

Synthesis, Characterizations and Absorption Spectral Studies of Novel 2-Arylidene-1-dicyanomethyleneindane Dyes

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ABSTRACT. The synthesis and the absorption properties of methine dyes formed by Knoevenagel condensation of aromatic aldehydes with 1-dicyanomethyleneindane (**2**) afforded novel series of dyes (**5a-k**) absorbing in the region of 490-593 nm. The substituents on the aromatic aldehyde have remarkable effects on the visible absorption maxima of the new dyes. Increasing the solvent polarity had pronounced effects on the absorption maxima.

Introduction

Methine dyes (*e.g.*, **1**) based on indane-1,3-dione are typical donor-acceptor chromophors, 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 the 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 counterpart derived from 1-indanone.

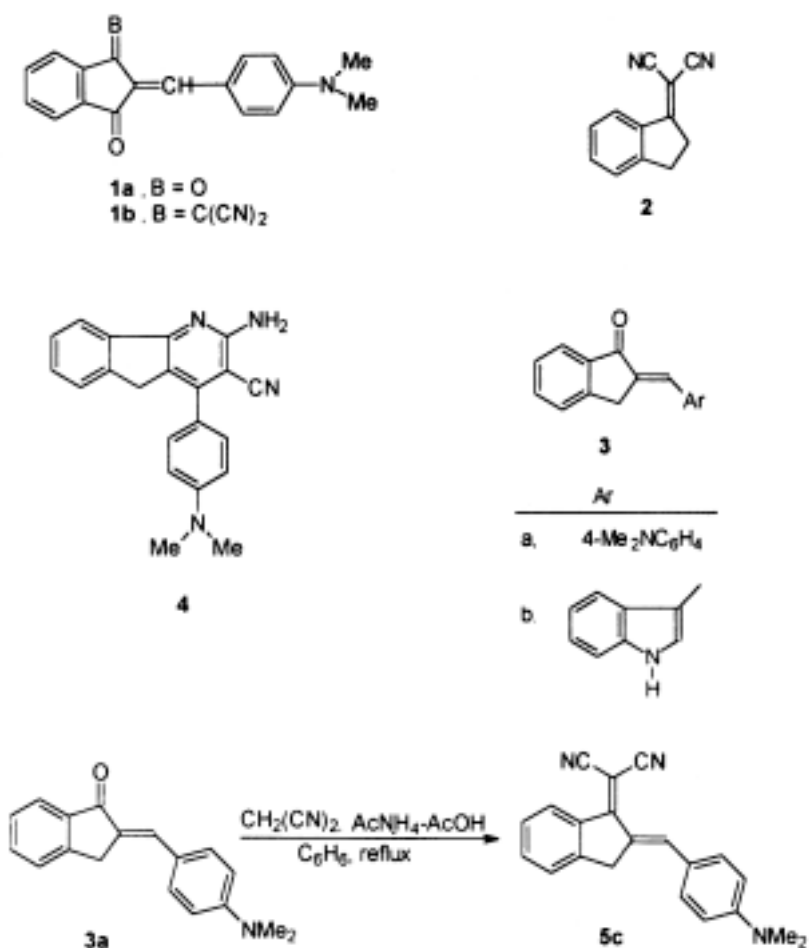
Results and Discussion

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, 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 was 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 chalcone **3a** with malononitrile in ethanol using pipyridene as a base gave unidentified products. It has been reported in 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]. Although, heating under reflux for six hours chalcone (**3a**) and 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).



Scheme 1

The low yield of Knoevenagel product (**5c**) promoted us to look for alternative procedure to get better yield. So when the condensation was attempted started with 1-dicyanomethyleneindane (**2**) and 4-dimethylaminobenzaldehyde in dry THF using a secondary amine such as diethyl or piperidine, dye (**5c**) was obtained in 80% yield (Scheme 2). This procedure was adapted for the synthesis of dyes (**5a-k**). The physical and analytical data are summarized in Table 1. The dyes (**5a-k**) exhibited a CN absorption bands in their IR spectra in the region of 2197-2222 cm^{-1} , moreover their ^1H -nmr spectra showed a low field singlet in the region of 9.80-10.40 ppm attributed to the olefinic protons (Table 2).

TABLE 1. Physical and analytical data of synthesized dyes 5 a-k.

