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Synthesis of heteroaryl pyridone methine dyes

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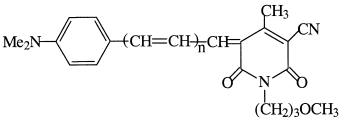
Abstract

The synthesis of furyl, thienyl and indole methine dyes derived from *N*-substituted-3-cyano-4-methyl-6-hydroxyl-2-pyridones has been achieved by condensation of pyridones with heteroaryl aldehydes. In addition, 5-amino-3-cyano-4-methyl-6-hydroxyl-1-ethyl-2-pyridone was synthesized and nitrosated to give an azamethine dye. The absorption properties of these novel cyanine dyes were investigated in various solvents. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pyridone; Methine dyes; Cyanine dyes

1. Introduction

During the past two decades, azo disperse dyes derived from 2-pyridones as coupling components (e.g. **1a** and **1b**) have proved to be important colorants [1, 2]. Disperse dyes obtained by coupling heterocyclic compounds with 2-pyridones have been reported by Nermin [3], and Bello [4] synthesized methine dyes from the condensation of pyridones with *N*,*N*-dimethylaminobenzenealdehydes (e.g. **2**). Würthner [5] simplified the required two steps, formylation and condensation, by developing a one-pot synthesis involving a DMF/Ac_2O medium (Fig. 1), but the starting material was limited to highly electron-rich aromatic compounds.



So far little attention has been paid to polymethine dyes derived from heteroaryl aldehydes. Such compounds are of interest because they should possess absorptions at long wavelengths and high molar extinction coefficients. In the present study, new pyridone polymethine dyes **5a–5f**, **6a–6d**, and **7a–b** were prepared by condensing pyridones with furyl, thienyl and indole aldehydes **2a–2c**, **3a–b**, **4** in alcohol. The furyl, thienyl and indole systems were chosen because of their wide availability and relatively high reactivity. The solubility and spectroscopic characteristics of methine dyes from **1a** and **1b** were compared. In addition, intermediate **8** was synthesized, nitrosated, and condensed with pyridone **1a** to give azamethine dye **9**.

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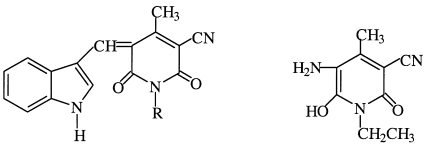
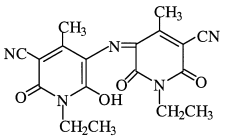


7a R=C_2H_5, **7b** R=$C_{12}H_{25}$

8



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2. Results and discussion

2.1. Syntheses

N-Substituted-3-cyano-4-methyl-6-hydroxy-2-pyridones were prepared by condensing ethylcyanoacetate and ethylamine or dodecylamine at 120 °C [6]. The products were purified by recrystallisation from alcohol/water.

Thiophene-2-aldehyde and indole-3-aldehyde were prepared using the conventional Vilsmier reaction [7,8]. Fufural, thiophene-2-aldehyde reacted with acetoaldehyde to give 2-furyl and thienyl acrolein [9,10]. 5-(2-Furyl)-2,4-pentadienal was also synthesized from acetoaldehyde and fufural [9].

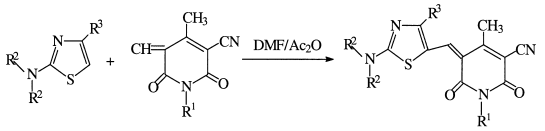


Fig. 1. One-pot synthesis of methine dyes [5].

