

Synthesis and Absorption Spectral Properties of Bis-methine Dyes Exemplified by 2,5-Bis-arylidene-1-dicyanomethylene-cyclopentanes

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Received November 25, 2002

A range of methine dyes has been synthesized by condensation of highly electronegative active methylene compound dicyanomethylenecyclopentane derived from cyclopentanone with the formyl group of substituted benzaldehydes. The electronic absorption spectroscopic properties of the dyes were investigated. In general, substituents on the aromatic aldehyde moiety have a significant effect on the visible absorption maxima of the dyes; increasing the solvent polarity also showed a pronounced effect on the absorption maxima.

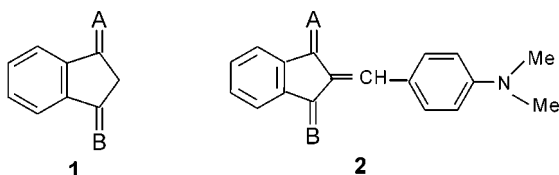
Key Words : Bis-methine dyes, Malononitrile, Cyclopentanone, Dicyanomethylenecyclopentane, Chalcones

Introduction

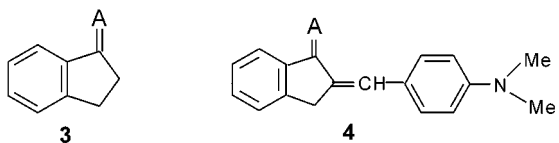
A broad class of dyestuff and colorants are based on electron donor-acceptor (D- π -A) chromogens. Such compounds have found many applications such as in dyeing of fabric, coloring of toners, and in image forming and optical information storage technologies. Some of these compounds are also used as sources of tunable (dye laser) radiation.¹⁻⁷

Methine dyes (e.g. **2**) based on indan-1,3-dione **1a** are typical donor-acceptor chromogens and are generally yellow to orange in colour with high absorption intensity.⁸

Replacement of the oxygen of one of the carbonyl groups in **2a** by a more powerful electron acceptor dicyanomethylene groups give dye **2b**, which has absorption maximum at much longer wavelengths with some reduction in intensity.⁹ Further modification of dye **2b** by replacing the second carbonyl group by dicyanomethylene group (e.g. **2c**), results



1, 2
a A = B = O
b A = O, B = C(CN) ₂
c A = B = C(CN) ₂

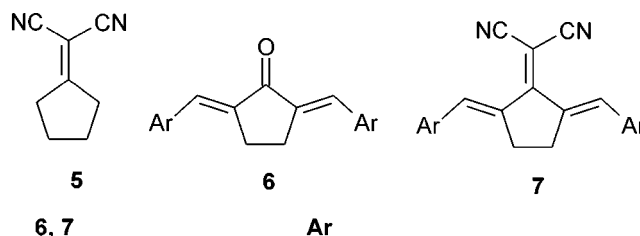


3, 4
a A = O
b A = C(CN) ₂

in dyes with absorption up to 625 nm.⁹

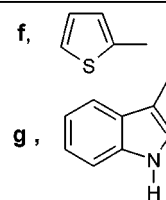
Recently, we have reported the synthesis of new dyes **4a** and **4b** by condensation of 1-indanone **3a** and 1-dicyanomethyleneindane **3b** and aromatic aldehydes.¹⁰

Dye **4b** absorbs at shorter wavelength than **2b** by some 84 nm and some 46 nm to longer wavelength than **2a**. In the present investigation, the synthesis, colour and constitution of new dyes **7a-g** prepared by condensation of dicyanomethylenecyclopentane **5** and aromatic aldehydes will be discussed.



