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Azo Dyes Derived from 4(5)-Cyano-5(4)-Hydroxyimidazole

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ABSTRACT

The synthesis of a series of azo colorants from diazotised arylamines and 4(5)-cyano-5(4)-hydroxyimidazole is described. The dyes exhibit large bathochromic shifts of visible absorption maxima relative to analogous dyes derived from carbocyclic coupling components. Some preliminary spectra data are reported.

1 INTRODUCTION

The use of heterocyclic intermediates in the synthesis of azo disperse dyes is well documented. In addition to their wide utilisation as diazo components,[1,2] industrial applications as coupling components have been mainly centred on yellow dyes derived from pyridones and pyrazolones. Other intermediates which couple in the hetero ring have also been described, typically, *N*-substituted 2-aminothiazoles,[3,4] *N*-substituted 2-aminothiophenes,[4] 2-methylindoles,[5] and 2-dialkylaminofurans.[6]

Imidazole derivatives have been extensively investigated for both colorant and pharmaceutical end-use. As diazo components in dyes, 5-amino-1-methyl-4-nitroimidazole[7] and 5-amino-2,4-dimethylimidazole[8,9] have been reported, but the main emphasis, in the context of disperse dyes, has been on 4-amino-5-cyanoimidazole[10] and, especially, 2-amino-4,5-dicyanoimidazole.[11–13] The latter compound is obtained by condensation of diaminomaleonitrile with cyanogen chloride;[14–16] its diazo compound is stated to be an explosive.[14,15]

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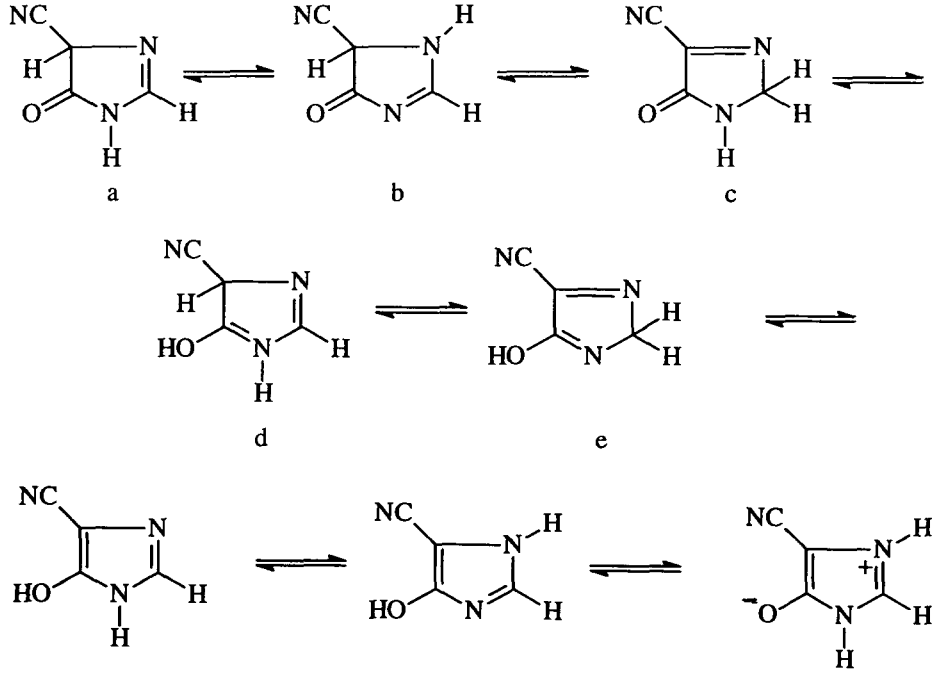
Additionally, various derivatives of 2-amino-4,5-dicyanoimidazole with *N*-substitution of the hetero atom, e.g. *N*-CH_2CN,[17,18] *N*-CH_3,[19] *N*-C_2H_5[20] and *N*-CH_2Ph,[21] and also 2-amino-4(5)-carboethoxy-5(4)-cyanoimidazole[22] have been described as useful diazo components.

