ELSEVIER

Dyes and Pigments, Vol. 30, No. 3, pp. 173–182, 1996

0143-7208/96 $15.00 + 0.00

0143-7208(95)00075-5

Synthesis of Some 2- and 7-Pyrenyl Substituted Thiazolo[3,2-*a*]pyridine Derivatives

Jyh Jian Chen & Ing Jing Wang*

Department of Textile Engineering, National Taiwan Institute of Technology, Taipei, Taiwan, 107672, Republic of China

(Received 31 July 1995; accepted 4 September 1995)

ABSTRACT

A series of 5-amino-2-arylidene-6,8-diethoxycarbonyl-3-oxo-7-pyrenyl-7H-thiazolo-[3,2-a]pyridine derivatives and 5-amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-aryl-7H-thiazolo[3,2-a]pyridine derivaives were prepared by cyclization of 5-subsitiuted-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazoles and ethyl 2-cyano-3-substituted acrylates.

1 INTRODUCTION

Pyrenes containing a heteroaromatoic ring system have been reported as having useful fluorescent whitening agent characteristics.[1–3] In previous papers, we have reported the syntheses of pyrenyl pyridine[4] and pyrenyl pyridone[5–6] derivatives and an evaluation of these compounds as fluorescent colorants for polyester. We report here the syntheses of some new pyrenyl compounds derived from 7*H*-thiazolo[3,2-*a*]pyridine derivatives; the syntheses of 7*H*-thiazolo[3,2-*a*]pyridine has been previously reported.[7–9] The 2- and 7-pyrenyl substituted thiazolo-[3,2-*a*]pyridine derivatives were synthesized according to the method for 7*H*-thiazolo[3,2-*a*]pyridine described by Kambe *et al.*[10] The spectral characteristics and colour assessment on polyester fabrics are discussed.

