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Synthesis and Colour Assessment of Some 3-Cyano-4-Pyrenyl-6-Substituted-2-Pyridone Derivatives

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ABSTRACT

A series of 3-cyano-4-pyrenyl-6-substituted-2-pyridone derivatives was prepared by the cyclization of ethyl 2-cyano-3-pyrenyl acrylate with aryl methyl ketones in the presence of ammonium acetate. The structures of the compounds were confirmed by spectral and element analysis. The fluorescence and colour parameters of the 3-cyano-4-pyrenyl-6-substituted-2-pyridones were also investigated.

1 INTRODUCTION

In a previous paper[1] we have reported that 3-acetylpyrene as starting material reacted with ethyl 2-cyano-3-substituted acrylate to give a series of 3-cyano-4-substituted-6-pyrenyl-2-pyridone derivatives, which exhibited a greenish-blue to green fluorescence. We report here on some new substituted pyridone derivatives using 3-pyrenecarbaldehyde as starting material; this was synthesized from pyrene and dichloromethyl methyl ether by Friedel-Crafts reaction. Ethyl 2-cyano-3-pyrenyl acrylate, a derivative of 3-pyrenecarbaldehyde, reacted with various ketone compounds to give a series of 3-cyano-4-pyrenyl-6-substituted-2-pyridone derivatives. These compounds were applied as disperse dyes on polyester fabrics and their colour properties were studied.

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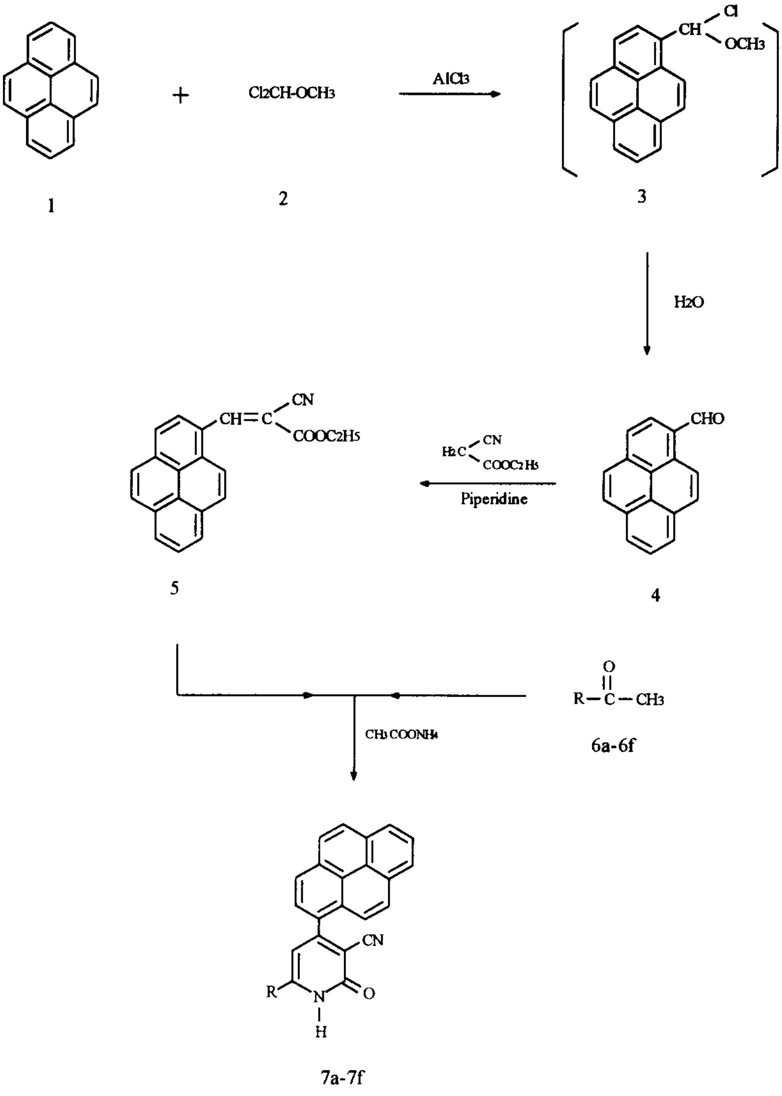
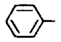
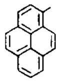
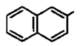


Compound	R	Compound	R
6a 7a		6d 7d	
6b 7b		6e 7e	
6c 7c		6f 7f	

Scheme 1

2 RESULTS AND DISCUSSION

2.1 Preparation and spectral characteristics

The preparation of the 3-cyano-4-pyrenyl-6-substituted-2-pyridones (**7a–7f**) is shown in Scheme 1.