6, 7 Ar

a	4-Me ₂ N-C ₆ H ₄
b	2-MeO-C ₆ H ₄
c	3,4-(MeO) ₂ -C ₆ H ₃
d	2,5-(MeO) ₂ -C ₆ H ₃
e	3,4-OCH ₂ O-C ₆ H ₃



Results and Discussion

Synthesis of dyes. Chalcones **6a-g** were prepared *via* Aldol condensation of 1-cyclopentanone and appropriate aldehydes (Table 1). When chalcone **6a** and malononitrile were heated under reflux in the presence of ammonium acetate, gave exclusively the pyridine derivative **8** shown in Scheme 1. This is in agreement with similar observations reported in the literature.¹¹

The IR spectrum of the pyridine derivatives **8** showed absorption bands at 3350, 3227 cm⁻¹ and an absorption band at 2215 cm⁻¹ for amino and cyano groups respectively.

It has been reported in the literature that α,β -unsaturated

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Table 1. Characterization Data of Chalcones **6a-g**

Dye No.	Yield (%)	m.p. (°C)	Molecular formula	(% Found (calculated))		
				C	H	N
6a	63	120	C ₂₃ H ₂₆ N ₂ O	79.52 (79.77)	7.85 (7.51)	7.85 (8.09)
6b	67	155	C ₂₁ H ₂₀ O ₃	78.63 (78.75)	5.98 (6.25)	
6c	66	157	C ₂₃ H ₂₄ O ₅	72.49 (72.63)	6.28 (6.32)	
6d	88	210	C ₂₃ H ₂₄ O ₅	72.52 (72.63)	6.43 (6.32)	
6e	44	250	C ₂₁ H ₁₆ O ₅	72.51 (72.41)	4.43 (4.60)	
6f	55	140	C ₁₅ H ₁₂ S ₂ O	65.87 (66.17)	4.67 (4.41)	
6g	77	170	C ₂₃ H ₁₈ N ₂ O ₂	81.46 (81.65)	5.51 (5.33)	8.36 (8.23)

ketones, when heated with malononitrile in benzene using a catalytic amount of ammonium acetate-acetic acid as a base under a Deanstark trap, gave the desired Knoevenagel condensation product.^{12,13} However, heating under reflux for 8 hrs the chalcone **6a**, malononitrile and ammonium acetate-acetic acid in benzene gave **7a** as shown in Scheme 2 in very low yield. The low yield of Knoevenagel product **7a** promoted us to look for an alternative procedure to obtain a better yield.

Among those procedures a solid state Knoevenagel

reaction which reported in 1993 in which a catalytic amount of CdI was used as a catalyst.¹⁴ Moreover, when the reaction was carried in ethanol in the presence of piperidine as a base, 4H-pyran derivative **9** was obtained as yellow crystals in good yield (Scheme 2). In this case, the Knoevenagel condensation was not taking place but the Michael addition was facilitated. On the other hand, if the highly electro-negative active methylene **5** was condensed with benzaldehydes such as 4-dimethylaminobenzaldehyde in ethanol or in THF no Knoevenagel products were identified.

However, a reasonable yield of dyes **7a-g** was obtained when the dicyanomethylenecyclopentane **5** and the aromatic aldehyde were fused at 140 °C for about three hours. This procedure was adopted for the synthesis of dyes **7a-g**, analytical data for which are summarized in Table 1. Dyes **7a-g** exhibited CN absorption bands in their IR spectra in the region of 2205-2230 cm⁻¹ (Table 3), and their ¹H-NMR spectra showed a down field singlet in the region of δ 7.0-8.0 ppm, attributed to olefinic protons (Table 4). ¹³C-NMR data are summarized in Table 5.

Electronic absorption spectroscopic properties. Absorption spectra were recorded in chloroform, acetone and acetonitrile; the results obtained are summarized in Table 6. Dye **7a**, which was obtained from 4-dimethylaminobenzaldehyde and compound **5**, absorbs at 542 nm in chloroform, with molar extinction coefficient of 5000 dm³·mol⁻¹·cm⁻¹. Changing the donor from dimethylamino to methoxy group as for dye **7b**, which prepared from 2-methoxybenzaldehyde,

