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Synthesis and characterization of dyes exemplified by 2-arylidene-1-dicyanomethyleneindane

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Abstract

The synthesis of methine dyes formed by Knoevenagel condensation of aromatic aldehydes with 1-dicyanomethylene indane 2 afforded a novel series of dyes absorbing in the region 490–593 nm. Substituents on the aromatic aldehyde moiety have a significant effect on the visible absorption maxima of the dyes; increasing the solvent polarity also had a pronounced effect on the absorption maxima. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Methine dyes (e.g. **1**) based on indane-1,3-dione are typical donor–acceptor chromophores, and are generally yellow to orange in colour with a high absorption intensity [1]. Replacement of the oxygen of one of the carbonyl groups in **1a** by the more powerful electron acceptor dicyanomethylene groups gives dye **1b**, which has absorption maximum at much higher wavelengths with some reduction in intensity [2]. However, there is no report in the literature describing the synthesis of dyes based on 1-dicyanomethyleneindane. In the present paper the synthesis of dyes based on 1-dicyanomethyleneindane is described and compared with some of their analogues derived from 1-indanone.

2. Results and discussion

2.1. Synthesis of dyes

For comparison purposes, chalcones **3a** and **3b** were prepared via Aldol condensation of 1-indanone and the appropriate aldehyde. Heating under reflux the chalcone **3a** and malononitrile in ethanol, using ammonium acetate as a base, gave exclusively a cyclized product, 2-amino-4-(4′-dimethyleaminophenyl)-3-cyano-5H-indeno[1,2]pyridine **4**, and no Knoevenagel condensation product was isolated. This is in agreement with similar observations reported in the literature [3,4].

The IR spectrum of the cyclized product **4** showed absorption bands at 3341, 3231 and 2209 cm^{-1} for NH_2 and the cyano group respectively. Similar reaction of the chalcone **3a** with malononitrile in ethanol using piperidine as a base gave unidentified products. It has been reported in

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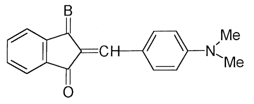
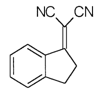
the literature that α,β-unsaturated ketones, when heated with malononitrile in benzene using a catalytic amount of ammonium acetate–acetic acid as a base under a Dean-Stark trap, gave the desired Knoevenagel condensation product [5,6]. However, heating under reflux for 6 h the chalcone **3a**, malononitrile and a catalytic amount of ammonium acetate and acetic acid in benzene gave 2-[4-dimethylaminobenzylidene]-1-dicyanomethyleneindane **5c**, the yield was very low (Scheme 1).

The low yield of the Knoevenagel product **5c** prompted us to look for an alternative procedure to obtain a better yield. When the condensation was effected with 1-dicyanomethyleneindane **2** and 4-dimethylaminobenzaldehyde in dry THF using a secondary amine, such as diethylamine or piperidine, dye **5c** was obtained in 80% yield (Scheme 2). This procedure was adapted for the synthesis of dyes **5a–k**, analytical data for which are summarized in Table 1. Dyes **5a–k** exhibited CN absorption bands in their IR spectra in the region of 2197–2222 cm^{-1}, and their H^1-NMr spectra showed a low field singlet in the region of 9.8–10.4 ppm, attributed to the olefinic protons (Table 2).



1a, B = O
1b, B = C(CN)$_2$



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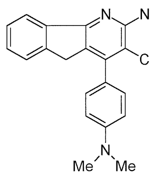

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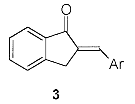
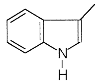
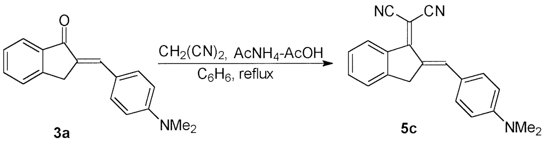


3

	Ar
a,	4-Me$_2$NC$_6$H$_4$
b,	



Scheme 1.