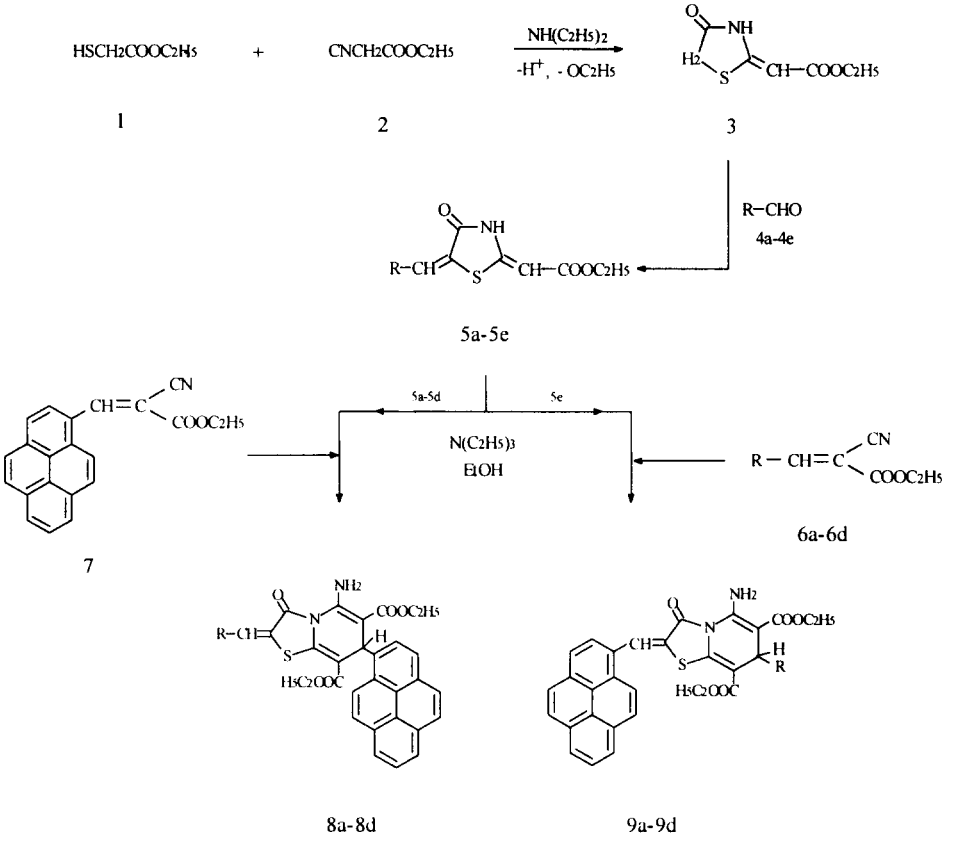
2 RESULTS AND DISCUSSION

2.1 Preparation and spectral characteristics

The synthetic routes used for the preparation of the 5-amino-2-arylidene-

*Corresponding author.

6,8-diethoxycarbonyl-3-oxo-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridine derivatives (**8a–d**) and 5-amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-aryl-7*H*-thiazolo[3,2-*a*]pyridine derivatives (**9a–d**) are shown in Scheme 1.



Compounds					R
4a	5a	6a	8a	9a	Phenyl
4b	5b	6b	8b	9b	4-Dimethylaminophenyl
4c	5c	6c	8c	9c	4-Methoxyphenyl
4d	5d	6d	8d	9d	4-Methylphenyl
4e	5e				Pyrenyl

Scheme 1.

Reaction of 2-ethoxycarbonylmethylene-4-oxo-tetrahydrothiazole (**3**)[11] with various aldehydes (**4a–e**) in the presence of a base catalyst yielded the pale yellow to orange coloured 5-substituted-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazoles (**5a–e**). The IR spectra of these compounds showed characteristic imine (=NH) absorption bands at 3249–3251 cm^{-1} and two carbonyl absorption bands at 1696–1708 cm^{-1} (ester) and 1679–1690 cm^{-1} (on ring). The ^1H NMR spectra of compounds **5a–d** in DMSO-d_6 showed a 1H singlet at δ 5·55–5·63 due to =CH— for ethoxycarbonylmethylene and a 1H singlet at δ 7·42–7·50 due to the arylidene —CH=. A broad absorption band at δ 11·95–12·22 was attributed to 1H of the imine group. Compound **5e** in chloroform-*d* showed a multiplet (8H) at δ 7·95–8·42 and a 1H doublet at δ 8·60–8·67 due to the pyrenyl group. Data for compounds **5a–e** are listed in Table 1.

The 7*H*-thiazolo[3,2-*a*]pyridine derivatives (**8a–d**) containing a pyrenyl group at the 7-position were obtained by reaction of 5-arylidene-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazoles (**5a–d**) and ethyl 2-cyano-3-pyrenyl acrylate (**7**), and the corresponding 7*H*-thiazolo[3,2-*a*]pyridine derivatives (**9a–d**) with a pyrenylidene group at the 2-position were synthesized by reaction of 5-pyrenylidene-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (**5e**) with ethyl 2-cyano-3-aryl acrylates (**6a–d**).[5] The IR spectra of compounds **8a–d** and **9a–d** showed characteristic amino absorption at 3368–3396 and 3259–3290 cm^{-1}. The ^1H NMR spectra in chloroform-*d* showed a singlet at δ 6·05–6·08 attributed to the 1H of the 7-position on the thiazolo[3,2-*a*]pyridine ring, and a broad absorption at δ 8·7–8·86 attributed to 2H of the amino group. The chemical shift of the pyrenyl group of compounds **9a–d** ($CDCl_3$ + CF_3COOD) was in the region δ 8·20–8·88 ppm, the amino absorption overlapping in the multiplet of the pyrenyl group. Full data for compounds **8a–d** and **9a–d** are listed in Tables 2 and 3.