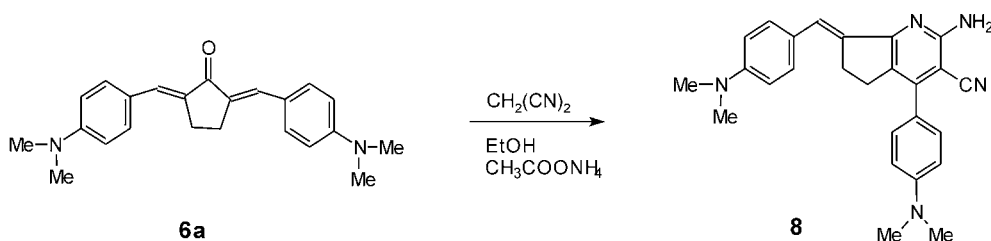
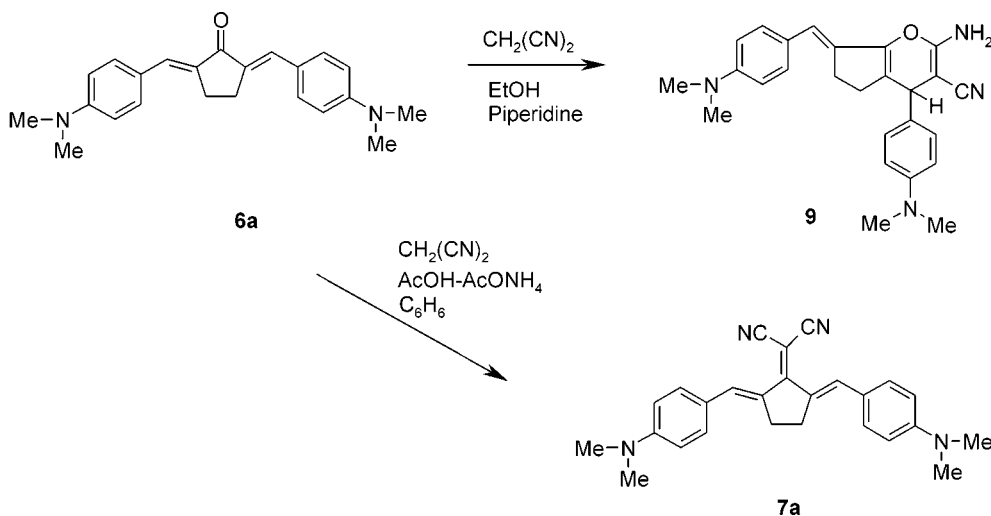
**Scheme 1****Scheme 2**

Table 2. Characterization Data of Dyes **7a-g**

Dye No.	Yield (%)	m.p. (°C)	Molecular formula	(% Found (calculated))		
				C	H	N
7a	16	233	C ₂₆ H ₂₆ N ₄ O ₄	77.95 (78.18)	6.31 (6.59)	14.01 (14.21)
7b	67	122	C ₂₄ H ₂₀ N ₂ O ₂	78.04 (78.26)	5.68 (5.43)	7.39 (7.61)
7c	66	125	C ₂₆ H ₂₄ N ₂ O ₄	72.64 (72.89)	5.46 (5.60)	6.61 (6.54)
7d	75	199	C ₂₆ H ₂₄ N ₂ O ₄	72.68 (72.89)	5.46 (5.60)	6.38 (6.54)
7e	44	189	C ₂₄ H ₁₆ N ₂ O ₂	72.43 (72.72)	4.25 (4.04)	6.85 (7.07)
7f	55	168	C ₁₈ H ₁₂ N ₂ S ₂	67.43 (67.50)	3.64 (3.75)	8.56 (8.75)
7g	77	189	C ₂₆ H ₁₈ N ₄	80.68 (80.82)	4.54 (4.66)	14.32 (14.50)

Table 3. IR Spectral Data of Chalcones **6a-g** and Dyes **7a-g**

Entry No.	ν_{\max} (cm ⁻¹)			
	6		7	
	C=C	C=O	C=C	CN
a	1589	1689	1607	2175
b	1594	1679	1657	2225
c	1597	1680	1645	2207
d	1616	1708	1640	2206
e	1597	1682	1657	2224
f	1589	1649	1657	2225
g	1609	1682	1637	2203