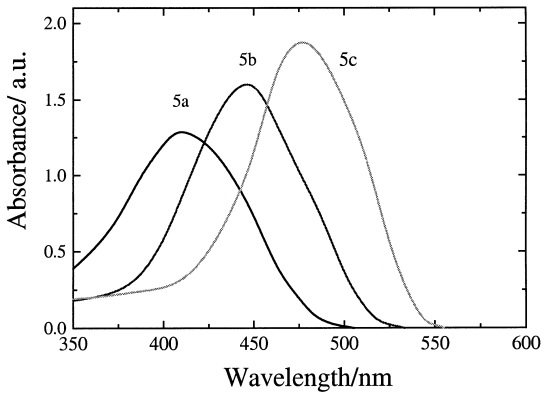
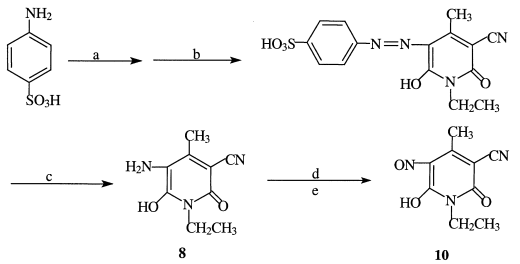


Fig. 2. Absorption spectra of dyes **5a**, **5b**, and **5c** in acetone (2×10^5 M).

The aminohydroxypyridone **9** was synthesized by a variant of a previously described method [11], which involves the intermediacy of azo compound **8** (Scheme 1). The nitroso pyridone **10** was prepared by a modification of a known procedure [12]. The product of the final step was converted to free base upon treatment with sodium carbonate solution. The target methine and azamethine dyes were obtained by condensation of the appropriate aldehydes or nitroso pyridone with *N*-substituted-3-cyano-4-methyl-6-hydroxyl-2-pyridones at room temperature.

2.2. Absorption spectral data

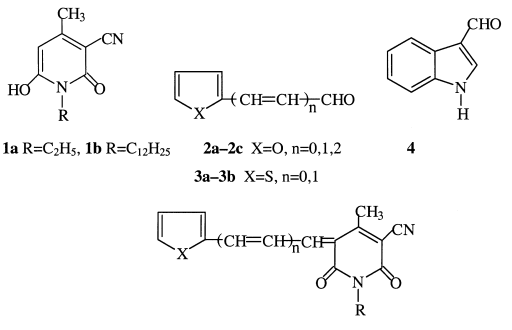
The absorption spectral data recorded on dyes prepared in this study are listed in Table 2, and they show the pronounced bathochromic effects of introducing a polymethine chain. Dye **5a**, which was obtained by condensation of **1a** with fufural, absorbed at 405 nm in acetone. Increasing the length of the conjugated system by replacing fufural with 2-furyl acrolein yielded dye **5b**, which absorbed at 448 nm with a molar extinction coefficient of 7.9×10^4. Further increases in λ_{max} and ε_{max} were achieved by extending the conjugated system using 5-(2-furyl)-2,4-pentadienal (shown in Fig. 2). It has been reported that the aggregation of azacyanine dyes in solution caused band broadening and a decrease in λ_{max} [13]. In the present study, we found that fufural-based dyes also afforded narrower absorption bands and longer λ_{max}, as the number of the vinyl groups was increased. The half-



8 **10**

Scheme 1. (a) HCl/$NaNO_2$, 0–5 °C; (b) NaOH/1a; (c) NaOH/$Na_2S_2O_4$, rt; (d) HCl/$NaNO_2$, 0–5 °C; (e) Na_2CO_3/H_2O.

bandwidths for dyes **5a**, **5b** and **5c** were 60, 75 and 95 nm, respectively, which suggests that aggregation decreased in solution as chain length increased. Similar results were obtained in the thiophene series, as a 36 nm difference existed between the λ_{max} values for **6a** and **6b**.



1a R=C_2H_5, **1b** R=$C_{12}H_{25}$ **2a–2c** X=O, n=0,1,2 **4**

3a–3b X=S, n=0,1

5a–5c X=O, n=0,1,2 R=C_2H_5 **5d–5f** X=O, n=0,1,2 R=$C_{12}H_{25}$

6a–6b X=S, n=0,1 **6c–6d** X=S, n=0,1

Replacement of *N*-ethyl in the pyridone moiety with a dodecyl group also shifted the absorption maximum to slightly longer wavelengths. For instance, dye **5f** absorbed at 10 nm higher than **5c**. In Table 2, it can be seen that the indole system caused a bathochromic effect of approximately 40 nm relative to the furan and thiophene systems. Replacement of the O-atom with an S-atom resulted in a modest bathochromic shift (2–9 nm). Based on MO calculations, we know that molecular planarity was altered significantly by this substitution, leading to a decrease in λ_{max}. The furan and thiophene based methine dyes exhibited a negative solvatochromism, with a 24 nm red shift in λ_{max} in chloroform versus acetone. The spectra of indole based dyes **7a** and **7b** did not exhibit such a solvent dependence.