Electronic absorption spectra of the 7H-thiazolo[3,2-*a*]pyridine derivatives **8a–d** and **9a–d** in DMF showed λ_{max} in the range 380–455 nm and 443–450 nm, and are listed in Table 4.

2.2 Colour assessment

The colour of dyed fabrics was assessed in term of tristimulus colorimetry. Table 5 shows the values of the Helmholtz coordinates (λ_D, $Y\%$, $P\%$) and the position of the colour using the CIELAB colour coordinates (L^*, h^*_{ab}, C^*_{ab}). In CIELAB, the hue angle of yellow is in the range 88–103°;[12,13] the colour positions of compounds **8a–d** and **9a–d** are distributed in the yellow–green area, with hue angle h^*_{ab} of 90·96–98·56° and radial chroma C^*_{ab} of length 40·90–74·37. The dominant wavelength and purity are 572–575 nm

TABLE 1
IR and ^{1}H NMR Spectra of 5-Substituted 2-Ethoxycarbonylmethylene-4-oxotetrahydrothiazole Derivatives (**5a–e**)

Compound	*IR* ν^{KBr} *(cm^{-1})*	*^{1}H NMR* δ *(ppm)*	
5a	3251 [=NH]	1·18–1·23	[*t*,3H, –CH_2–CH_3]
	1708 [–C=O; ester]	4·08–4·15	[*q*, 2H, –CH_2–CH_3]
	1688 [–C=O; ring]	5·63	[*s*, 1H, =CH–$COOC_2H_5$]
		7·42–7·63	[*m*, 6H, C_6H_5–CH= and phenyl]
		12·22	[*br*, 1H, =NH]
			(DMSO-d_6)
5b	3250 [=NH]	1·18–1·22	[*t*, 3H, –CH_2–CH_3]
	1701 [–C=O; ester]	2·99	[*s*, 6H, –$N(CH_3)_2$]
	1679 [–C=O; ring]	4·07–4·14	[*q*, 2H, –CH_2–CH_3]
		5·55	[*s*, 1H, =CH–$COOC_2H_5$]
		6·81–7·46	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·42	[*s*, 1H, C_6H_4–CH=]
		11·95	[*br*, 1H, =NH]
			(DMSO-d_6)
5c	3251 [=NH]	1·18–1·22	[*t*, 3H, –CH_2–CH_3]
	1708 [–C=O; ester]	3·81	[*s*, 3H, –OCH_3]
	1688 [–C=O, ring]	4·07–4·14	[*q*, 2H, –CH_2–CH_3]
		5·59	[*s*, 1H, =CH–$COOC_2H_5$]
		7·09–7·59	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·50	[*s*, 1H, C_6H_4–CH=]
		12·10	[*br*, 1H, =NH]
			(DMSO-d_6)
5d	3249 [=NH]	1·18–1·23	[*t*, 3H, –CH_2–CH_3]
	1696 [–C=O; ester]	2·35	[*s*, 3H, –CH_3]
	1685 [–C=O; ring]	4·07–4·14	[*q*, 2H, –CH_2–CH_3]
		5·60	[*s*, 1H, =CH–$COOC_2H_5$]
		7·23–7·52	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·50	[*s*, 1H, C_6H_4–CH=]
		12·15	[*br*, 1H, =NH]
			(DMSO-d_6)
5e	3250 [=NH]	1·24–1·29	[*t*, 3H, –CH_2–CH_3]
	1701 [–C=O; ester]	4·15–4·22	[*q*, 2H, –CH_2–CH_3]
	1690 [–C=O; ring]	5·73	[*s*, 1H, =CH–$COOC_2H_5$]
		7·95–8·42	[*m*, 9H, pyrene–CH= and pyrenyl]
		8·60–8·67	[*d*, 1H, H-2 on pyrene]
		11.16	[*br*, 1H, =NH]
			($CDCl_3$)

TABLE 2

IR and ^{1}H NMR Spectra of 5-Amino-2-arylidene-6,8-diethoxycarbonyl-3-oxo-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridine Derivatives (**8a-d**)