Table 4. ¹H-NMR-Data of Chalcones **6a-g** and Their Analogues Dicyanomethylene Derivatives **7a-g**

Compound No.	-(CH ₂ -)	Aromatic protons	Olifinc protons	Others
6a	3.02	6.78-7.38	7.71	3.04 (CH ₃) ₂ N
6b	3.02	6.93-7.52	8.00	3.89 (CH ₃ O)
6c	3.10	6.92-7.22	7.53	3.92 (2CH ₃ O)
6d	3.00	6.86-7.08	7.95	3.80, 3.81 (2CH ₃ O)
6e	2.95	6.8-7.11	7.67	5.95 (-OCH ₂ O-)
6f	2.95	7.14-7.54	7.98	
6g	2.90	7.95-7.18	7.98	9.02 (NH)
7a	2.19	6.69-7.74	7.08	3.09 (CH ₃) ₂ N
7b	2.20	6.91-7.35	7.09	3.74 (CH ₃ O)
7c	2.19	6.86-7.67	7.03	3.83, 3.86 (2CH ₃ O)
7d	2.19	6.93-7.31	7.05	3.79 (2CH ₃ O)
7e	2.19	6.88-7.26	7.03	5.95 (-OCH ₂ O-)
7f	2.20	7.17-7.52	7.47	
7g	2.19	7.18-7.75	7.35	9.02 (NH)

resulted in absorption at 411nm in chloroform. In increasing the number of the donating group as in the case in dyes **7c**, **7d** and **7e** the shift of absorption to longer wavelength compared to **7b** was observed (Table 6). The presence of the methoxy groups in position 3 and 4 showed bathochromic

Table 5. ¹³C-NMR-Data of Dicyanomethylene Derivatives **7a-g**

Compound No.	δ
7a	26.78, 39.85, 82.63, 111.67, 115.44, 124.16, 135.21, 138.39, 143.7, 151.01, 167.79
7b	26.21, 55.80, 81.00, 111.30, 115.33, 120.5, 123.67, 128.88, 132.52, 134.36, 143.45, 161.80, 170.90
7c	25.91, 56.05, 82.63, 112.63, 114.40, 115.44, 128.23, 129.11, 142.32, 145.32, 145.57, 148.71, 149.78, 170.19
7d	26.11, 55.61, 55.80, 81.00, 112.28, 115.01, 115.88, 124.11, 124.2, 130.48, 145.09, 152.05, 155.23, 173.29
7e	26.78, 82.63, 102.02, 112.55, 115.44, 127.92, 128.72, 142.44, 147.91, 148.14, 148.14, 148.32, 170.19
7f	26.37, 82.10, 115.44, 129.76, 133.59, 134.32, 136.47, 142.50, 142.5, 167.79
7g	29.43, 73.45, 112.09, 115.72, 116.35, 118.90, 120.54, 123.65, 127.12, 129.23, 131.26, 133.04, 136.23, 159.08

Table 6. UV-Visible Spectral Data of Chalcones **6a-g** and Their Analogues Dicyanomethylene Derivatives **7a-g**

Dye No.	λ_{\max} (nm)			ϵ_{\max}
	(dm ³ mol ⁻¹ cm ⁻¹)			
	CHCl ₃	Acetone	CH ₃ CN	CH ₃ CN
6a	466	379	404	2360
6b	379	376	372	3368
6c	387	384	394	3067
6d	401	395	383	6893
6e	398	—	394	4004
6f	376	365	372	5604
6g	435, 356	432, 412	353	1361
7a	542	533	543	5000
7b	411	410	404	3327
7c	450	467	440	1070
7d	486	495	480	4091
7e	445	461	450	8523
7f	452	475	461	5941
7g	489	481	506	6189

shift compared to the presence of the methoxy groups in position 2 and 5.