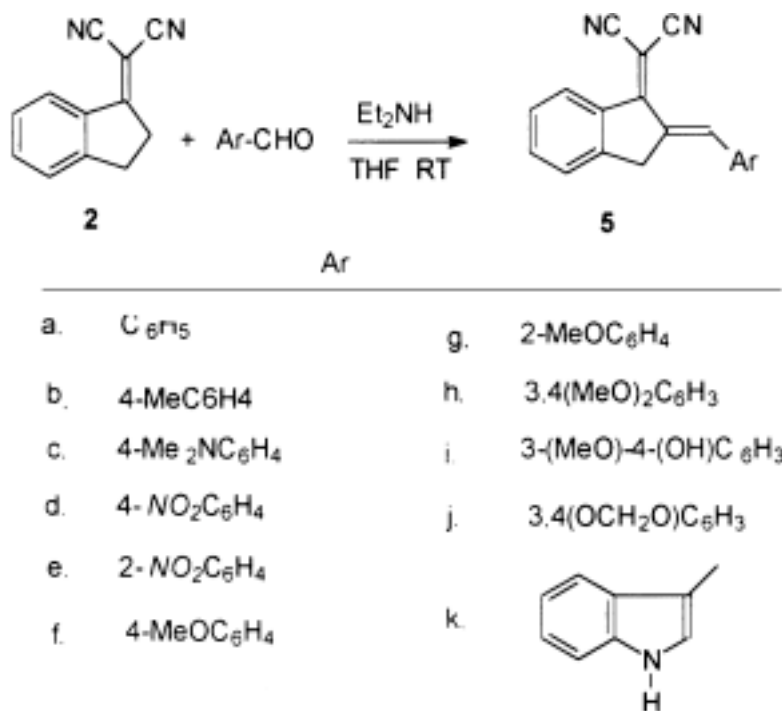
Dye no.	Yield (%)	m.p. (°C)	Molecular formula	% Found (calculated)		
				C	H	N
5a	95	180	$\text{C}_{19}\text{H}_{12}\text{N}_2$	84.82 (85.07)	4.62 (4.48)	10.21 (10.48)
5b	42	103	$\text{C}_{20}\text{H}_{14}\text{N}_2$	85.05 (85.10)	4.63 (4.96)	9.76 (9.93)
5c	80	215	$\text{C}_{21}\text{H}_{17}\text{N}_3$	80.82 (81.03)	5.23 (5.46)	13.41 (13.50)
5d	75	141	$\text{C}_{19}\text{H}_{11}\text{N}_2\text{O}_2$	72.75 (72.84)	3.65 (3.51)	13.24 (13.42)
5e	52	162	$\text{C}_{19}\text{H}_{11}\text{N}_3\text{O}_2$	72.68 (72.84)	3.74 (3.51)	13.11 (13.42)
5f	72	121	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$	80.32 (80.54)	4.82 (4.70)	9.22 (9.40)
5g	97	107	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$	80.45 (80.54)	4.93 (4.70)	9.34 (9.40)
5h	55	109	$\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$	76.64 (76.83)	4.92 (4.88)	8.29 (8.53)
5i	61	110	$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2$	76.22 (76.43)	4.65 (4.46)	8.73 (8.92)
5j	65	122	$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$	76.78 (76.92)	3.94 (3.84)	8.87 (8.97)
5k	70	200	$\text{C}_{21}\text{H}_{13}\text{N}_3$	83.54 (83.72)	4.54 (4.32)	13.84 (13.95)

TABLE 2. ^1H -NMR and IR data of synthesized dyes 5 a-k.

Dye no.	δ				$\nu_{\text{max}} / \text{cm}^{-1}$	
	Ar - H	CH_2	= C - H	Others	C = C	C
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

TABLE 2. Contd.

Dye no.	δ				$\nu_{\max} / \text{cm}^{-1}$	
	Ar - H	CH ₂	= C - H	Others	C = C	C
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,	3.47	10.2		1663, 1655	2191
	4.70					



Scheme 2

Visible Absorption Spectroscopic Properties

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

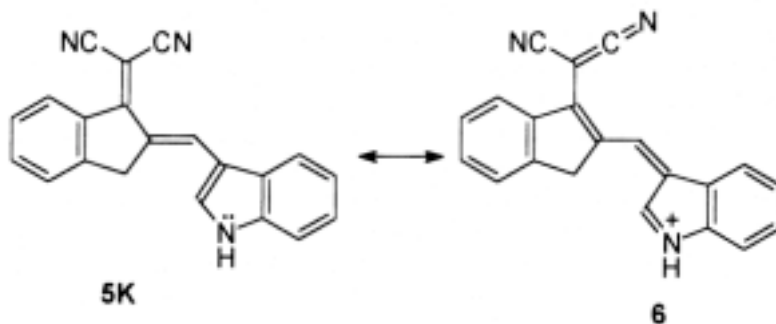
Each dye showed two absorption bands, the parent dye (**5a**) showed an absorption band at 495 nm in chloroform, and much more intense band at 378 nm. Likewise dye (**5c**) showed no absorption bands at 516 and 362 nm in chloroform. The introduction of donating groups into the para position of the phenyl group caused a remarkable 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 at 543 nm. Similar pattern was found for some of the synthesized dyes. By inspection the data of 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 shifts of the visible bands. Dye (**5g**) containing a methoxy group in position 2 absorbs at higher wavelength compared to dye (**5f**) containing the same substituent in position 4, this may be explained in term of the steric effect. The introduction of a second methoxy group provided further bathochromic shift, for example dye (**4h**) 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**). (3) The introduction of 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 parent dye **5a** is also an evidence of the donor-acceptor character of these dyes (see $\Delta\lambda$ values, Table 3). The visible absorption band of dye (**5k**) involves a $\pi-\pi^*$ transition through the conjugation 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 novel 1-dicyanomethylene dyes (**5c**) and (**5k**) with their 1-indanone derivatives (**3a**) and (**3b**) reveals the excellent electron accepting properties of the dicyanomethylene in producing a large bathochromic shifts of the maximum absorption bands.