Rieche *et al.*[2] reported the introduction of an aldehyde group using dichloromethyl-alkyl ethers in presence of a Friedel-Crafts catalyst in methylene chloride as solvent. The reaction of pyrene (**1**) with dichloromethyl methyl ether (**2**) in the presence of aluminium chloride gave the precursor **3**, which was then hydrolysed to give 3-pyrenecarbaldehyde (**4**). Ethyl 2-cyano-3-pyrenyl acrylate (**5**) was prepared by condensation of compound **4** with ethyl cyanoacetate; cyclisation of this with ketones (**6a–6f**) in the presence of excess ammonium acetate gave the 3-cyano-4-pyrenyl-6-substituted-2-pyridones (**7a–7f**).

The IR spectra of compounds **4** and **5** showed characteristic carbonyl absorption at 1680 cm^{-1} and 1718 cm^{-1} and their ^{1}H-NMR spectra in $CDCl_3$ showed a 1H doublet at δ = 9·19–9·22 ppm and 8·81–8·84 ppm, attributed to the proton at the 2-position of the pyrene ring.[3]

The IR spectra of the 3-cyano-4-pyrenyl-6-substituted-2-pyridones (**7a–7f**) showed a sharp absorption band at 2219–2222 cm^{-1} corresponding to the cyano group in the pyridone ring. Compounds **7a–7f** can be considered to exist in two tautomeric forms. In the IR spectra, the strong absorption at 1635–1650 cm^{-1} could be assigned to the carbonyl group signal of the lactam form. However, the ^{1}H-NMR spectra (DMSO-d_6) showed a broad signal at δ = 12·49–13·32 ppm, attributed to the OH proton of the enolic form.[4] A singlet at δ = 6·77–7·16 ppm is attributed to the 1H at the 5-position of pyridone ring. Spectral data for compounds **4**, **5** and **7a–7f** are listed in Table 1.

2.2 Absorption and fluorescence in DMF

The absorption and fluorescence emission maxima of 3-cyano-4-pyrenyl-6-substituted-2-pyridones (**7a–7f**) in dimethylformamide are listed in Table 2. The absorption of compounds **7c–7f** resulted in a bathochromic shift with respect to compound **7a**. The presence of a naphthyl group (in **7b**) at the 6-position of the pyridone ring resulted in a hypsochromic shift. Compound **7e**, with a pyridyl group on the pyridone ring, showed the lowest fluorescence emission wavelength at 482 nm in DMF, while the presence of a naphthyl group (in **7b**), fluorenyl group (in **7c**) and pyrenyl group (in **7d**) resulted in a green fluorescence emission in the range 498–505 nm.

TABLE 1

IR and ^{1}H NMR of 3-Pyrenecarbaldehyde (**4**), Ethyl 2-Cyano-3-Pyrenyl Acrylate (**5**) and 3-Cyano-4-Pyrenyl-6-Substituted-2-Pyridones (**7a–7f**)

Compound number	*IR* ν *KBr (cm^{-1})*	*^{1}H-NMR: δ (ppm) (DMSO-d_6)*	
4	1680 [—C=O]	7·88–8·25	[m, 8H, pyrene]
		9·19–9·22	[d, 1H, H-2 on pyrene]
		10·63	[s, 1H, CHO on pyrene] (CDCl$_3$)
5	1718 [—C=O]	1·43–1·48	[t, 3H, —CH$_2$—$\underline{\text{CH}_3}$]
	2215 [—C≡N]	4·43–4·50	[q, 2H, —$\underline{\text{CH}_2}$—CH$_3$]
		8·02–8·31	[m, 8H, pyrenyl]
		8·81–8·84	[d, 1H, H-2 on pyrene]
		9·33	[s, 1H, —CH=C—] (CDCl$_3$)
7a	1647 [—C=O]	6·97	[s, 1H, 5-position on pyridone]
	2219 [—C≡N]	7·49–7·93	[m, 5H, phenyl on pyridone]
		8·05–8·45	[m, 9H, pyrenyl]
		12·98	[br, 1H, OH on pyridone]
7b	1635 [—C=O]	7·16	[s, 1H, 5-position on pyridone]
	2222 [—C≡N]	7·59–9·06	[m, 16H, naphthyl and pyrenyl]
		13·07	[br, 1H, OH on pyridone]
7c	1650 [—C=O]	7·04	[s, 1H, 5-position on pyridone]
	2220 [—C≡N]	7·39–8·94	[m, 18H, fluorenyl and pyrenyl]
		13·21	[br, 1H, OH on pyridone]
7d	1649 [—C=O]	6·77	[s, 1H, 5-position on pyridone]
	2219 [—C≡N]	8·05–8·52	[m, 18H, two pyrenyl]
		13·32	[br, 1H, OH on pyridone]
7e	1646 [—C=O]	7·16	[s, 1H, 5-position on pyridone]
	2222 [—C≡N]	7·47–7·50	[d, 1H, H-3 on pyridine]
		7·56–7·59	[q, 1H, H-5 on pyridine]
		7·97–8·46	[m, 9H, pyrenyl]
		8·75–8·76	[d, 1H, H-6 on pyridine]
		12·49	[br, 1H, OH on pyridone]
7f	1640 [—C=O]	6·77–6·79	[q, 1H, H-4 on furan]
	2222 [—C≡N]	6·90	[s, 1H, 5-position on pyridone]
		7·68–7·70	[d, 1H, H-3 on furan]
		7·98–7·99	[d, 1H, H-5 on furan]
		8·04–8·44	[m, 9H, pyrenyl]
		12·95	[br, 1H, OH on pyridone]