Imidazole and its derivatives have also been reported in the context of their use as coupling components, e.g. imidazole,[23] 2-methylimidazole,[24,25] 4,5-alkyl/arylimidazoles,[26,27] and 4,5-diphenylimidazole.[28,29] 2-Arylazo derivatives of 4,5-dimethylimidazole absorb at *c.* 40 nm longer wavelength than isomeric 5-arylazo derivatives of 2,4-dimethylimidazole.[26]

Certain substituted 5-hydroxyimidazoles have been shown to exhibit cytotoxic activity towards viruses, bacteria and cancer cells, e.g. Bredinin,[30] an imidazole nucleoside shown by X-ray crystallography to be 4-carbamoyl-1-β-D-ribofuranosylimidazolium-5-olate,[31] and its aglycone, 4-carbamoylimidazolium-5-olate.[32] Many anologues have been similarly evaluated,[33,34] and some anticarcinogenic activity has also been reported[35] for 4(5)-cyano-5(4)-hydroxyimidazole [4(5)-cyanoimidazolium-5(4)-olate] (**I**) and for various *O*-acyl derivatives thereof.[36] Structures **Ia–h** illustrate the tautomeric forms for **I**.[37]

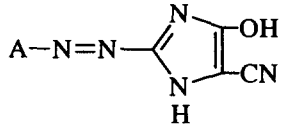


I

N-substituted derivatives of **I**, e.g. *N*-carboxylates, have fungicidal properties[38] and 2-(methyleneamino) derivatives have plant growth regulating activity.[39]

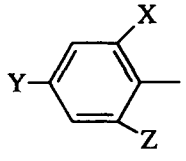
I can be obtained by dehydration of the 4-carbamoyl derivative,[35] and also via initial interaction of cyanoacetic acid and formamide.[34] It has also been obtained by initial conversion of the carbamoyl derivative to thiocarbamoyl, followed by methylation and subsequent hydrolysis to the 4-C(O)SMe derivative, treatment of which with $HgCl_2$ in the presence of methylamine gave **I** (15% yield in final stage).[40]

We report here the synthesis of, and electronic spectra for, a series of monoazo compounds **II** derived from the use of **I** as coupling component, and an initial evaluation of structure–property relationships in such compounds. (The formula **II** depicts only one of many possible tautomeric forms).



II

in which A is



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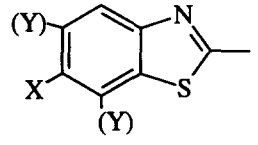

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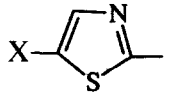

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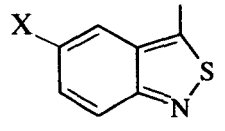


VI

2 EXPERIMENTAL

2.1 4(5)-Cyano-5(4)-hydroxyimidazole (I)

*Stage 1. 2-Cyano-*N*-formylacetamide*

Cyanoacetic acid (47·5 g, 0·5 mole) was dissolved in acetic anhydride (100 ml) by stirring at 70–75°C for 10 min. Formamide (22·5 g, 0·5 mole)

was added and the solution stirred at 80°C for 3 h. After reducing the volume (Rotavapor), an orange viscous mass resulted, which crystallised on addition of ethyl acetate (20 ml). The orange crystals were filtered, washed with ethyl acetate and then with dry ether; yield 29·6 g (48%), m.p. 118–122°C. This product was used directly in Stage 2; recrystallisation from ethyl acetate (Norit) gave, from 1 g, as first crop material, 0·8 g pale straw coloured prisms, m.p. 138–139°C (lit.[41] m.p. 139–140°C); *m/z* (EI) 112, M^+, 8%; 84, $[M\text{-}CO]^+$, 64%; 44, 100%.