Based on perturbation theory it was anticipated that the replacement of the terminal CH moiety by an N-atom would cause a bathochromic shift. To confirm these theoretical results, we synthesized dye **9** from aminopyridone **8**. The resultant dye had λ_{max} at 584 nm in acetone, which surpassed most of its analogs. The results in Table 2 indicate that dye **9** was sensitive to solvent polarity. It was also found that an increase in solvent polarity (dielectric constant) resulted in an increase in λ_{max} (Table 3). This behavior indicates that the excited state of dye **9** was stabilized by interactions with polar solvents.

3. Experimental

^{1}H NMR spectra were recorded on Brüker DRX instrument at 300 and 500 MHz, and EI mass spectra (70 eV) were recorded using a Hitachi M-1108 spectrometer. UV/visible absorption spectra were recorded on a Perkin Elmer 40P instrument and an Italy MOD 1106 analyzer was used for element analysis.

3.1. 3-Cyano-4-methyl-6-hydroxyl-1-ethyl-2-pyridone (***1a***) *[6]*

A mixture of ethylcyanoacetate (10 ml, 0.1 mol) and ethylamine (25.9 g, 0.3 mol, 60–70%) was stirred until a solution was obtained, and then ethylacetoacetate (12.5 ml, 0.1 mol) was added. The mixture was stirred under reflux for 8 h at 120 °C and then cooled to room temperature. The solution was diluted with water (100 ml) and acidified with hydrochloric acid (20%) to give **1a** as a white solid. The mixture was filtered, and the solid was washed with water and dried. Purification by recrystallisation from alcohol gave an 81% yield. IR: ν_{max} (KBr): –C=O 1658 cm^{-1}, –CN 2210 cm^{-1}

3.2. 3-Cyano-4-methyl-6-hydroxy-1-dodecyl-2-pyridone (**1b**)

The preparation of **1b** employed the procedure described above for **1a**. Purification by recrystallisation from alcohol/water (1:1) afforded a 78% yield. IR: ν_{max} (KBr): –C=O 1655 cm^{-1}, –CN 2210 cm^{-1}

3.3. 2-Furyl acrolein (***2b***) *[7]*

Fufural (9.6 g, 0.1 mol) was added to aqueous acetaldehyde (20 ml, 40%) and the solution was added dropwise to sodium hydroxide (60 ml, 8%) over 2 h, with vigorous stirring at 0 °C. The reaction mixture was stirred for another hour at this temperature and the precipitate was collected by filtration, washed with cold water, and dried to give 11.3 g crude product. Purification by vacuum distillation gave 9.5 g **2b** (78%), b.p. 94–97 °C (9 mmHg).