Compound	*IR* ν^{KBr} *(cm^{-1})*	*^{1}H NMR* δ *(ppm)*	
8a	3392, 3270 [$-NH_2$]	0·78–0·87	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1702 [–C=O; ester]	3·66–4·04	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
	1655 [–C=O; ring]	6·08	[*s*, 1H, ring =$\underline{CH}$–]
		7·38–8·15	[*m*, 13H, phenyl and pyrenyl]
		7·78	[*s*, 1H, $C_6H_5-\underline{CH}$=]
		8·75–8·78	[*d*, 1H, H-2 on pyrenyl]
		8·79	[*br*, 2H, $-NH_2$]
			($CDCl_3$)
8b	3368, 3259 [$-NH_2$]	0·79–0·89	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$
	1705 [–C=O; ester]	3·03	[*s*, 6H, $-N(CH_3)_2$]
	1658 [–C=O; ring]	3·65–4·05	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
		6·08	[*s*, 1H, ring =$\underline{CH}$–]
		6·69–7·56	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·72	[*s*, 1H, $C_6H_4-\underline{CH}$=]
		7·81–8·15	[*m*, 8H, pyrenyl]
		8·78–8·81	[*d*, 1H, H-2 on pyrenyl]
		8·86	[*br*, 2H, $-NH_2$]
			($CDCl_3$)
8c	3383, 3264 [$-NH_2$]	0·78–0·88	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1702 [–C=O; ester]	3·83	[*s*, 3H, $-OCH_3$]
	1686 [–C=O; ring]	3·68–4·04	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
		6·06	[*s*, 1H, ring =$\underline{CH}$–]
		6·95–7·60	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·74	[*s*, 1H, $C_6H_4-\underline{CH}$=]
		7·78–8·15	[*m*, 8H, pyrenyl]
		8·75–8·79	[*d*, 1H, H-2 on pyrenyl]
		8·80	[*br*, 2H, $-NH_2$]
			($CDCl_3$)
8d	3396, 3266 [$-NH_2$]	0·77–0·87	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1716 [–C=O; ester]	2·38	[*s*, 3H, $-CH_3$]
	1689 [–C=O; ring]	3·65–4·06	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
		6·05	[*s*, 1H, ring =$\underline{CH}$–]
		7·23–7·54	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·75	[*s*, 1H, $C_6H_4-\underline{CH}$=]
		7·77–8·24	[*m*, 8H, pyrenyl]
		8·75–8·78	[*d*, 1H, H-2 on pyrenyl]
		8·78	[*br*, 2H, $-NH_2$]
			($CDCl_3$)

TABLE 3
IR and ^{1}H NMR Spectra of 5-Amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-aryl-7*H*-thiazolo[3,2-*a*]pyridine Derivatives (**9a–d**)