Stage 2. 4(5)-cyano-5(4)-hydroxyimidazole
2-Cyano-*N*-formylacetamide (22·4 g, 0·02 mole) was stirred vigorously into ice-water (150 ml) containing sodium nitrite (14 g, 0·02 mole); whilst maintaining a temperature of 0–5°C, the liquor was adjusted to pH 4 by dropwise addition of hydrochloric acid. After stirring for a further 15 min, the temperature was allowed to rise to ambient and sodium dithionite (75 g) added (effervescence), during which time the temperature rose to 70–75°C and the liquor decolourised. After stirring at 70–75°C for 30 min, the liquor was refrigerated overnight. The resulting pale lemon-yellow crystalline product was filtered and washed with ice-cold water; yield 16·3 g (75%). Recrystallisation from water (Norit) gave colourless needles, m.p. > 360°C (darkens from 220–230°C) (lit.[34] 360°Cd); *m/z* (EI) 109, M^+, 100%; 82, M-HCN, 18%; 81, M-CO, 11%; 66, M-HCNO, 17%; 54, M-HCN-CO, 73%; 28, $[CO]^+$, 55%.

2.2 Synthesis of azo compounds II

Method A
A solution of sodium nitrite (0·7 g, 0·01 mole) in ice-water (5 ml) was added to a solution (or fine suspension) of the arylamine (0·01 mole) in ice-water (25 ml) and conc. HCl (5 ml). After stirring for 1 h, excess nitrite was removed with sulphamic acid and the liquor filtered. To the filtrate (0–5°C) was added finely powdered 4(5)-cyano-5(4)-hydroxyimidazole and the pH adjusted to 4·5–5 by addition of 10% aq. NaOH, and maintained at this value. The precipitated dye was filtered after 20 min, washed with ice-water and air-dried.

Method B
The arylamine (0·01 mole) was stirred at 20°C into nitrosylsulphuric acid prepared from sodium nitrite (0·7 g) and conc. H_2SO_4 (10 ml). After diazotising for 2 h, the liquor was stirred into ice (50 g), excess nitrite removed with sulphamic acid and finely powdered imidazole derivative (0·01 mole) added rapidly. The pH was adjusted to 4·5–5·0 by addition

of 40% aq. NaOH, during which time the product precipitated. It was filtered (rapidly) after 10–15 min and washed thoroughly with ice-water prior to drying in air.

As a variation to this method, sulphamic acid was added to the diazo liquor, followed by the coupling component. After stirring for 15 min the mixture was run rapidly into ice-water (600 ml). After the addition, during which pH was controlled around 4–5, the liquor was stirred for 5–10 min and then filtered and the product washed as above.

Method C

The appropriate heterocyclic amine (0·01 mole) was stirred into phosphoric acid (20 ml) and the suspension diluted with acetic acid 3:1 (5 ml) and cooled to 0°C. Sodium nitrite (0·7 g) was added portionwise, maintaining 0°C and diazotisation then continued for 2–3 h. After addition of sulphamic acid, the liquor was added to a vigorously stirred suspension of 4(5)-cyano-5(4)-hydroxyimidazole (1·09 g, 0·01 mole) in ice-water (60 g), maintaining the pH 4·5–5 by addition of 40% aq. NaOH. After addition was complete, the liquor was stirred for 10–15 min and the product isolated as above.

2.3 Dye purification

Where appropriate, the products were dissolved in dry acetone (minimal volume) at 0–5°C, the solution treated with activated charcoal, filtered rapidly and solvent removed immediately using a Rotavapor (ambient bath temperature). The majority of products thus obtained showed negligible contamination as shown by TLC on Eastman Chromagram Sheets, Type 13181, Silica Gel, using toluene : ethyl acetate : glacial acetic acid 7 : 2 : 3 as eluant. Some dyes, particularly those from heterocyclic and di-nitro substituted carbocyclic diazo components, showed minor traces of yellow contaminants (estimated 5%). Further purification attempts tended to be self-defeating (see Section 3). Yields of dyes were in the 65–75% region for those products obtained in high purity direct from the reaction liquor and which were not purified further (e.g. dyes from aniline, 4-anisidine, 2,4-dimethoxyaniline, 4-nitroaniline and 4-aminoacetanilide). Somewhat higher yields of other dyes (85–95%) in the crude form were obtained, reducing after purification to 70–75%. The more stable dyes gave mass spectra showing the appropriate molecular ion at 15–40% relative abundance, with high intensity ions (one of which was the base peak of the spectrum) arising from fission of the C—N bands of the azo group; typically, dye **III.1** (aniline), *m/z* (E.I.) 213, M^+, 21%; 105, 24%; 77, 100%; dye **III.5** (4-nitroaniline), *m/z* (E.I.) 258, M^+, 37%; 150, 51%;