Table 1
Data for the methine and azamethine dyes prepared in this study

Dye	Yield (%)	Appearance	Melting point (°C)	Elemental analysis		C	H	N
5a	95	Yellow needles	176–178	$C_{14}H_{12}N_2O_3$	Calcd	65.62	4.72	10.93
					Found	65.57	4.63	10.97
5b	96	Dark red needles	214–216	$C_{16}H_{14}N_2O_3$	Calcd	68.08	5.00	9.92
					Found	68.16	5.08	9.99
5c	95	Dark green leaflets	181–182	$C_{18}H_{16}N_2O_3$	Calcd	70.12	5.23	9.09
					Found	70.05	5.15	9.01
5d	97	Yellow needles	159–160	$C_{24}H_{32}N_2O_3$	Calcd	72.70	8.13	7.06
					Found	72.50	8.19	6.99
5e	96	Dark red needles	173–175	$C_{26}H_{34}N_2O_3$	Calcd	73.90	8.11	6.63
					Found	73.81	8.17	6.51
5f	94	Dark green leaflets	136–138	$C_{28}H_{36}N_2O_3$	Calcd	74.97	8.09	6.24
					Found	75.03	8.01	6.20
6a	95	Yellow needles	228–229	$C_{14}H_{12}N_2O_2S$	Calcd	61.75	4.44	10.29
					Found	61.71	4.41	10.22
6b	96	Dark red needles	216–217	$C_{16}H_{14}N_2O_2S$	Calcd	64.41	4.73	9.39
					Found	64.59	4.71	9.49
6c	97	Yellow needles	158–159	$C_{24}H_{32}N_2O_2S$	Calcd	72.95	8.08	3.40
					Found	72.89	8.02	3.32
6d	95	Dark red needles	158–161	$C_{26}H_{34}N_2O_2S$	Calcd	71.20	7.81	6.39
					Found	71.05	7.74	6.34
7a	96	Yellow powder	252–253	$C_{18}H_{15}N_3O_2$	Calcd	74.98	5.30	9.20
					Found	74.87	5.21	9.15
7b	96	Red powder	> 300	$C_{28}H_{35}N_3O_2$	Calcd	75.47	7.92	9.43
					Found	75.38	7.83	9.39
9	94	Dark green needles	187–188	$C_{18}H_{17}N_5O_4$	Calcd	58.85	4.66	19.06
					Found	58.79	4.57	19.02

3.4. 5-(2-Furyl)-2,4-pentadienal (***2c***) *[9]*

Fufural (24.0 g, 0.25 mol) was added to sodium hydroxide (500 ml, 7.5%), and aqueous acetaldehyde (50 ml, 40%) was added at 20 °C over 2.5 h with vigorous stirring. Following neutralization with cold acetic acid, the mixture was extracted with ether. The extract was washed with water and dried over anhydrous sodium sulfate. Solvent removal and vacuum distillation of the dark red oil gave 22.5 g (61%) **2c**, b.p. 130–150 °C (16 mmHg).

3.5. Thiophene-2-aldehyde (***3a***) *[9]*

A solution of thiophene (21.0 g, 0.25 mol) and DMF (23.0 g, 0.32 mol) was stirred under a reflux condenser equipped with a calcium chloride drying

Table 2
Absorption spectral data for some methine and azamethine dyes

Dye	λ_{max} (nm)		ε_{max} (in CH_3COCH_3)
	$CHCl_3$	CH_3COCH_3	(1 mol^{-1} cm^{-1})
5a	417	405	64,000
5b	458	448	79,000
5c	498	474	91,200
5d	418	410	27,200
5e	459	453	30,600
5f	500	484	39,100
6a	420	414	41,000
6b	462	450	46,500
6c	421	416	31,700
6d	464	453	34,400
7a	467	467	75,500
7b	468	469	33,800
9	506	584	33,200

tube as phosphorus oxychioride (48 g, 0.31 mol) was added slowly. The reaction mixture was carefully heated at 90 °C for 3 h using a steam bath, cooled, and then poured into a beaker containing 300 g cracked ice. The solution was neutralized by adding saturated sodium acetate and the oily layer was extracted into diethyl ether. The ether solution was washed free of all traces of acid using sodium bicarbonate solution (5%), dried with anhydrous sodium sulfate, and concentrated. Vacuum distillation of the red oil gave 20.5 g (73%) **3a**, b.p. 66–68 °C (4 mmHg).

3.6. 2-Thienyl acrolein (*3b*) [10]

Sodium hydroxide (5 g) was dissolved in ethyl alcohol (60 ml) and water (120 ml), and freshly distilled thiophene-2-aldehyde (22.5 g, 0.22 mol) was added over 15 min. Aqueous acetaldehyde (50 g, 40%) was added at 0 °C over 3 h with vigorous stirring. The reaction mixture was held at this temperature for an additional 15 min. Following neutralization with ice-cold acetic acid the mixture was extracted with diethyl ether, and the extract was washed with water and dried over anhydrous sodium sulfate. Vacuum distillation yielded 15 g (54%) **3b**, b.p. 122–130 °C (16 mmHg).