The introduction of the heterocyclic group such as dye **7f** and **7g** which were prepared from 2-thiophenecarboxaldehyde and indole-3-carboxaldehyde respectively, showed bathochromic shift of visible absorption bands; dye **7g** absorbs at 489nm with large band width *ca.* 180 nm, which is a large bathochromic shift. The UV-Visible spectrum of dye **7a** is shown in Figure 1 in acetonitrile as a representative example.

The large bathochromic shift of visible absorption of 4-dimethylamino derivative **7a** (542 nm in chloroform) relative to the less powerful donating groups such as the methoxy *e.g.* in **7c** typifies the donor-acceptor character of the system. Increasing the solvent polarity causes bathochromic shift, indicating that the visible absorption band of dyes **7a-g** involves a π - π^* transition through the conjugated system.

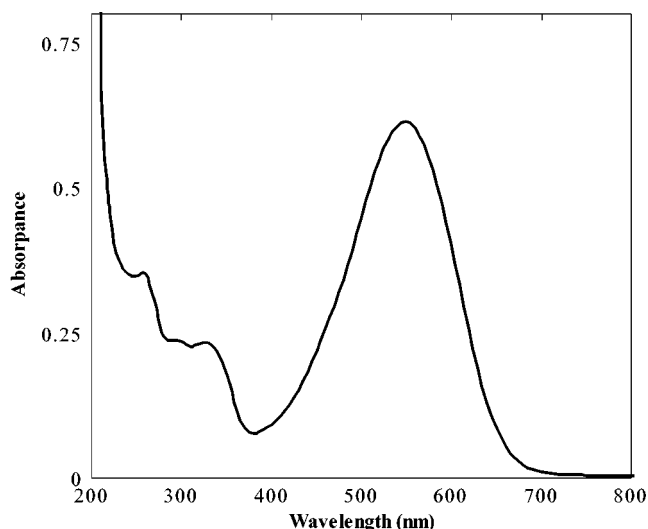


Figure 1. UV-Visible Spectrum of Dye **7a** in acetonitrile.

The excited state receiving a large contribution from polar charge transfer is obtained by the migration of electrons from the nitrogen atom to the dicyanomethylene moiety (Scheme 4).

Comparison of the dicyanomethylene **7a-g** with their corresponding chalcones **6a-g** showed the excellent electron accepting properties of the dicyanomethylene moiety in producing large bathochromic shifts (Table 6).

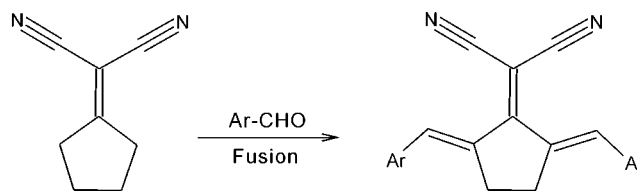
Conclusions

The solventless Knoevenagel condensation of aromatic aldehydes and dicyanomethylenecyclopentane afforded new 2,5-bisarylidene methine dyes. The substituents on the aromatic aldehydes play an important role in the colour of the new dyes.

Experimental Section

Melting points were recorded on a Thomas-Hover capillary melting apparatus without correction. IR spectra were taken on KBr disks on a Nicolet Magna 520 FTIR spectrophotometer. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 on a Bruker DPX 400 MHz. Spectrometer using TMS as an internal standard. Microanalysis were carried out using a Perkin-Elmer 240B analyzer. UV-Visible spectra was recorded on a Shimadzu 260 spectrometer.