122, 100%; dye **III.7** (2-bromo-4-nitroaniline), *m/z* (E.I.) 336, M^+, 58%; 228, 76%; 200, 100%. Other dyes tended to show the molecular ion at very low abundance, with relatively intense $[M-43]^+$ ions corresponding to loss of HCNO from the coupler residue, and base peak at *m/z* 27 (HCN).

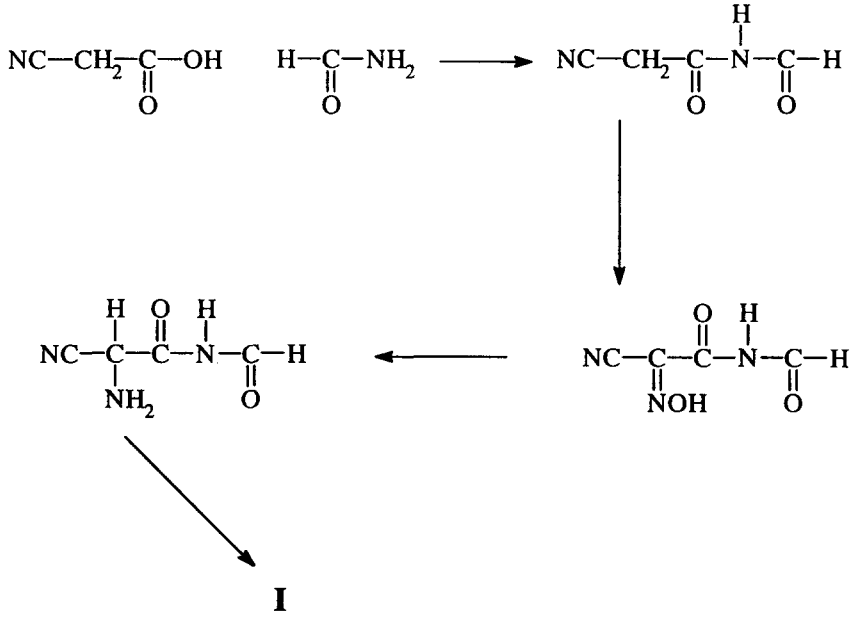
2.4 General

All reagents were of laboratory grade (Aldrich) and were used without further purification.

Mass spectra were recorded on an AEI MS902, and electronic spectra on a Philips PV8730 spectrophotometer (at dye concentrations in the region $2–3 \times 10^{-5}$ M).

3 RESULTS AND DISCUSSION

4(5)-Cyano-5(4)-hydroxyimidazole (**I**) has been prepared by dehydration of 4(5)-hydroxy-5(4)-imidazolecarboxamide,[35] which can be derived by interaction of aminomalonamide and ethyl orthoformate;[42] the C^{14} labelled analogue has also been synthesised from C^{14} carbonyl labelled aminomalonamide and ethyl formiminoester.[43] In this present investigation **I** was obtained by initial interaction of cyanoacetic acid and formamide,



Scheme 1. Synthesis of 4(5)-cyano-5(4)-hydroxyimidazole (**I**).

giving *N*-cyanoacetylformamide (Scheme 1). Previous data on this synthesis[41] report a 36% recovery of purified product. The 'crude' reaction product obtained in the present work was in 48% yield, and of sufficient purity to be used directly in the subsequent stage without the necessity of prior recrystallisation. Further reaction of *N*-cyanoacetylformamide with nitrous acid gave the hydroxyimino derivative, reduction of which with sodium dithionite afforded, via intermediate amine formation, **I** in yields (78%) of similar order to those reported[34] for conversion of the purified starting material (76%).