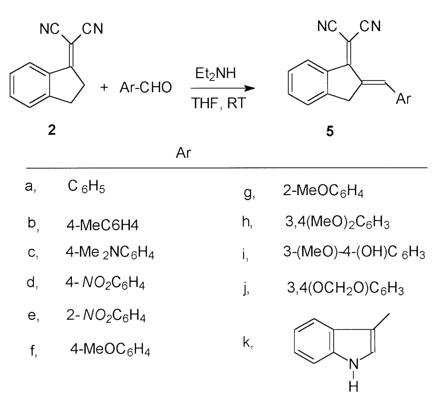
2.2. Visible absorption spectroscopic properties

Absorption spectra were recorded in chloroform and in acetonitrile, with molar extension coefficients being measured in acetonitrile; the results are summarized in Table 3.

Each dye showed two absorption bands. The parent dye **5a** showed an absorption band at 495 nm in chloroform and a much more intense band at 378 nm. Similarly dye **5c** showed two absorption bands at 516 and 362 nm in chloroform. The introduction of donating groups into the para position of the phenyl group caused a significant bathochromic shift; for instance, dye **5c** was 21 nm red shifted when compared with the parent dye **5a**. In acetonitrile the visible band of dye **5c** was displaced to 543 nm. A similar pattern was found for the other synthesized dyes. From the data in Table 3, the following observations can be drawn.

(a) The large bathochromic shift of the visible absorption of the dimethylamino derivative **5c** (516 nm in chloroform) relative to **5a** typifies the donor–acceptor character of the system.

(b) The introduction of an electron-donating group such as methoxy in different positions (i.e. 2, 3 and 4) of the aromatic ring of the arylidene moiety causes a pronounced bathochromic shift of the visible bands.



Scheme 2.

Table 1
Characterisation data of dyes **5a–k**

Dye No.	Yield (%)	m.p (°C)	Molecular formula	(%) Found (calculated)		
				C	H	N
5a	95	180	$C_{19}H_{12}N_2$	84.82 (85.07)	4.62 (4.48)	10.21 (10.48)
5b	42	103	$C_{20}H_{14}N_2$	85.05 (85.10)	4.63 (4.96)	9.76 (9.93)
5c	80	215	$C_{21}H_{17}N_3$	80.82 (81.03)	5.23 (5.46)	13.41 (13.50)
5d	75	141	$C_{19}H_{11}N_2O_2$	72.75 (72.84)	3.65 (3.51)	13.24 (13.42)
5e	52	162	$C_{19}H_{11}N_3O_2$	72.68 (72.84)	3.74 (3.51)	13.11 (13.42)
5f	72	121	$C_{20}H_{14}N_2O$	80.32(80.54)	4.82 (4.70)	9.22 (9.40)
5g	97	107	$C_{20}H_{14}N_2O$	80.45 (80.54)	4.93 (4.70)	9.34 (9.40)
5h	55	109	$C_{21}H_{16}N_2O_2$	76.64 (76.83)	4.92 (4.88)	8.29 (8.53)
5i	61	110	$C_{20}H_{14}N_2O_2$	76.22 (76.43)	4.65 (4.46)	8.73 (8.92)
5j	65	122	$C_{20}H_{12}N_2O_2$	76.78 (76.92)	3.94 (3.84)	8.87 (8.97)
5k	70	200	$C_{21}H_{13}N_3$	83.54 (83.72)	4.54 (4.32)	13.84 (13.95)