3.7. Indole-3-aldehyde (*4*) [8]

Freshly distilled phosphorus oxychioride (5.5 ml, 0.26 mol) was added with stirring to freshly distilled DMF (18 ml) over a 30 min period, with cooling via an ice-salt bath. To the resultant yellow colored formylation complex was added a solution of indole (6.25 g, 0.052 mol) in DMF (7 ml) over 1 h, at a rate such that the temperature did not rise above 10 °C. Once the solution was well mixed, the temperature of the viscous solution was raised to 35 °C and the reaction mixture was stirred efficiently for 1 h. At that point, crushed ice (40 g) was added to the stirred mixture, giving a clear solution. A solution of sodium hydroxide (40 ml, 37%) was added dropwise with stirring and the resultant suspension was heated rapidly to the boiling point and allowed to cool to room temperature. Refrigeration overnight gave a precipitate that was collected, washed with water and dried, yielding 7.2 g (95%) **4**, m.p. 196–198 °C.

3.8. Condensation of *1a/1b* with heteroaryl aldehydes

A mixture of the aldehyde (5 mmol) and **1a**/**1b** (5 mmol) was stirred at room temperature in absolute ethanol (40 ml) for 2 h. The product was collected, washed with ethanol and recrystallised from acetone. Yields, m.p., NMR and combustion data for the products are summarised in Tables 1 and 4.

Table 3
The absorption maximum (λ_{max}) of dye **9** in various solvents

Solvents	Chloroform	Ethyl acetate	Propanol	Acetone	DMF
Dielectric constant [14]	4.8	6.0	20.3	20.7	36.7
λ_{max} (nm)	506	566	574	584	586