Tautomer possibilities for **I** are extensive and, as examples, eight different forms have been suggested for 2,4-disubstituted imidazol-5-ones[37] and also for imidazoline-5(4)-ones.[44] The extremely facile reactivity of **I** with diazonium cations would imply an appreciable amount of an enolic configuration under the pertinent reaction conditions, as has been noted for imidazol-4-ones generally.[45] Thus, instantaneous coupling occurred on addition of 4-nitroaniline, diazotised by conventional methods, to **I** in aq. NaOH; when **I** was applied in a strongly acidic environment, little coupling occurred. Whilst such coupling procedures gave azo derivatives of good homogeneity, similar couplings using arylamines which required nitrosylsulphuric acid diazotisation media gave products heavily contaminated with yellow products. Attempted removal of these by conventional column chromatography or by recrystallisation procedures only compounded the problem and resulted in extensive dye degradation. The dyes were degraded on silica gel before any effective separation could be made, and exposure to hot solvents, particularly of an ethanolic nature, tended to have a similar effect during recrystallisation.

When contamination with the yellow by-products was less extensive, it was found that their satisfactory elimination could be effected by dissolving the dyes in cold dry acetone (or ethyl acetate, or ether, or mixtures thereof), treating the solution with activated charcoal, and removing the solvent *in vacuo* at ambient temperature. This procedure was best carried out rapidly; prolonged solvent contact and/or heat application was detrimental, particularly with products derived from diazo components containing strong electron acceptor centres.

It was therefore advantageous for the generation of a range of dyes **II** that the initial diazotisation–coupling product contained minimal by-products. The procedures outlined in Section 2.2 gave such products; the coupling medium was optimised to *c.* pH 4·5–5 and the products isolated immediately coupling was complete, as even relatively short (30 min) delays in isolation resulted in increased contamination. With many heterocyclic amines and heavily electron-acceptor substituted anilines, only minimal dye remained if isolation was delayed for 1–2 h.

TABLE 1
Electronic Spectra Data for Dyes **II**

Dye	*X*	*Y*	*Z*	*Absorption in ethanol*		λ_{max} *(nm) of carbocyclic dye*[a]	$\Delta\lambda$ *(nm)*
				λ_{max} *(nm)*	$\varepsilon_{max} \times 10^4$		
III.1	H	H	H	474	3·27	397	77
III.2	H	OMe	H	477	3·12	398	79
III.3	OMe	OMe	H	500	2·99	—	
III.4	H	$NHCOCH_3$	H	488	4·11	409	79
III.5	H	NO_2	H	531	3·40	451	80
III.6	Cl	NO_2	H	554	3·61	474	80
III.7	Br	NO_2	H	555	3·74	476	79
III.8	CN	NO_2	H	576	3·49	505	71
III.9	Br	NO_2	Br	500	1·77	418	82
III.10	NO_2	NO_2	Cl	582	2·68	500	82
III.11	NO_2	NO_2	Br	583	2·44	501	82
III.12	Br	NO_2	CN	576	3·37	509	67
IV.1	H	H	H	550	2·22	495	55
IV.2	Cl	(Cl)	(Cl)[b]	556	2·85	510	46
IV.3	SO_2Me	H	H	562	3·08	516	46
IV.4	NO_2	H	H	569	3·77	527	42
V.1	H	—	—	520	2·81	471	49
V.2	NO_2	—	—	596	1·59[c]	554	42
VI.1	H	—	—	578	2·89	526	52
VI.2	NO_2	—	—	625	3·14	570	55

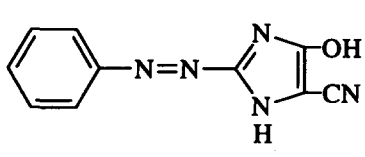
[a] Coupling component *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline; data from Refs 46–49.
[b] Isomer mixture of 5,6- and 6,7-derivatives.
[c] Absorption at 596 nm diminishes on solution standing, additional band at 536 nm appears.

