dyes. All the dyes were recrystallized from toluene and characterized by microanalysis. Yield, melting points and characterization data are summarized in Table 1.

Electronic spectra data

The visible absorption of the dyes was measured in dichloromethane and toluene, and molar extinction coefficients calculated for the toluene solution; the results obtained are summarized in Table 2.

Dye **3**, which was obtained by condensation of **2** with 4-*N*,*N*-dimethyl aminobenzaldehyde, absorbs at 526 nm in dichloromethane, with molar extinction coefficient of $6{\cdot}61 \times 10^4$ l mol^{-1} cm^{-1}. Increasing the length of the alkyl chain by replacing the methyl group by ethyl, and further introduction of a hydroxyl group, yields dye **4**, which absorbs at 533 nm in the same solvent, viz. a bathochromic shift of 7 nm; the intensity of the resulting dyes was significantly increased from $6{\cdot}61 \times 10^4$ to $1{\cdot}09 \times 10^5$ l mol^{-1} cm^{-1}. Increase in the chain length of the vinyl group (cf. **3** with **5**) also results in a bathochromic shift. For example, dye **3** absorbs

TABLE 1
Yields and Characterization Data for the Dyes

Dye	*Yield (%)*	*Appearance*	*Melting point (°C)*	*Elemental analysis (%)*			
					C	*H*	*N*
3	85·5	Red lustrous crystals	208		($C_{20}H_{23}N_3O_3$)		
				Calc.	67·98	6·51	11·90
				Found	68·00	6·50	11·90
4	71·0	Red lustrous crystals	176		($C_{22}H_{27}N_3O_4$)		
				Calc.	66·49	6·80	10·58
				Found	66·15	6·95	10·68
5	79·0	Dark solid	215		($C_{22}H_{25}N_3O_3$)		
				Calc.	69·47	6·84	11·05
				Found	69·10	6·50	10·75
6a	89·0	Dark blue leaflets	188–190		($C_{19}H_{22}N_4O_3$)		
				Calc.	64·41	6·21	15·81
				Found	64·45	6·15	15·45
6b	93·0	Dark blue leaflets	172		($C_{21}H_{26}N_4O_3$)		
				Calc.	65·97	6·81	14·66
				Found	65·95	6·70	14·25
6c	82·0	Dark blue leaflets	205		($C_{23}H_{29}N_5O_4$)		
				Calc.	62·72	6·81	15·90
				Found	62·40	6·50	15·60
6d	65·0	Dark blue leaflets	180		($C_{19}H_{22}N_4O_4$)		
				Calc.	61·62	6·10	15·14
				Found	61·95	6·20	15·20
6e	60·0	Dark blue leaflets	182		($C_{21}H_{25}N_4O_4$)		
				Calc.	63·31	6·53	14·10
				Found	63·40	6·60	14·10
6f	65·0	Dark blue leaflets	207		($C_{25}H_{33}N_5O_4$)		
				Calc.	64·24	7·06	14·98
				Found	64·30	7·10	14·10
8	47·0	Dark blue leaflets	214		($C_{27}H_{35}N_5O_4$)		
				Calc.	65·72	7·10	14·19
				Found	65·60	7·20	14·45

at 526 nm in dichloromethane, whereas the vinylogue **5** absorbs at 612 nm, viz. a bathochromic shift of 86 nm. Dye **4** is relatively insensitive to solvent polarity; there is only a 6 nm difference between λ_{max} in dichloromethane and in toluene. This contrasts with the pronounced positive solvatochromism of **5**, where a difference in λ_{max} of 58 nm is observed in the same two solvents. Dye **4** also has a significantly narrower bandwidth

TABLE 2
Spectroscopic Data for the Dyes

Dye	λ_{max} *(nm)*		ε_{max} *(CH_2Cl_2)* *($l\ mol^{-1}\ cm^{-1}$)*	$\Delta\lambda_{max}$ *(nm)* *(CH_3Cl_2 − toluene)*
	CH_2Cl_2	*Toluene*		
3	526	508	66 100	18
4	533	527	109 850	6
5	612	554	76 470	58
6a	582	560	26 100	22
6b	586	562	28 400	24
6c	594	587	49 300	7
6d	580	568	70 000	12
6e	582	571	71 000	1
6f	597	588	49 600	9
8	610	601	48 900	9

than dye **3**. The high intensity and narrow bandwidth observed for **4** may be related to some form of intramolecular hydrogen bonding. The IR spectrum of dye **4** shows broad bands in the region of 3000 cm^{-1}, normally attributed to hydrogen bonded hydroxyl groups. The solvent insensitivity of the hydroxy-substituted dye **4**, relative to **5** and **3**, may also be attributed to strong intramolecular hydrogen bonding, which effectively limits specific interaction with polar solvents.

The introduction of an additional vinyl unit into **3** to give vinylogue **5** significantly displaces the visible absorption band to longer wavelengths. Thus dye **5** is blue and absorbs at 612 nm in dichloromethane, a bathochromic shift of *c*. 86 nm relative to **3**. The positive solvatochromism of dye **5** (*c*. 58 nm) (Table 2) shows that the dye molecule is more polar in the excited state than the ground state.

Replacement of the carbon bridge in **3** by nitrogen, as in dye **6a**, results in a displacement of the visible band from 526 to 582 nm in the same solvent. This is in agreement with simple perturbational molecular orbital theory, which predicts that any factor increasing the electronegativity at this position will cause a bathochromic shift of visible absorption bands.

Dyes **6** show the same positive solvatochromism as **3**, but the aza substitution causes a large decrease in absorption intensity, and the molar absorption coefficients of **6a** and **6b** are approximately 50–60% lower than those of the corresponding dyes **3** and **4**. However, the intensities of the *ortho* hydroxy dyes **6d** and **6e** are significantly higher relative to other dyes in the same series, and this may be attributed to intramolecular hydrogen bonding between the carbonyl oxygen atom and the hydroxy group which enhances the planarity of these dyes.

