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

A. M. ASIRI
Department, Faculty of Science
King Abdul-Aziz University
Jeddah 21589, P.O. Box 80203, Saudi Arabia

(Received 3rd January, 2002, revised 8th August, 2003)

Summary: 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 had a pronounced effect on the absorption maxima.

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 the more powerful electron acceptor dicyanomethylene groups give dye **2b**, which has absorption maximum at much higher 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 in dyes absorbing up to 625 nm [9].

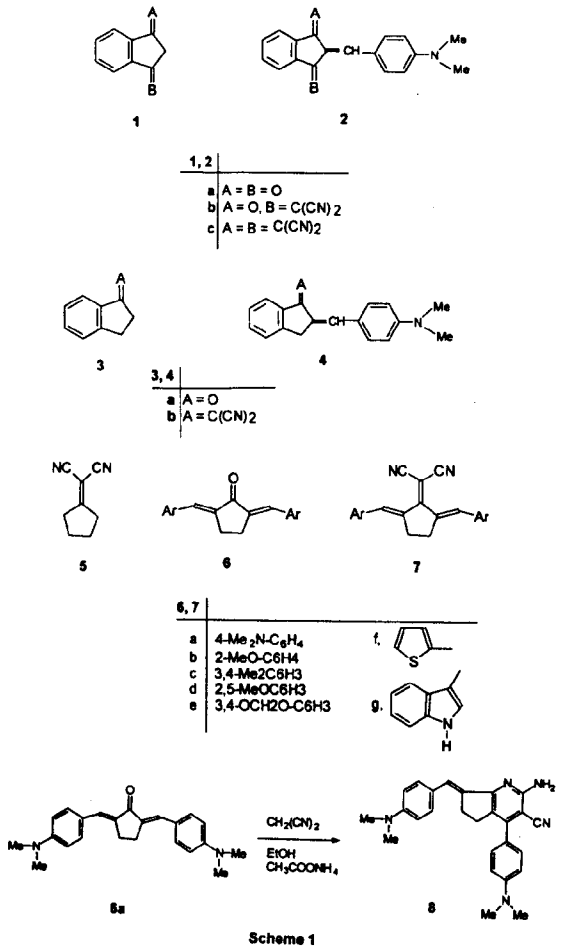
Recently,[10] we have reported the synthesis of new dyes **4a** and **4b** by condensation of 1-indanone **3a** and 1-dicyanomethyleneindane **3b** and aromatic aldehydes.

Dye **4b** absorbs some 84 nm to lower wavelength than **2b** 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 dicyanomethylene-cyclopentane **5** will be discussed.

Results and Discussion

Synthesis of dyes

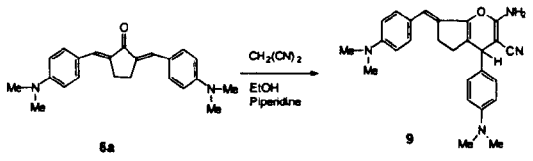
Chalcones **6a-g** were prepared via Aldol condensation of 1-indanone and appropriate aldehyde (Table 1). When chalcone **6a** and malononitrile were heated under reflux in the presence of ammonium acetate, gave exclusively the pyridine **8** derivative shown in scheme 1. This in agreement with similar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



Scheme 1

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

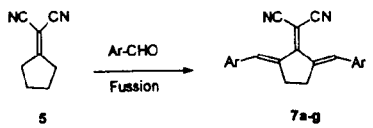
It has been reported in the literature that α,β-unsaturated ketones, when heated with malononitrile in benzene using a catalytic amount of ammonium acetate-acetic acid as a base under a Dean-Stark trap, gave the desired Knoevenagel condensation product [12,13]. However, heating under reflux for 8hr the 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.



Scheme 2

Among those procedures a solid state Knoevenagel reaction which reported by 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-pyrane derivative **9** was obtained as yellow crystals in good yield (scheme 2). In this case, the Knoevenagel condensation was not taking place and the Michael addition was facilitated.

On the other hand, if the hieghly electronegative active methylene **5** was condensed with benzaldehydes such as 4-dimethylaminobenzaldehyde in ethanol or in THF no Knoevenagel product were identified (Scheme 3).