2.4 Colour assessment

The assessment of colour-dyed fabrics was made in terms of tristimulus colorimetry.[5] Figure 1 shows the CIELAB coordinates of compounds **7a–7f** on polyester fabrics. The values of the CIELAB coordinate (L^*, h^*_{ab}, C^*_{ab}) are listed in Table 3. According to Richter[6] and McLaren,[7] the

TABLE 2
Absorption and Fluorescence Spectra Data of 3-Cyano-4-Pyrenyl-6-Substituted-2-Pyridones (**7a–7f**) in Dimethylformamide

Compound number	λ_{max} *(nm)*	*Log* ε	λ_{em} *(nm)*
7a	383	4·54	489
7b	373	4·40	503
7c	410	4·31	505
7d	387	4·43	498
7e	384	4·16	482
7f	392	4·26	488

position of the colour is distributed in the yellow-green area with hue angle h^*_{ab} 101·34–115·63° and radial chroma C^*_{ab} of length 33·89–93·16. In Table 3, the Helmholtz coordinates of compounds **7a–7f** are reported and according to the colour distribution described by Kelly,[8] the colours of compounds **7a–7f** are distributed as follows:

Compounds **7e**, **7f**: yellow-green
Compounds **7a–7d**: greenish-yellow

Figure 2 shows the position of the deviation of hue angle and radial chroma of compounds **7b–7f**, in comparison with those of compound **7a** as model compound. The dyed fabrics showed a greener hue and a shorter radial chroma than for compound **7a**, for those compounds where *R* is a heteroaromatic group, i.e. furyl group (in **7e**) or pyridyl group (in **7f**). The compounds with a naphthyl group (in **7b**), fluorenyl group (in **7c**) or pyrenyl group (in **7d**) at the 6-position of pyridone ring have a yellower hue and high colour purity, and are suitable as disperse dyes for polyester fabrics.

TABLE 3
Colour Data of Compounds **7a–7f** on Polyester

Compound number	*Helmholtz coordinate*			*CIELAB*		
	Dominant wavelength λ_D *(nm)*	*Luminance factor* *Y (%)*	*Purity* *P (%)*	L^*	h^*_{ab} *(degrees)*	C^*_{ab}
7a	571	74·63	52·10	89·22	103·40	54·08
7b	570	75·06	74·69	89·42	103·75	83·56
7c	570	76·06	80·68	89·89	102·70	93·16
7d	571	68·41	75·91	86·21	101·34	81·73
7e	567	61·55	31·80	82·67	115·63	33·89
7f	569	77·32	43·76	90·47	108·46	47·16