Table 2
H^1-NMR and IR data of dyes **5a–k**

Dye No.	δ				ν_{max}/cm^{-1}	
	Ar-H	CH_2	=C-H	Others	C=C	C≡N
5a	6.7–7.8	3.35	10.2		1705, 1610	2222
5b	6.7–7.9	3.41	10.1	2.4 (CH_3)	1699, 1600	2219
5c	6.8–7.8	3.58	9.85	3.2 (Me_2N)	1703, 1601	2204
5d	6.9–8.2	3.73	9.90		1700, 1644	2208
5e	6.8–8.1	3.53	9.95		1710, 1636	2202
5f	6.7–8.3	3.62	9.95	3.9 (MeO)	1681, 1602	2205
5g	6.9–8.1	3.65	10.4	4.1 (MeO)	1685, 1607	2201
5h	7.0–8.2	3.75	9.90	3.95 2xMeO	1679, 1644	2197
5i	6.6–8.28	3.73	9.80	3.90 MeO	1678, 1642	2198
5j	7.0–8.3	3.68	9.80	4.10 OCH_2	1684, 1640	2215
5k	6.8–8.4, 4.70	3.47	10.2		1663, 1655	2191

Table 3
UV-visible data of dyes **5a–k**

Dye No.	λ_{max} (log ε)/CH_3CN		$\lambda_{max}/CHCl_3$		Δλ[a]
	Band 1	Band 2	Band 1	Band 2	
5a	360 (3.43)	497 (2.01)	378	495	0.0
5b	392 (3.35)	578 (2.11)	410	595	99
5c	365 (3.87)	543 (3.83)	362	516	21
5d	380 (3.66)	532 (3.11)	380	550	55
5e	347 (3.75)	578 (3.48)	355	589	94
5f	393 (3.44)	573 (2.79)	370	562	67
5g	393 (3.42)	583 (2.76)	421	588	93
5h	385 (4.23)	581 (2.85)	363	586	91
5i	382 (4.20)	575 (2.51)	428	570	75
5j	380 (4.11)	505 (2.01)	400	492	−3
5k	381 (4.21)	585 (2.88)	343	593	98

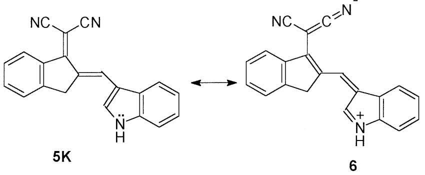
[a] $\Delta\lambda = \lambda$max (band 2 dyes **5b–k**)$-\lambda$max (band 2 dye **5a**) in chloroform.

Dye **5g**, containing a methoxy group in position 2, absorbs at higher wavelength compared to dye **5f** containing the same substituent in position 4, and this may be explained in terms of steric effects. The introduction of a second methoxy group resulted in a further bathochromic shift; for example dye **4h** which has two methoxy groups in positions 3 and 4, showed visible absorption at 586 nm in chloroform. However, the 3,4-(methylenedioxy) substituted dye **5j** showed a hypsochromic shift of 3 nm compared to the parent dye **4a**. The introduction of a heterocyclic group as the arylidene moiety, such as indol-3-yl, resulted in blue dyes with absorption maxima at 593 nm and an absorption tail above 750 nm. This large bathochromic shift of the visible absorption band compared to the parent dye **5a** is also evidence of the donor–acceptor character of these dyes (see $\Delta\lambda$ values Table 3).

The visible absorption band of dye **5k** involves a π–$\pi*$ transition through the conjugated system, the excited state receiving a large contribution from polar charge transfer migration of electrons from the nitrogen atom to the dicyanomethylene moiety (Scheme 3). Comparison of the 1-dicyanomethylene dyes **5c** and **5k** with their 1-indanone derivatives **3a** and **3b** reveals the excellent electron accepting properties of the dicyanomethylene moiety in producing large bathochromic shifts.

3. Experimental

Melting points were recorded on a Thomas–Hoover capillary melting apparatus without correction. IR spectra were taken on KBr disks on a Nicolet Magna 520 FTIR spectrometer, H^1-NMR were recorded in $CDCl_3$ on a Brucker DPX 400 MHz spectrometer using TMS as internal standard. Microanalyses were carried out using a Perkin–Elmer 240B analyzer. UV-visible spectra were recorded on a Shimadazu 260 spectrometer.



Scheme 3.