Electronic spectra data for dyes **II** in absolute ethanol are shown in Table 1, together with corresponding data for dyes derived from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline, a related OH/CN substituted carbocyclic coupling component. The influence of the cyano–hydroxy substitution in the imidazole coupler is very pronounced. Dyes from imidazole are essentially yellow, e.g. 4-chloro-2-aminoanisole → imidazole, λ_{max} 384 nm.[23] The dye from 4-nitroaniline and imidazole, synthesised in this present study for reference, had λ_{max} 385 nm in ethanol; the 4-nitroaniline derivative from **I** (**III.5**) had λ_{max} 530 nm, a shift of 145 nm.

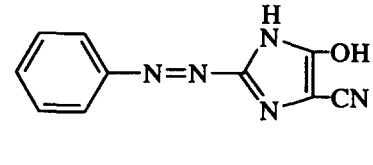
Compared with the carbocyclic analogues derived from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline, $\Delta\lambda$ values are generally of the order of 70–80 nm for most dyes, decreasing, as the electron withdrawing nature of the diazo moiety increases, to *c.* 40–50 nm for dyes derived from the thiazole based diazo components (**IV–VI**).

Within the range of diazo components used, λ_{max} values range from 474 nm (**III.1**) to 625 nm (**VI.2**), viz $\Delta\lambda$ 151 nm, compared with $\Delta\lambda$ 173 nm for analogous dyes from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline. The bathochromic shifts resulting from substitution of electron acceptor groups into the diazo component of dyes **III** are similar to those in the carbocyclic analogues, e.g. 4'-nitro, $\Delta\lambda$ 57 nm in dyes **III**, $\Delta\lambda$ 54 nm in the carbocyclic dyes; 2'-bromo-4'-nitro-6'-cyano, $\Delta\lambda$ 102 nm and 112 nm. This implies the polar effects of the substituents are similar in each series, and hence suggests an essentially azo configuration (in ethanol) for dyes **III**, although more extensive tautomerism is possible in these dyes.

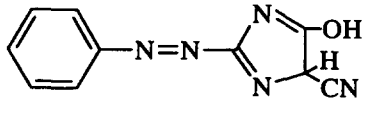
The tautomerism in imidazolones has been noted above, and this could lead to several different configurations of the azo form, typified by structures **VII–XI** for the aniline derived dye **III.1**.



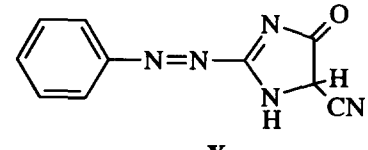
VII



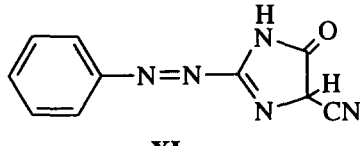
VIII



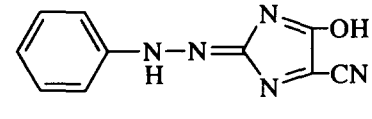
IX



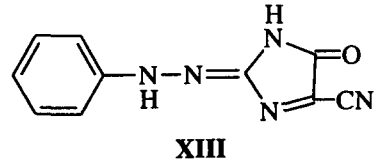
X



XI



XII



XIII

Azo–hydrazone tautomerism could give rise to structures such as **XII** and **XIII**. Increase in the electron-acceptor nature of the diazo moiety will introduce additional polar effects and also influence the relative contributions of the various possible tautomers.

Dyes **II** can be regarded as 2,4-disubstituted imidazol-5-ones and it has been noted[42] in such compounds that the 4-substituent has a major influence on the tautomeric equilibria, but that the 2-substituent has only a minor influence, and solvent effects do not greatly alter the equilibrium. However,