Compound	*IR* ν^{KBr} *(cm^{-1})*	*^{1}H NMR* δ *(ppm)*	
9a	3396, 3290 [$-NH_2$]	1·55–1·78	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1701 [–C=O, ester]	4·59–4·70	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
	1691 [–C=O; ring]	6·45	[*s*, 1H, ring =$\underline{CH}$–]
		7·44–7·70	[*m*, 5H, phenyl]
		7·56	[*s*, 1H, pyrene–$\underline{CH}$=]
		8·35–8·80	[*m*, 10H, pyrenyl and $-NH_2$]
		9·41–9·49	[*d*, 1H, H-2 on pyrenyl]
			($CDCl_3$ + CF_3COOD)
9b	3386, 3267 [$-NH_2$]	1·62–1·80	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1702 [–C=O; ester]	3·67	[*s*, 6H, $-N(CH_3)_2$]
	1685 [–C=O; ring]	4·50–4·88	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
		6·47	[*s*, 1H, ring = $\underline{CH}$–]
		7·59	[*s*, 1H, pyrene–$\underline{CH}$=]
		7·78–7·95	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		8·35–8·88	[*m*, 10H, pyrenyl and $-NH_2$]
		9·57–9·59	[*d*, 1H, H-2 on pyrenyl]
			($CDCl_3$ + CF_3COOD)
9c	3390, 3284 [$-NH_2$]	1·47–1·63	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1701 [–C=O; ester]	4·05	[*s*, 3H, $-OCH_3$]
	1687 [–C=O; ring]	4·37–4·71	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
		6·31	[*s*, 1H, ring =$\underline{CH}$–]
		7·12–7·30	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·44	[*s*, 1H, pyrene–$\underline{CH}$=]
		8·20–8·70	[*rn*, 10H, pyrenyl and $-NH_2$]
		9·38–9·44	[*d*, 1H, H-2 on pyrenyl]
			($CDCl_3$ + CF_3COOD)
9d	3393, 3286 [$-NH_2$]	1·68–1·85	[*m*, 6H, $-CH_2-\underline{CH_3} \times 2$]
	1701 [–C=O; ester]	2·73	[*s*, 3H, $-CH_3$]
	1691 [–C=O; ring]	4·70–4·80	[*m*, 4H, $-\underline{CH_2}-CH_3 \times 2$]
		6·52	[*s*, 1H, ring =$\underline{CH}$–]
		7·41–7·60	[*dd*, 4H, 2,6- and 3,5- position on phenyl]
		7·57	[*s*, 1H, pyrene–$\underline{CH}$=]
		8·41–8·88	[*m*, 10H, pyrenyl and $-NH_2$]
		9·55–9·62	[*d*, 1H, H-2 on pyrenyl]
			($CDCl_3$ + CF_3COOD)

TABLE 4
Absorption Spectra Data of Compounds **5a–e**, **8a–d** and **9a–d** in DMF

Compound	λ_{max} *(nm)*	*Log* ϵ
5a	359	4·51
5b	422	4·32
5c	374	4·45
5d	365	4·46
5e	422	4·57
8a	380	4·67
8b	455	4·44
8c	395	4·64
8d	383	4·65
9a	443	4·59
9b	450	4·58
9c	448	4·58
9d	444	4·59

TABLE 5
Colour Data of Compounds **8a–d** and **9a–d** on Polyester

Compound	*Helmholtz coordinate*			*CIELAB*		
	Dominant wavelength λ_D *(nm)*	*Luminance factor* Y*(%)*	*Purity* P*(%)*	L*	h^*_{ab} *(degrees)*	C^*_{ab}
8a	574	73·55	42·64	88·71	95·52	41·50
8b	574	73·55	42·17	88·71	94·84	40·90
8c	573	74·85	47·58	89·32	97·55	47·39
8d	574	71·15	50·06	87·56	93·99	48·51
9a	575	68·83	69·00	96·42	90·96	69·27
9b	572	72·97	70·35	88·43	98·56	74·37
9c	574	70·09	65·08	87·04	92·29	64·97
9d	574	69·32	64·16	86·66	92·12	63·59

and 42·17–70·35%. The colours of the compounds are distributed in the greenish–yellow area as defined by Kelly's colour-name map.[14,15] It was found that the dominant wavelength was only slightly influenced by the substituents on the phenyl ring. Both the dominant wavelength and purity of the 2-pyrenylidine-7-aryl-7*H*-thiazolo[3,2-*a*]pyridines (**9a–d**) were larger than those of 2-arylidine-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridines (**8a–d**). Compounds **9a–d** were also suitable as disperse dyes for polyester.

3 EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a JASCO Hc-2 FT- IR/IR-3 using the KBr technique. The ^1H 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 Finnegan TSQ-700 mass spectrometer. Absorption spectra were recorded on a Milton Roy Spectronic Genesys 5 recording spectrophotometer, at concentrations of 5×10^{-5} M.