3.1. *1-Dicyanomethylenindane **2***

Anhydrous sodium acetate (6.5 g, 0.076 mol) was added to a stirred solution of 1-indanone (10 g, 0.075 mol), and malononitrile (5.1 g, 0.75 mol) in absolute ethanol (100 ml) at 25°C. The reaction mixture was stirred for 2 h, diluted with water and acidified to pH 3–4 with hydrochloric acid. The solid formed was filtered off, washed with water followed by a small amount of ethanol. The crude product was recrystallised from ethanol to give **2** as off-white powder (11.5 g, 84%), m.p. 146–48°C (Found: C, 80.3; H, 4.23; N, 15.9%. $C_{12}H_8N_2$ requires C, 80.0; H, 4.44; N, 15.6 %); H^1-NMr: δ_H 7.1–8.4, 3.3 (2H, *t*, CH_2), 3.1 (2H, *t*, CH_2), ν_{max} cm^{-1} 2222 (CN), 1570.

3.2. *General procedure for the synthesis of chalcones **3a** and **3b***

A solution of sodium hydroxide (20 ml, 10%) was added dropwise to a well stirred solution of indan-2-one (15 ml) and the appropriate aldehyde (15 ml) in ethanol (25 ml) at room temperature. The reaction mixture was stirred for 2 h and then added to a mixture of ice and hydrochloric acid. The precipitates were filtered off, washed thoroughly with water and finally with ethanol, and dried, and recrystallised from ethanol.

3.3. *2-(4-Dimethylaminobenzylidene)indan-2-one **3a***

Yellow needles, 89% yield, m.p. 156–158°C. Found: C, 82.13; H, 6.46; N, 5.32. $C_{18}H_{17}NO$ requires C, 81.88; H, 6.23; N, 5.45%.

3.4. *2-(Indol-3-yl)indan-2-one **3b***

Yellow crystals, 94% yield, m.p. 160–162°C. Found: C, 83.22; H, 5.34; N, 5.65. $C_{18}H_{13}NO$ requires C, 83.40; H, 5.02; N, 5.41%.

*3.5. Synthesis of 2-amino-4-(4′-dimethyleamino-phenyl)-3-cyano-5H-indeno[1,2]- pyridine **4***

A solution of the chalcone **3a** (1.5 g, 5.7 mmol), malononitrile (0.4 g, 5.7 mmol) and ammonium acetate (1.1 g, 11.4 mmol) in absolute ethanol (50 ml) was heated under reflux for 3 h. The red solid product was collected by filtration and recrystallized from ethanol to give compound **4**. Yield 1 g (60%), m.p. 240–242°C. Found: C, 76.32; H, 5.86; N, 17.96. $C_{20}H_{18}N_4$ requires C, 76.43; H, 5.73; N, 17.83%. $\nu_{max}\,cm^{-1}$ 3341, 3231 (NH_2), 2209 (CN), 1570 (C=C).

*3.6. Synthesis of dye **5c** by condensation of chalcone **3a** and malononitrile*

A mixture of chalcone **5a** (0.5 g, 1.9 mmol), malononitrile (0.13 g, 1.9 mmol) and a catalytic amount of ammonium acetate–acetic acid mixture in dry benzene (20 ml) was heated under reflux for 6 h. The reaction mixture was cooled and poured into ice; the dark red solid separated, was collected by filtration and washed with cold ethanol and dried. The solid was recrystallized from a mixture of dichloromethane-toluene giving the dye **5c** as dark red crystals (0.09 g, 15% yield). Characterisation data of this compound are similar to that prepared by the following procedure and are listed in Tables 1–3.

*3.7. General procedure for the synthesis of dyes **5a–k** by condensation of aromatic aldehydes and 1-dicyanomethyleneindane **2***

A mixture of the appropriate aldehyde (10 mmol), 1-dicyanomethyleneindane **2** (10 mmol) and diethylamine (10 mmol) in dry THF (25 ml) was stirred at room temperature for 3 h. The reaction mixture was then poured into crushed ice (100 g) and the separated solid dye was collected and recrystallized from a dichloromethane-toluene mixture. Yield, melting points and analytical data are listed in Table 1. H^1-NMR and infrared data are summarized in Table 2.

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