Scheme 3

However, a reasonable yield of dyes **7a-g** was obtained when the dicyanomethylenecyclopetane **5** and the aromatic aldehyde were fussed 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 2), and their H^1-NMR spectra showed a low field singlet in the region of δ 8.5-8.1 ppm, attributed to olefinic protons (Table 3).

Table 1:Characterizations Data of Chalcones 6a-g

Dye No.	Yield (%)	m.p. (°C)	Molecular formula	(%) Found(calculated) C	H	N
6a	63	120	$C_{23}H_{26}N_2O$	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	$C_{15}H_{12}S_2O$	65.87 (66.17)	4.67 (4.41)	
6g	77	170	$C_{23}H_{18}N_2O_2$	81.46 (81.65)	5.51 (5.33)	8.36 (8.23)

Table-2: IR Spectral Data of Chalcones 6a-g and Dyes 7a-g

Entry No.	vmax (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 3:H-NMR-Data of Chalcones 6a-g and their Analogues Dicyanomethylene Derivatives 7a-g

Comp. No.	$-(CH_2)-$	Aromatic protons	Oliefinc protons	Others
6a	3.02	6.78-7.38	7.71	3.04 $(CH_3)_2N$
6b	3.02	6.93-7.52	8.00	3.89 (CH_3O)
6c	3.10	6.92-7.22	7.53	3.92 (2CH3O)
6d	3.00	6.86-7.08	7.95	3.80, 3.81 ($2CH_3O$)
6e	2.95	6.8-7.11	7.67	5.95 ($-OCH_2O-$)
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 $(CH_3)_2N$
7b	2.20	6.91-7.35	7.09	3.74(CH_3O)
7c	2.19	6.86-7.67	7.03	3.83, 3.86 ($2CH_3O$)
7d	2.19	6.93-7.31	7.05	3.79 ($2CH_3O$)
7e	2.19	6.88-7.26	7.03	5.95 ($-OCH_2O-$)
7f	2.20	7.17-7.52	7.47	
7g	2.19	7.18-7.75	7.35	9.02 (NH)

Electronic Absorption Spectroscopic Properties

Absorption spectra were recorded in chloroform in acetone and acetonitrile; the results obtained are summarized in table 4.

Dye **7a**, which was obtained from 4-dimethylaminobenzaldehyde and compound **5**, absorbs at 542nm in chloroform, with molar extinction coeffi-

Table-4:Uv Visible Spectral Data of Chalcones 6a-g and their Analogues Dicyanomethylene Derivatives 7a-g

Dye No.	λ_{max} (nm)			ε_{max} ($dm^3mol^{-1}cm^{-1}$)
	$CHCl_3$	Acetone	CH_3CN	CH_3CN
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

cient of 5000 $dm^3.mol^{-1}cm^{-1}$. Changing the donor from dimethylamino to methoxy group as for dye **7b**, which prepared from 2-methoxybenzaldehyde, absorbs at 411nm in cholroform.

In increasing the number of the donating group as the case in dyes **7c**, **7d** and **7e** shift of the absorption to longer wavelength compared to **7b** (Table 4). The presence of the methoxy group in positions 3 and 4 showed bathochromic shift compared to the presence of the methoxy group in positions 2 and 5.

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

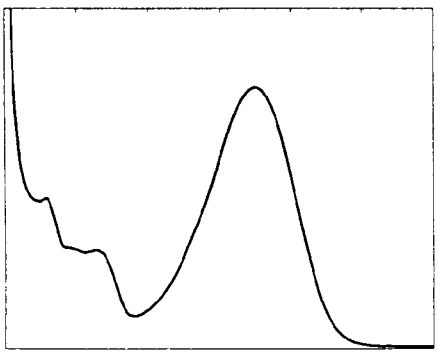
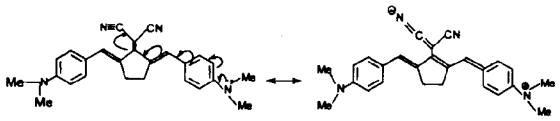


Fig. 1: UV-Visible Spectrum of dye **7a** in acetonitrile

The large bathochromic shift of visible absorption of 4-dimethylamino derivative **7a** (542nm in chloroform) relative to the less powerful donating groups such as the methoxy e.g. **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 $\pi-\pi^*$ 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 4).