TABLE 3. UV-Visible data of synthesized dyes 5a-k.

Dye no.	$\lambda_{\max} (\log \epsilon) / \text{CH}_3\text{CN}$		$\lambda_{\max} (\log \epsilon) / \text{CHCl}_3$		$\Delta\lambda$
	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

$\Delta\lambda = \lambda_{\max} (\text{band2 dyes 5b-k}) - \lambda_{\max} (\text{band2 dye 5a})$ in chloroform.



Scheme 3

Experimental

Melting points were recorded on a Thomas-Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer, $^1\text{H-NMR}$ were recorded in CDCl_3 on a Bruker 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 Shimadzu 260 spectrometer for solutions.

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), malononitrile (5.1 g, 0.075 mol) in absolute ethanol (100 ml) at 25°C . The reaction mixture was stirred for two hours, diluted with water and acidified to pH 3-4 with hydrochloric acid. The solid formed was filtered off, washed with water followed by small amount of ethanol. The crude product was recrystallised from ethanol to give **2** as off-weight powder (11.5 g, 84%), m.p. $146\text{--}8^\circ\text{C}$ (Found: C, 80.3; H, 4.23; N, 15.9%. $\text{C}_{12}\text{H}_8\text{N}_2$ requires C, 80.0; H, 4.44; N, 15.6%); ^1H nmr: δ_{H} 7.1-8.4, 3.3 (2H, t, CH_2), 3.1 (2H, t, CH_2), $\nu_{\text{max}}/\text{cm}^{-1}$ 2222 (CN), 1570.

General procedure for the synthesis of chalcones (3a) and (3b): A solution of sodium hydroxide (20 ml, 10%) was added drop-wise 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 two hours 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. Analytical samples were recrystallized from ethanol.

2-(4-Dimethylaminobenzylidene)indan-2-one- (3a): Yellow needles, 89% yield, m.p. $156\text{--}158^\circ\text{C}$. Found: C, 82.13; H, 6.46; N, 5.32. $\text{C}_{18}\text{H}_{17}\text{NO}$ requires C, 81.88; H, 6.23; N, 5.45%.

2-(Indol-3-yl)indan-2-one (3d): Yellow crystals, 94% yield, m.p. 160-162°C. Found: C, 83.22; H, 5.34; N, 5.65. C₁₈H₁₃NO requires C, 83.40; H, 5.02; N, 5.41%

Synthesis of 2-amino-4(4'-dimethyleaminophenyl)-3-cyano-5H-indeno[1,2]-pyridine (4): A solution of chalcone (**3a**) (1.5 g, 5.7 mmol), malonotrile (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 hours. The red solid product was collected by filtration and recrystallized from ethanol to give the title compound (**4**). Yield 1.0 g (60%), m.p. 240-242°C. Found: C, 76.32; H, 5.86; N, 17.96. C₂₀H₁₈N₄ requires C, 76.43; H, 5.73; N, 17.83%. $\nu_{\max}/\text{cm}^{-1}$ 3341, 3231 (NH₂), 2209 (CN), 1570 (C = C).

Synthesis of dye 5c by condensation of chalcone 3a and malonotrile: A mixture of chalcone **5a** (0.5 g, 1.9 mmol), malonotrile (0.13 g, 1.9 mmol) and catalytic amount of ammonium acetate-acetic acid mixture in dry benzene (20 ml) was heated under reflux for six hours. 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). The physical and analytical data of this compound are similar to that prepared by the following procedure and are listed in Tables 1, 2 and 3.

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 diethyl amine (10 mmol) in dry THF (25 ml) was stirred at room temperature for 3 hours. The reaction mixture was then poured into crushed ice (100 g) and the separated solid dye was collected and recrystallized from dichloromethane-toluene mixture. Yield, melting points and analytical data are listed in Table 1. H¹-nmr and infrared data are summarized in Table 2.

References

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اصطناع ، توصيف وخواص الامتصاص الضوئي لأصباغ جديدة مثلة في 2-أرايلدين-1-ثنائي سيانوميثيلين اندان

عبد الله محمد عسيري

قسم الكيمياء ، كلية العلوم ، جامعة الملك عبد العزيز

جدة - المملكة العربية السعودية

المستخلص . الاصطناع والخواص الضوئية لأصباغ مايثين مكونة من تكائف كنفينا جل لألدهيد عطري مع 1-ثنائي سيانوميثيلين اندان (2) أعطى مجموعة جديدة من الأصباغ (5 a-k) لها امتصاص في المجال من 490-593 nm . وجد أن المستبدلات في الحلقة العطرية للألدهيد لها تأثير كبير على قمم الامتصاص في المجال المرئي . زيادة قطبية المذيب لها تأثير على موقع الامتصاص .