TABLE 2
Effect of Solvent (Dielectric Constant) on λ_{max}

Dye	*Toluene* (2·38)	*Diethyl ether* (4·34)	*Ethyl acetate* (6·02)	*Acetic acid* (6·15)	*Acetone* (20·7)	*Ethanol* (24·6)	*DMF* (36·7)	*DMSO* (46·7)	*Water* (~80)	*Formamide* (109)
III.1	536	534	485	491	494	474	512	507	461	482
III.2	565	561	510	500	512	478	514	506	460	487
III.5	532	526	482	480	571	531	588	580	506	539

in **II**, the influence of the azo moiety in the 2-position is significant, as noted above. Solvent effects are also very apparent. Table 2 illustrates changes in λ_{max} for the parent dye from aniline (**II.1**) and of representative dyes containing an electron-donor (**III.2**, 4-anisidine) and electron-attracting substituent (**III.5**, 4-nitroaniline) in a range of solvents of differing dielectric constants (all data recorded within 15 min of preparation of dye solution).

It is clearly apparent that solvent shifts are not directly relatable to solvent polarity (on the basis of dielectric constant values), and also differ significantly with substitution in the diazo component. Thus, whilst the aniline (**III.1**) and 4-anisidine (**III.2**) have λ_{max} at longer wavelength in ethyl acetate (ε = 6·02) than in formamide (ε = 109), the 4-nitroaniline based dye (**III.5**) absorbs at appreciably longer wavelength in the latter solvent. All three dyes absorb at lower wavelength in formamide than in DMSO and DMF, and in water, whilst λ_{max} is at a lower wavelength than in ethyl acetate for **III.1** and **III.2**, it is at a longer wavelength for the electron-acceptor substituted **III.5**. In the solvents of lowest dielectric constant (toluene and diethyl ether used; dyes were insoluble in cyclohexane) λ_{max} were at considerably higher wavelengths than in any other solvent used for the aniline and 4-anisidine dyes, but with the 4-nitroaniline dye, whilst λ_{max} was at longer wavelength than in e.g. ethyl acetate, it was at lower wavelength than in solvents of higher dielectric constant, although values in toluene and formamide were very similar.

Where colorants exist in both azo and hydrazone configurations, e.g. 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols, the hydrazone form has λ_{max} at the longer wavelength and can be evaluated from spectra in acetic acid relative to ethanol, in which both tautomers exist;[50] $\Delta\lambda$ values between the two forms are of the order of 60–70 nm. In dyes **III**, whilst λ_{max} are at longer wavelengths in acetic acid for the aniline (**III.1**, 17 nm) and 4-anisidine dyes (**III.2**, 22 nm), the 4-nitroaniline dye (**III.5**) is 51 nm more bathochromic in ethanol. Within the solvents used, overall variations in λ_{max} were 75 nm for **III.1** (536 nm in toluene, 461 nm in water), 105 nm

for **III.2** (565 nm in toluene, 460 nm in water) and 108 nm for **III.5** (588 nm in DMF, 480 nm in acetic acid).

It is evident that different tautomeric forms are present in different solvents, depending on the nature of both the solvent (dielectric constant and possible solute–solvent interactions) and the diazo moiety. Such factors also influence dye stability; thus, in ethanol, the 4-nitroaniline dye (**III.5**) showed, after 3 days, a significant decrease in the intensity of the long wavelength absorption band and the development of lower wavelength bands. After 1 week, only species absorbing at *c.* 440 nm were present. Further details on stability factors in different solvents will be reported later.

CONCLUSIONS

4(5)-Cyano-5(4)-hydroxyimidazole is readily sourced from the widely available precursors cyanoacetic acid and formamide. This compound couples with diazotised arylamines, giving azo derivatives showing large bathochromic shifts relative to analogous carbocyclic dyes derived from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline. The extensive possibilities of both keto–enol and azo–hydrazone tautomerism in the dyes is demonstrated by their widely divergent absorption parameters in different solvents, in several of which they degrade rapidly. Solvent effects and dye instability, with possible rapid interconversion between species, renders absolute dye characterisation in solvent media problematical; ^{1}H and ^{13}C NMR studies will be reported separately. The dyes were extensively susceptible to degradation under conventional colouration conditions used for disperse dyes on synthetic-polymer fibres, giving dull yellow to brownish-yellow dyeings, and therefore have no value in this respect.

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