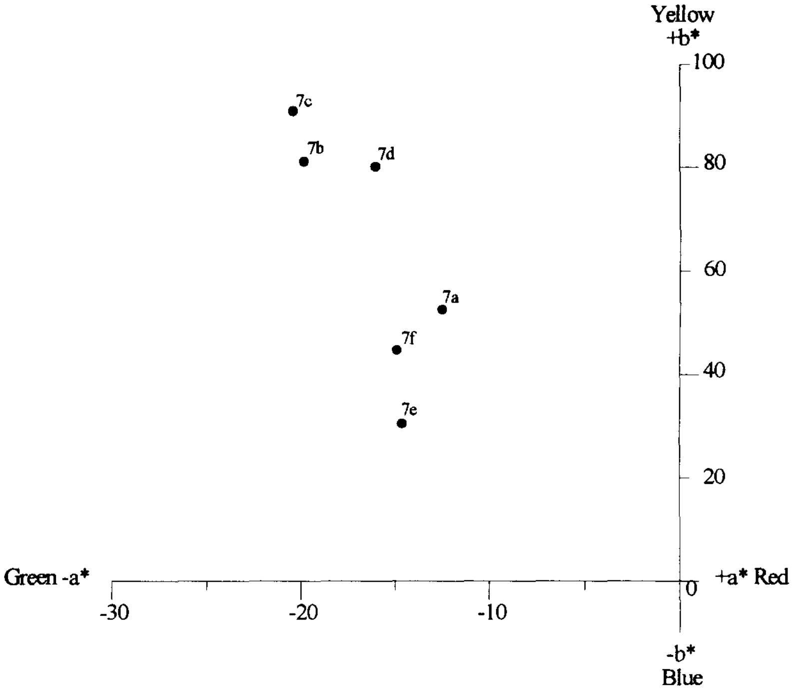


Fig. 1. CIELAB colour coordinates (L^*, a^* and b^*) of 3-cyano-4-pyrenyl-6-substituted 2-pyridone derivatives (**7a**–**7f**) on polyester fabrics.

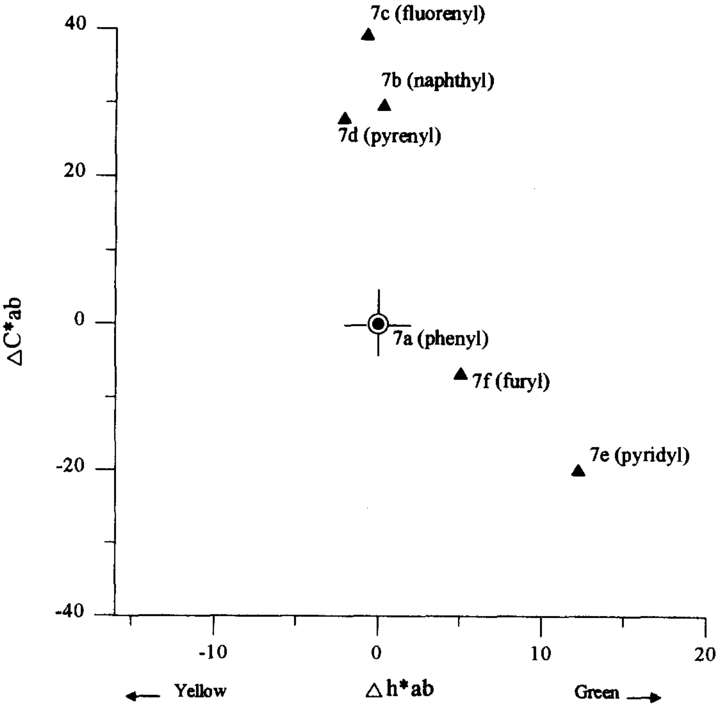


Fig. 2. Diagram of ΔC^*_{ab} plot of Δh^*_{ab} (**7a** as model compound).

3 EXPERIMENTAL

All melting point are uncorrected. IR spectra were recorded on a JASCO Hc-2 FT-IR/IR-3 using the KBr technique. The ^{1}H-NMR spectra were determined with a JUM-FX-100 (JEOL) FT-NMR spectrometer using TMS as internal standard. The mass spectra were determined on a FINNIGAN TSQ-700 mass spectometer. Absorption spectra were recorded on a Shimadzu UV-240 recording spectrophotometer and fluorescence spectra were recorded on a Perkin-Elmer LS 50 luminescence spectrometer. The concentration of solution used for measurement was 5×10^{-5} m.

3.1 Dyeing and colour assessment

The dyebaths were prepared from the dispersed compounds (1% omf) with an amphoteric dispersol-levelling agent (1 g l^{-1}) to a final liquor ratio of 20:1 w/w. The pH value of the bath was adjusted to 4–5 with acetic acid (10%). The polyester sample, previously wetted, was placed into the liquor at 25–30°C. The temperature was raised at 2°C min^{-1} to 130°C, and dyeing continued for 2 h. After cooling, the dyed fabrics were washed and dried. The colour parameters and fluorescence of the dyed polyester fabrics were measured using the Applied Colour System, CS-5 chroma-sensor, model 502 using D_{65} source and ultraviolet radiation.