3.1 5-Phenylidene-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (5a)

A mixture of 2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (**3**; 1·87 g, 0·01 mol), benzaldehyde (**4a**; 1·06 g, 0·01 mol), ethanol (30 ml) and triethylamine (1 ml) was refluxed for 3–4 h. After reaction, a pale yellow product precipitated, which was filtered and recrystallized from ethanol to give pale yellow crystals (60%), m.p. 193–196°C (P^+ at *m/e* 275). Calculated for $C_{14}H_{13}NO_3S$: C, 61·08; H, 4·76; N, 5·09. Found: C, 61·04; H, 4·79; N, 5·03.

Compounds **5b–c** were similarly prepared.

3.2 5-[4-(Dimethylamino)phenylidene]-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (5b)

Recrystallized from EtOH as orange crystals (70%), m.p. 233–235°C (P^+ at *m/e* 318). Calculated for $C_{16}H_{18}N_2O_3S$: C, 60·36; H, 5·70; N, 8·80. Found: C, 60·31; H, 5·75; N, 8·74.

3.3 5-(4-Methoxyphenylidene)-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (5c)

Recrystallized from EtOH as pale yellow crystals (71%), m.p. 167–170°C (P^+ at *m/e* 305). Calculated for $C_{15}H_{15}NO_4S$: C, 59·00; H, 4·96; N, 4·59. Found: C, 58·92; H, 4·99; N, 4·52.

3.4 5-(4-Methylphenylidene)-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (5d)

Recrystallized from EtOH as pale yellow crystals (73%), m.p. 180–182°C (P^+ at *m/e* 289). Calculated for $C_{15}H_{15}NO_3S$: C, 62·27; H, 5·23; N, 4·84. Found: C, 62·19; H, 5·34; N 4·72.

3.5 5-Pyrenylidene-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (5e)

Recrystallized from EtOH as orange crystals (78%), m.p. 176–178°C (P^+ at *m/e* 399). Calculated for $C_{24}H_{17}NO_3S$: C, 72·16; H, 4·29; N, 3·51. Found: C, 72·10; H, 4·30; N, 3·44.

3.6 5-Amino-2-phenylidene-6,8-diethoxycarbonyl-3-oxo-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridine (8a)

A mixture of 5-phenylidene-2-ethoxycarbonylmethylene-4-oxotetrahydrothiazole (**5a**; 1 g, 0·0036 mol), ethyl 2-cyano-3-pyrenylacrylate (**7**; 1·17 g, 0·0036 mol), EtOH (50 ml) and triethylamine (1 ml) was refluxed for 10 h. During the reaction, the yellow product precipitated. The crude product was filtered and recrystallized from $CHCl_3$ to give yellow crystals (55%), m.p. 273–275°C (P^+ at *m/e* 600). Calculated for $C_{36}H_{28}N_2O_5S$: C, 71·98; H, 4·70; N, 4·67. Found: C, 71·78; H, 4·76; N, 4·51.

Compounds **8b–d** and **9a–d** were similarly prepared.

3.7 5-Amino-2-[4-(dimethylamino)phenylidene]-6,8-diethoxycarbonyl-3-oxo-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridine (8b)

Recrystallized from $CHCl_3$ as yellow crystals (63%), m.p. 270–273°C (P^+ at *m/e* 643). Calculated for $C_{38}H_{33}N_3O_5S$: C, 70·89; H, 5·17; N, 6·53. Found: C, 70·83; H, 5·25; N, 6·47.

3.8 5-Amino-2-(4-methoxyphenylidene)-6,8- diethoxycarbonyl-3-oxo-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridine (8c)

Recrystallized from $CHCl_3$ as yellow crystals (58%), m.p. 260–264°C (P^+ at *m/e* 630). Calculated for $C_{37}H_{30}N_2O_6S$: C, 70·46; H, 4·80; N, 4·44. Found: C, 70·32; H, 4·93; N, 4·32.