Table 4
^{1}H NMR spectral data of the methine dyes

Dye	^{1}H NMR (300/500 MHz) (CD_3COCD_3)
5a	8.68 (*d*, 1H, *J* = 2.2 Hz, fur-H), 8.22 (*d*, 1H, *J* = 3.3 Hz, fur-H), 7.92 (*s*, 1H, –CH=), 6.93 (*dd*, 1H, *J* = 3.4, 1.9 Hz, fur-H), 3.97 (*q*, 2H, CH_2), 2.68 (*s*, 3H, CH_3), 1.17 (*t*, 3H, CH_3)
5b	8.58 (*dd*, 1H, *J* = 15.2, 11.9 Hz, –CH=), 7.90 (*d*, 1H, *J* = 2.4 Hz, fur-H), 7.87 (*d*, 1H, *J* = 11.3 Hz, –CH=), 7.52 (*d*, 1H, *J* = 15.3 Hz, –CH=), 7.06 (*d*, 1H, *J* = 3.5 Hz, fur-H), 6.73 (*dd*, 1H, *J* = 3.5, 1.8 Hz, fur-H), 3.95 (*q*, 2H, CH_2), 2.58 (*s*, 3H, CH_3), 1.16 (*t*, 3H, CH_3)
5c	8.25 (*dd*, 1H, *J* = 14.5, 11.9 Hz, –CH=), 7.82 (*d*, 1H, *J* = 12.2 Hz, –CH=), 7.76 (*d*, 1H, *J* = 1.7 Hz, fur-H), 7.48 (*m*, 1H, –CH=), 7.03–7.15 (*m*, 2H, –CH=), 6.83 (*d*, 1H, *J* = 3.4 Hz, fur-H), 6.63 (*dd*, 1H, *J* = 3.4, 1.8 Hz, fur-H), 3.92 (*q*, 2H, CH_2), 2.57 (s, 3H, CH_3), 1.15 (*t*, 3H, CH_3)
5d	8.68 (*d*, 1H, *J* = 2.3 Hz, fur-H), 8.22 (*d*, 1H, *J* = 3.3 Hz, fur-H), 7.92 (*s*, 1H, –CH=), 6.93 (*dd*, 1H, *J* = 3.4, 1.9 Hz, fur-H), .91 (*q*, 2H, CH_2), 2.58 (*s*, 3H, CH_3), 1.23–1.55 (*m*, 20H, CH_2), 0.87 (*t*, 3H, CH_3)
5e	8.56 (*dd*, 1H, *J* = 15.0, 11.9 Hz, –CH=), 7.91 (*d*, 1H, *J* = 2.5 Hz, fur-H), 7.89 (*d*, 1H, *J* = 11.8 Hz, –CH=), 7.50 (*d*, 1H, *J* = 15.3 Hz, –CH=), 7.06 (*d*, 1H, *J* = 3.5 Hz, fur-H), 6.73 (*dd*, 1H, *J* = 3.5, 1.7 Hz, fur-H), 3.91 (*q*, 2H, CH_2), 2.58 (*s*, 3H, CH_3), 1.23–1.55 (*m*, 20H, CH_2), 0.87 (*t*, 3H, CH_3)
5f	8.25 (*dd*, 1H, *J* = 14.7, 11.8 Hz, –CH=), 7.82 (*d*, 1H, *J* = 12.2 Hz, –CH=), 7.76 (*d*, 1H, *J* = 1.7 Hz, fur-H), 7.48 (*m*, 1H, –CH=), 7.03–7.15 (*m*, 2H, –CH=), 6.83 (*d*, 1H, *J* = 3.5 Hz, fur-H), 6.63 (*dd*, 1H, *J* = 3.5, 1.8 Hz, fur-H), 3.91 (*q*, 2H, CH_2), 2.58 (*s*, 3H, CH_3), 1.23–1.55 (*m*, 20H, CH_2), 0.87 (*t*, 3H, CH_3)
6a	8.51 (*s*, 1H, –CH=), 8.29 (*d*, 1H, *J* = 5.1 Hz, thio-H), 8.18 (*d*, 1H, *J* = 3.4 Hz, thio-H), 7.42 (*dd*, 1H, *J* = 5.0, 4.1 Hz, thio-H), 4.01 (*q*, 2H, CH_2), 2.71 (*s*, 3H, CH_3), 1.19 (*t*, 1H, CH_3)
6b	8.58 (*dd*, 1H, *J* = 15.1, 11.5 Hz, –CH=), 7.95 (*d*, 1H, *J* = 3.5 Hz, thio-H), 7.88 (*d*, 1H, *J* = 5.2 Hz, thio-H), 7.85 (*d*, 1H, *J* = 12.1 Hz, –CH=), 7.58 (*d*, 1H, *J* = 14.9 Hz, –CH=), 7.25 (*dd*, 1H, *J* = 4.9, 3.9 Hz, thio-H), 3.95 (*q*, 2H, CH_2), 2.70 (*s*, 3H, CH_3), 1.17 (*t*, 1H, CH_3)
6c	8.50 (*s*, 1H, –CH=), 8.28 (*d*, 1H, *J* = 5.1 Hz, thio-H), 8.18 (*d*, 1H, *J* = 3.4 Hz, thio-H), 7.41 (*dd*, *J* = 5.0, 3.9 Hz, 1H, thio-H), 3.96 (*q*, 2H, CH_2), 2.70 (*s*, 3H, CH_3), 1.23–1.42 (*m*, 20H, CH_2), 0.88 (*t*, 3H, CH_3)
6d	8.58 (*dd*, 1H, *J* = 15.1, 11.5 Hz, –CH=), 7.93 (*d*, 1H, *J* = 3.5 Hz, thio-H), 7.88 (*d*, 1H, *J* = 5.1 Hz, thio-H), 7.84 (*d*, 1H, 1H, *J* = 12.0 Hz, –CH=), 7.58 (*d*, 1H, *J* = 14.8 Hz, –CH=), 7.26 (*dd*, 1H, *J* = 4.9, 3.9 Hz, thio-H), 3.94 (*q*, 2H, CH_2), 2.69 (*s*, 3H, CH_3), 1.23–1.40 (*m*, 20H, CH_2), 0.86 (*t*, 3H, CH_3)
7a (DMSO-d_6)	9.62 (*s*, 1H, ind-H), 8.31 (*s*, 1H, –CH=), 7.32–8.18 (*m*, 4H, ind-H), 3.98 (*q*, 2H, CH_2), 2.67 (*s*, 3H, CH_3), 1.14 (*t*, 3H, CH_3)
7b (DMSO-d_6)	9.60 (*s*, 1H, ind-H), 8.39 (*s*, 1H, –CH=), 7.36–8.10 (*m*, 4H, ind-H), 3.90 (*q*, 2H, CH_2), 2.75 (*s*, 3H, CH_3), 1.23–1.29 (*m*, 20H, CH_2), 0.84 (*t*, 3H, CH_3)