3.2 3-Pyrenecarbaldehyde (4)

Pyrene (4·88 g, 0·02 mole) and aluminium trichloride (2·66 g, 0·02 mole) were added to dichloromethane (200 ml) and the mixture was cooled below 5°C. The mixture was stirred vigorously and dichloromethyl methyl ether (2·3 g, 0·02 mole) in dichloromethane (6 ml) was slowly added over 1 h. The resulting solution was stirred at 5–10°C for 3–4 h. The mixture was poured over 600 g ice-water and stirred for 20 min. The organic layer was dried ($MgSO_4$) and solvent removed. The residual oil was crystallized from ethanol to give yellow crystals (65%), m.p. 122–125°C (P^+ at *m/e* 230). Calculated for $C_{17}H_{10}O$: C, 88·67; H, 4·38. Found: C, 88·61; H, 4·40.

3.3 Ethyl 2-cyano-3-pyrenyl acrylate (5)

A mixture of ethyl cyanoacetate (1·13 g, 0·01 mole), 3-pyrenecarbaldehyde (**4**; 2·30 g, 0·01 mole), ethanol (50 ml) and piperidine (1 ml) was stirred at 40–45°C until the reaction was completed (about 3–4 h). During the reaction, the orange product precipitated. The crude product was filtered and recrystallized from ethanol to give orange crystals (70%), m.p. 136–138°C (P^+ at *m/e* 325). Calculated for $C_{22}H_{15}NO_2$: C, 81·20; H, 4·65; N, 4·31. Found: C, 81·19; H, 4·66; N, 4·29.

3.4 3-Cyano-4-pyrenyl-6-phenyl-2-pyridone (7a)

A mixture of ethyl 2-cyano-3-pyrenyl acrylate (**5**; 1·625 g, 0·005 mole), acetophenone (**6a**; 0·6 g, 0·005 mole) and ammonium acetate (2 g) in ethanol (50 ml) was heated at reflux. During the reaction, the yellow product precipitated. The crude product was filtered, washed with acetone and recrystallized from chloroform as yellow crystals (45%), m.p. 318–320°C (P^+ at *m/e* 396). Calculated for $C_{28}H_{16}N_2O$: C, 84·82; H, 4·07; N, 7·07. Found: C, 83·94; H, 4·07; N, 6·90.

3.5 3-Cyano-4-pyrenyl-6-(2-naphthyl)-2-pyridone (7b)

Compound **7b** was prepared in a manner similar to that described above for **7a**. It was recrystallized from DMSO as yellow crystals (52%), m.p. 325–328°C (P^+ at *m/e* 446). Calculated for $C_{32}H_{18}N_2O$: C, 86·07; H, 4·07; N, 6·28. Found: C, 86·01; H, 4·12; N, 6·25.

3.6 3-Cyano-4-pyrenyl-6-(2-fluorenyl)-2-pyridone (7c)

Compound **7c** was prepared in a manner similar to that described above for **7a**. It was recrystallized from DMSO as yellow crystals (65%), m.p. 320–325°C (P^+ at *m/e* 484). Calculated for $C_{35}H_{20}N_2O$: C, 86·75; H, 4·16; N, 5·78. Found: C, 86·41; H, 4·28; N, 5·66.

3.7 3-Cyano-4-pyrenyl-6-(3-pyrenyl)-2-pyridone (7d)

Compound **7d** was prepared in a manner similar to that described above for **7a**. It was recrystallized from DMSO as yellow crystals (61%), m.p. 333–336°C (P^+ at *m/e* 520). Calculated for $C_{38}H_{20}N_2O$: C, 87·67; H, 3·88; N, 5·38. Found: C, 87·51; H, 3·94; N, 5·37.

3.8 3-Cyano-4-pyrenyl-6-(2-pyridyl)-2-pyridone (7e)

Compound **7e** was prepared in a manner similar to that described above for **7a**. It was recrystallized from chloroform as yellow-green crystals (41%), m.p. 292–294°C (P^+ at *m/e* 397). Calculated for $C_{27}H_{15}N_3O$: C, 81·59; H, 3·81; N, 10·58. Found: C, 81·29; H, 3·89; N, 10·25.

3.9 3-Cyano-4-pyrenyl-6-(2-furyl)-2-pyridone (7f)

Compound **7f** was prepared in a manner similar to that described above for **7a**. It was recrystallized from chloroform as yellow crystals (44%), m.p. 337–340°C (P^+ at *m/e* 386). Calculated for $C_{26}H_{14}N_2O_2$: C, 80·81; H, 3·65; N, 7·25. Found: C, 80·72; H, 3·74; N, 7·21.

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