3.9 5-Amino-2-(4-methylphenylidene)-6,8-diethoxycarbonyl-3-oxo-7-pyrenyl-7*H*-thiazolo[3,2-*a*]pyridine (8d)

Recrystallized from $CHCl_3$ as yellow crystals (68%), m.p. 242–245°C (P^+ at *m/e* 614). Calculated for $C_{37}H_{30}N_2O_5S$: C, 72·2; H, 4·92; N, 4·56. Found: C, 72·11; H, 4·96; N, 4·42.

3.10 5-Amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-phenyl-7*H*-thiazolo[3,2-*a*]pyridine (9a)

Recrystallized from $CHCl_3$ as yellow crystals (76%), m.p. 250–251°C (P^+ at

m/e 600). Calculated for $C_{36}H_{28}N_2O_5S$: C, 71·98; H, 4·70; N, 4·67. Found: C, 71·85; H, 4·81; N, 4·63.

3.11 5-Amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-(4-dimethylaminophenyl)-7*H*-thiazolo[3,2-*a*]pyridine (9b)

Recrystallized from $CHCl_3$ as yellow crystals (72%), m.p. 285–288°C (P^+ at *m/e* 643). Calculated for $C_{38}H_{33}N_3O_5S$: C, 70·89; H, 5·17; N, 6·53. Found: C, 70·77; H, 5·26; N, 6·41.

3.12 5-Amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-(4-methoxyphenyl)-7*H*-thiazolo[3,2-*a*]pyridine (9c)

Recrystallized from $CHCl_3$ as yellow crystals (68%), m.p. 270–271°C (P^+ at *m/e* 630). Calculated for $C_{37}H_{30}N_2O_6S$: C, 70·46; H, 4·80; N, 4·44. Found: C, 70·21; H, 4·93; N, 4·40.

3.13 5-Amino-2-pyrenylidene-6,8-diethoxycarbonyl-3-oxo-7-(4-methylphenyl)-7*H*-thiazolo[3,2-*a*]pyridine (9d)

Recrystallized from $CHCl_3$ as yellow crystals (80%), m.p. 252–254°C (P^+ at *m/e* 614). Calculated for $C_{37}H_{30}N_2O_5S$: C, 72·29; H, 4·92; N, 4·56. Found: C, 72·24; H, 4·99; N, 4·50.

REFERENCES

1. Atkinson, J. R, *British Patent* 1222970 (1971); *Chem. Abstr.*, **74** (1971)127557.
2. ICI, *French Patent* 1556896 (1969); *Chem. Abstr.*, **72** (1970) 45036.
3. Luethi, C., *Ger. Offen.* 2232729 (1973); *Chem. Abstr.*, **78** (1973) 125845.
4. Chen, J. J. & Wang, I. J., *Dyes and Pigments*, **26** (1994) 247.
5. Chen, J. J. & Wang, I. J., *Dyes and Pigments*, **27** (1995) 249.
6. Chen, J. J. & Wang, I. J., *Dyes and Pigments*, in press.
7. Reid, D. H., *The Chemical Society, London*, **1** (1970) 429.
8. Reid, D. H., *The Chemical Society, London*, **2** (1973) 695.
9. Reid, D. H., *The Chemical Society, London* **3** (1974) 653.
10. Kambe, S. & Saito, K., *Synthesis*, **12** (1977) 839.
11. Isidor, J. L. & McKee, R. L., *J. Org. Chem.*, **38** (1973) 3615.
12. McLaren K., *J. Soc. Dyers Colour.*, **92** (1976) 317.
13. McLaren K. & Taylor, P. F., *Color Res. Appl.*, **6** (1981) 75.
14. Agoston, G. A., *Color Theory and Application in Art and Design.* Springer, Berlin, 1979. p. 57.
15. Kelly, K. L., *J. Opt. Soc. Am.*, **33** (1943) 627.