*3.9. 5-Amino-3-cyano-4-methyl-6-hydroxyl-1-ethyl-2-pyridone (**8**)*

This compound was prepared from **1a** by a procedure similar to that described for the synthesis of *o*-xyloquinone [11]. Sulfanilic acid (10 g, 0.0575 mol) was dissolved in a solution of sodium carbonate (4.0 g) in water (40 ml) with slight heating when necessary. The resultant solution was cooled to 15 °C and a solution of sodium nitrite (4.2 g, 0.061 mol) in water (15 ml) was added. The mixture was poured into a beaker

containing conc. HCl (25 ml) and ice (60 g). This gray diazo salt mixture was left in an ice-water bath for 10–20 min while a solution of **1a** (10.3 g. 0.0575 mol) and sodium hydroxide (2.5 g) in water (40 ml) was prepared and cooled below 5 °C. Then the cold diazo salt suspension was slowly added with stirring to the cold alkaline pyridone solution. The mixture was allowed to stand for 3 h and then was diluted with sodium hydroxide (40%) until a clear solution was obtained. Sodium hydrosulfite (34 g, 0.2 mol) added in three portions and stirring was continued until the solution became light yellow. Hydrochloric acid (20%) was added to neutralize the excess sodium hydroxide and the precipitate was collected, washed with water and dried. The crude product was purified by heated with ethanol/acetone (1:1) to give **8** (76%). MS (*m*/*z*, rel. int.): 193 (M^+, 11), 165 (11), 94 (33), 93 (34), 77 (12), 67 (28), 66 (22), 52 (19), 44 (33); Anal. Calcd for $C_9H_{11}N_3O_2$: C, 55.90, N, 21.75, H, 5.74. Found C, 55.80, N, 21.48, H, 5.62.

3.10. Synthesis of compound *10* [12]

Compound **8** (1.93 g, 0.01 mol) was dissolved in a solution of sodium hydroxide (0.4 g) in water (15 ml) and acetic acid (3 ml) was added. A solution of sodium nitrite (0.7 g) in water (5 ml) was added dropwise over 15 min at a temperature below 5 °C. The mixture was stirred for 1 h and the yellow crystalline diazonium salt was converted to the free base by a dropwise addition of sodium carbonate (2 N) at 5 °C until the mixture became alkaline. Stirring was continued for 10 min and the precipitated dark green nitroso compound (**10**) was collected, washed with a little water and with ethanol/water (1:1). The product was dried in a dessicator over calcium chloride.

3.11. Synthesis of dye *9*

A mixture of nitroso compound **10** (1.0 g. 5 mmol) and **1a** (0.9 g, 5 mmol) in absolute ethanol (30 ml) was warmed to 60 °C and stirred at room temperature for 3 h. The precipitated dye was collected, washed with ethanol, and dried. Dye **9** was purified by recrystallisation from ethanol. ^{1}H NMR (500 MHz, CD_3COCD_3): 3.98 (*q*, 4H, CH_2), 2.57 (*s*, 6H, CH_3), 1.17 (*t*, 6H, CH_3). MS (EI, %): 204 (12), 203 (100), 202 (21), 177 (43), 175 (21), 133 (11), 76 (17)

4. Conclusions

Furyl, thienyl, and indole methine dyes can be conveniently prepared from *N*-substituted-3-cyano-4-methyl-6-hydroxyl-2-pyridones. As would be anticipated, these dyes display increasing λ_{max} and ε_{max} with increasing number of vinyl groups. The furan and thiophene structures exhibit a negative solvatochromism as solvent polarity increases. A nearly symmetrical azamethine dye was found to absorb at a much higher wavelength than the corresponding methine dyes, and its λ_{max} correlates with the dielectric constants of the solvents employed.

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