Dicyanomethylenecyclopentane (5). Anhydrous sodium acetate (10.0 g, 0.119 mol) was added to a stirred solution of



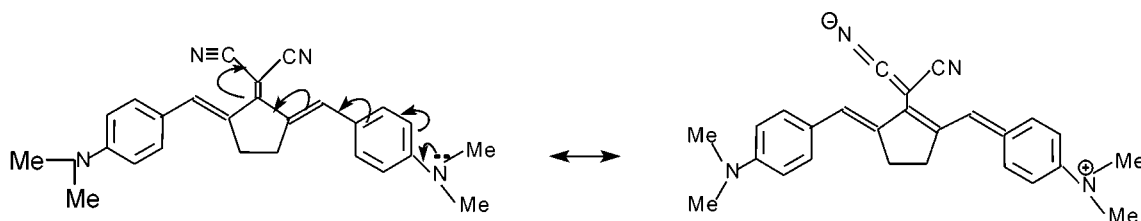
Scheme 3

cyclopentanone (10.0 g, 0.117 mol) and malononitrile (7.86 g, 0.119 mol) in absolute ethanol (100 mL) at 25 °C. The reaction mixture was stirred for 6 hrs, diluted with water and acidified to pH 3-4 with 6 N hydrochloric acid solution. The solid formed was filtered, washed with water followed by a small amount of ethanol. The crude product was recrystallized from ethanol to give **5** as off-white powder (12.5 g, 80%), m.p. 83-85 °C. *Anal.* Calculated for $\text{C}_8\text{H}_8\text{N}_2$: C, 72.73; H, 6.06; N, 21.21. Found: C, 72.56; H, 5.89; N, 21.43.

General procedure for the synthesis of chalcones (6a-g). A solution of sodium hydroxide (20 mL, 10%) in water was added dropwise to a well stirred solution of cyclopentanone (0.05 mole) and the appropriate aldehyde (0.1 mol) in ethanol (25 mL) at room temperature. The reaction mixture was stirred for two hours and then added to a mixture of ice and conc. hydrochloric acid. The precipitates were filtered, washed thoroughly with water and finally with ethanol, and dried. Analytical samples were recrystallized from ethanol (Table 1).

Preparation of the pyridine derivative (8). A solution of the chalcone **6a** (0.5 g, 1.43 mmol), malononitrile (0.1 g, 1.43 mmol) and ammonium acetate (0.33 g, 4.3 mmol) in absolute ethanol (25 mL) was heated under reflux for 3 hours. The solid product was collected by filtration and recrystallized from ethanol to give pyridine derivative **8** as orange powder (0.48 g, 82%), m.p. 220-222 °C. *Anal.* Calculated for $\text{C}_{26}\text{H}_{27}\text{N}_5$: C, 76.28; H, 6.60; N, 17.11%. Found: C, 76.35; H, 5.89; N, 17.37. $\nu_{\text{max}}/\text{cm}^{-1}$ 3350, 3227 (NH_2), 2215 (CN), 1580 (C=C).

Preparation of the pyran derivative (9). A mixture of chalcone **6a** (1.5 g, 4.3 mmol), malononitrile (0.28 g, 4.3 mmol) and absolute ethanol (20 mL) in the presence of a few drops of piperidine was refluxed in a water bath for 5 hrs. The amount of solvent was reduced by distillation under reduced pressure and allowed to cool. The precipitated solid was collected by filtration and crystallized from ethanol to give pyran **9** as yellow crystals (1.5 g, 85%), m.p. 153-155 °C. *Anal.* Calculated for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}$: C, 75.73; H, 6.80; N, 13.59. Found: C, 75.65; H, 6.98; N, 13.36; $^1\text{H NMR}$ δ 2.02, 2.41 (4H, m, CH_2), 2.91, 3.01 (12H, s, $(\text{CH}_3)_2\text{N}$), 4.24 (1H,



Scheme 4

s, Pyran-4H), 6.72-8.19 (8H, m, aromatic protons), 6.89 (1H, s, olefinic proton); ν_{\max} cm^{-1} 3380, 3290 (NH₂), 2220 (CN).

General procedure for the synthesis of dyes (7a-g). A mixture of cyclopentylidenemalonitrile (1 mmol) and aromatic aldehyde (2 mmol) was heated in an oil bath for 6 hrs. After cooling the reaction mixture to room temperature, ethanol (25 mL) was added and the precipitate was filtered and recrystallized from acetic acid (Table 2).

Acknowledgements. The financial support for this research from the scientific research council of King AbdulAziz University is gratefully acknowledged.

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