Scheme 4

Comparison of the dicyanomethylene **7a-g** with their counter part chalcones **6a-g** showed the excellent electron accepting properties of the dicyanomethylene moiety in producing large bathochromic shifts (Table 3).

Experimental

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, H^1-NMR spectra were recorded in $CDCl_3$ on a Brucker DPX 400 MHz. Spectrometer using TMS as internal standard. Microanalysis were carried out using a Perkin-Elmer 240B analyzer. UV-Visible spectra were recorded on a Shimadzu 260 spectrometer.

Dicyanomethylenecyclopentane (5)

Anhydrous sodium acetate (10.0g, 0.119mol) was added to a stirred solution of cyclopentanone (10.0g, 0.117mol) and malononitrile (7.86g, 0.119 mol) in absolute ethanol (100ml) at 25°C. The reaction mixture was stirred for 6hrs, 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 recrystallized from ethanol to give **5** as off-white powder (12.5g, 80%), m.p. 83-85 °C. *Anal.* Calculated for $C_8H_8N_2$:C, 72.73; H, 6.06; N, 21.21. Found: C, 72.56; H, 65.89; N, 21.43.

General procedure for the synthesis of chalcones (6a-g)

A solution of sodium hydroxide (20 ml, 10%) was added drop-wise to a well stirred solution of cyclopentanone (0.05mole) 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 hydrochloric acid. The precipitates were filtered off, 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 deriva-tive **8** as orange (0.48 g, 82%), m.p. 220-222°C. *Anal.* Calculated for $C_{26}H_{27}N_5$: C, 76.28; H, 6.60; N, 17.11%. Found: C, 76.35; H, 5.89; N, 17.37. ν_{max} /cm^{-1} 3350, 3227 (NH_2), 2215 (CN), 1580 (C=C).

Preparation of the pyrane 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 few drops of piperidine was refluxed on a water bath for 5hr. The 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 pyrane 9 as yellow crystals (1.5 g, 85 %), m.p. 153-155 °C. *Anal.* Calculated for $C_{26}H_{28}N_4O$: C, 75.73; H, 6.80; N, 13.59. Found: C, 75.65; H, 6.98; N, 13.36; ^{1}H NMR δ 2.02, 2.41 (4H, m, CH_2), 3.01 (6H, s, $(CH_3)_2N$), 4.24 (1H, s, Pyran-4H), 6.72-8.19 (8 H, m, aromatic protons), 6.89 (1H, s, olefinic proton); ν_{max} cm^{-1} 3380, 3290 (NH_2), 2220 (CN).

General procedure for the synthesis of dyes (7a-g)

A mixture of cyclopentylidenemalononitrile (1mmol) and aromatic aldehyde (2mmol) was heated in an oil bath for 6hrs. After cooling the reaction mixture to room temperature, ethanol (25ml) was added and the precipitate was filtered and recrystallized from acetic acid (Table 5).

Table 5:Characterizations Data of Dyes 7a-g

Dye No.	Yield (%)	m.p. (°C)	Molecular formula	(%) Found (calculated) C	H	N
7a	16	233	$C_{26}H_{26}N_4O_4$	77.95 (78.18)	6.31 (6.59)	14.01 (14.21)
7b	67	122	$C_{24}H_{20}N_2O_2$	78.04 (78.26)	5.68 (5.43)	7.39 (7.61)
7c	66	125	$C_{26}H_{24}N_2O_4$	72.64 (72.89)	5.46 (5.60)	6.61 (6.54)
7d	75	199	$C_{26}H_{24}N_2O_4$	72.68 (72.89)	5.46 (5.60)	6.38 (6.54)
7e	44	189	$C_{24}H_{16}N_2O_2$	72.43 (72.72)	4.25 (4.04)	6.85 (7.07)
7f	55	168	$C_{18}H_{12}N_2S_2$	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)

Conclusions

The solventles knovenagel condensation of aromatic aldehydes and dicanomethylenecyclopentane afforded a new 2,5-bis arylidene methine dyes. The subistitunets on the aromatic aldehydes play an important role in the colour of the new dyes.

Acknowledgements

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

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