As can be seen from the data in Table 2, additional bathochromic shifts can be obtained by enhancing the electron donor properties of the arylamine ring, for example by introducing an acetylamino group *ortho* to the nitrogen bridge. Thus **6c** has λ_{max} at 594 nm, a red shift of 8 nm relative to **6b**. Alternatively, the electron-donating effect of the amino group in **6b** can be enhanced by including the nitrogen atom in a fused six-membered ring, as in the tetrahydroquinoline derivative **8**. This maximizes overlap between the lone pair orbital on the nitrogen atom and the π-electron system of the molecule. Dye **8** absorbs at 610 nm in dichloromethane, a red shift of 16 nm relative to **6c**.

Stability properties

The stabilities of the methine and azamethine dyes in cellulose acetate film were assessed using the procedures described elsewhere[6,7] and the results obtained are summarized in Table 3.

The stability of many of the dyes was very poor and in some cases significantly inferior to that of the standard reference dye. The data in Table 3 show that there is no significant effect on either the thermal or photochemical stabilities of dye **3** when the conjugation is extended by an additional vinyl group, as in dye **5**. On the other hand, introduction of a hydroxy group *ortho* to the carbon bridge, as in dye **4**, results in a dye of very poor thermal stability. The photochemical stability of this dye is, however, similar to that of other dyes in the same series (Table 3).

Replacement of the carbon bridge by nitrogen gave good stability properties relative to the standard dye, and the thermal and photochemical stabilities of some of these dyes were of a similar order to the reference

TABLE 3
Stability Properties of the Dyes

Dye	*Thermal stability (% dye decomposed)*	*Photochemical stability (% dye faded)*
Standard dye	10·0	5·3
3	21·9	13·0
4	61·8	15·4
5	23·4	14·5
6c	13·0	7·4
6d	66·7	35·0
6e	75·6	45·3
6f	12·0	6·8
8	14·2	8·3

dye. However, the introduction of the hydroxy group *ortho* to the nitrogen bridge of these dyes had a significant deleterious effect on both the thermal and photochemical stabilities of the resulting dyes, and in particular dyes **6d** and **6e** were inferior to the reference dye. Dye **8**, from the tetrahydroquinoline coupler, had good light fastness and possessed good thermal stability, similar to other dyes in the series without the hydroxy group *ortho* to the nitrogen.

CONCLUSION

3-Cyano-4-methyl-6-hydroxyl-1-[3'-methoxypropyl]-2-pyridone readily condenses with the nitroso and formyl groups of *N*,*N*-dialkylamines to give dyes ranging from violet to cyan. Increasing the length of the vinyl group of the methine dyes results in bathochromic displacement of the visible absorption band. Introduction of a hydroxyl group *ortho* to the carbon bridge or nitrogen bridge also enhances the intensities of the resulting dyes. However, aza substitution generally causes a large decrease in the intensities of the dyes. Replacement of the carbon bridge by nitrogen improves the stabilities of the dyes but the presence of the hydroxy group *ortho* to the nitrogen or carbon bridge has a significant deleterious effect on the stability properties of the dyes.

EXPERIMENTAL

3-Cyano-4-methyl-6-hydroxy-1-[3'-methoxypropyl]-2-pyridone 2

A mixture of ethylcyanoacetate (28·2 cm^3) and 3-methoxypropylamine (72 cm^3) was stirred until a clear solution was obtained, and then ethylacetoacetate (39·3 cm^3) was added. The mixture was refluxed at 110°C for 9 h. The solution was diluted with water (400 cm^3) and acidified with hydrochloric acid to give **2** as a white solid. This was filtered, washed with water and dried (44·2 g, 62%, m.p. 201°C). ν_{max} (KBr) > C=O 1660 cm^{-1}, —CN 2210 cm^{-1}.

General procedure for nitrosating *N*,*N*-dialkylaryamines

The arylamine (0·031 mol) was dissolved in concentrated hydrochloric acid (13 cm^3) and finely crushed ice was added. Sodium nitrite solution (2·25 g in 4 cm^3) was added dropwise with stirring at 5°C, and after addition the mixture was allowed to stand for 1 h. The yellow crystalline hydrochloride salt precipitated and was converted directly to the free base by dropwise addition of sodium carbonate solution (2 N) at 5°C until the paste had become dark green and the mixture was alkaline. Stirring was continued for 10 min and the precipitated dark green nitroso compound was filtered, washed with a little water followed by a mixture of ethanol–water (1 : 1). The *para*-nitroso compound was dried in a dessicator over calcium chloride. Pure samples were obtained by recrystallization from petroleum ether (60–80°C).

Condensation of 2 with 4-formyl-*N*,*N*-dialkylarylamines

A mixture of the aldehyde (6 mmol) and **2** (6 mmol) was stirred at room temperature in absolute ethanol (50 cm^3) for 30 min. The crystalline product was filtered, washed with ethanol and recrystallized from ethanol. Yields, m.p. and microanalytical data are summarized in Table 1.

Condensation of 2 with 4-nitroso-*N*,*N*-dialkylarylamines

A mixture of the nitroso compound (6 mmol) and **2** (5 mmol) in absolute ethanol (30 cm^3) was warmed to 60°C and stirred at room temperature for 30 min. The precipitated dye was filtered, washed thoroughly with ethanol and dried. In the case of dyes **6d** and **6e**, the hydrochlorides of the nitroso compounds were used. The dyes were purified by recrystallization from toluene. Yields, m.p. and microanalytical data are summarized in Table 1.

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