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Synthesis and Electronic Absorption Spectra of New Coloring Matters Based on Donor-Conjugated-Acceptor Chromophores

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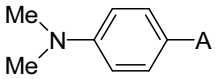
Abstract. New chromophores of the Donor-conjugated-acceptor types containing 4-N,N-dimethylaminobenzene as the donor-conjugated group are prepared with different types of acceptors. The electronic spectra were investigated in ethanol and acetonitrile to assess the effect of solvatochromic properties of these new dyes. The relative strength of the acceptor in producing large bathochromic shift was illustrated. Tricyanovinyl is the best acceptor used in this study to produce a larger bathochromic shift of the visible absorption, where as the least acceptor used is diethyl malonate.

Introduction

In chromophores exemplified by conjugated-donor-acceptor (D-π-A) system the color of a dye of this series is remarkably affected by one of the following structural modifications: (a) increasing the donor group releasing ability; (b) increasing the accepting ability of the acceptor group; (c) lengthening the conjugated system. Although increasing the conjugated system causes a pronounced bathochromic shift, yet it resulted in a remarkable decrease in the solubility of the dye in common organic solvents. Modification (a) is self-evident but modification, (b) needs further investigations. Our continuous interest in dyes absorbing at high wavelengths (*e.g.* blue and near-infrared regions) suitable for use with diode lasers in optical recording and other electro-optical areas[1,2],

encouraged us to look for a simple way to predict the effect of approach (b). The present paper, describes the use of UV-Visible spectroscopic data which can be used in a qualitative way to estimate the relative strength of different electron accepting groups of dyes having the general formula **1**.



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 FT-IR spectrometer. Microanalyses were carried out using a Perkin Elmer 240B analyzer. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for solutions (*c. f.*1×10^{-4} M).

General Procedure for the Condensation of 4-N,N-Dimethylamino Benzaldehyde and the Active Methylene Compounds

Method A [3]

To a refluxed solution of aldehyde (10 mmol) and the active methylene (10 mmol) in ethanol (50 ml) Piperidene (1 ml) was added. After the addition, the solution became darker and the reflux was continued for six hours, then the solution was left to cool to room temperature and the products deposited. The precipitate was filter and washed with cold water and finally with ethanol, dried and recrystallazied from the appropriate solvent (Tables 1 and 2).

Method B [4]

The aldehyde (10 mmol) and the active methylene (10 mmol) and cadmium iodide (CdI_2) (0.1 mmol) was mixed together and heated at 70 C for 5 min. The melt was then treated with 1% aqueous ethanol, filtered then washed with aqueous ethanol, dried and recrystalized from appropriate solvent (Tables 1 and 2).

Table 1. Physical and analytical data of synthesised dyes.

Dye no.	Yield (%)	m.p. (°C)	Preparation method +solvent of crystl.*	Molecular formulae	Calc. (Found) (%)		
					C	H	N
2a	89	185	A + E	$C_{12}H_{11}N_3$	73.10(73.31)	5.58(5.62)	21.32(21.11)
2c	85	105	A + E	$C_{14}H_{16}N_2O_2$	68.85(68.62)	6.56(6.45)	11.48(11.22)
2d	75	85	A + E	$C_{14}H_{17}NO_4$	63.88(63.65)	6.46(6.52)	5.32(5.55)
2e	84	150	D + E	$C_{16}H_{15}N_2F$	75.59(75.62)	5.90(5.75)	11.02(10.85)
2f	90	290	C + E	$C_{18}H_{16}N_4$	75.00(74.81)	5.56(5.34)	19.44(19.65)
2g	75	142	A + T	$C_{10}H_{12}N_2O_2$	62.50(62.32)	6.25(6.10)	14.58(14.67)
3a	94	232	B + T	$C_{13}H_{13}N_3O_3$	60.23(60.11)	5.02(4.82)	16.21(15.98)
3b	93	230	B + E	$C_{15}H_{17}N_3O_3$	62.72(62.45)	5.92(5.82)	14.63(14.45)
3c	98	242	B + T	$C_{13}H_{13}N_3O_2S$	56.73(56.55)	4.73(4.89)	15.27(15.45)
4a	89	156	A + E	$C_{18}H_{17}NO$	82.13(81.88)	6.46(6.23)	5.32(5.45)
4b	80	215	C + M	$C_{21}H_{17}N_3$	81.03(80.86)	5.46(5.23)	13.50(13.68)
5	78	195	D + E	$C_{19}H_{19}N_3O$	74.75(74.43)	6.23(6.11)	13.77(13.65)

* E = ethanol M = methanol T = toluene

Table 2. IR spectral data of synthesized dyes.

Dye no.	ν_{max}/cm^{-1}		
	C=O	C≡N	C=C
2a		2211	1615
2b		2213	1609
2c	1705	2210	1612
2d	1703		1610
2e		2205	1620
2f		2224	1590
2g		2224	1590
3a	1720, 1670		1610
3b	1713, 1660		1609
3c	1695, 1648		1612
4a	1680		1599
4b		2204	1601, 1705
5	1670		1622

Method C [5]

The aldehyde (10 mmol) and the active methylene (10 mmol) in dry THF (50 ml) were stirred at room temperature. Diethylamine (10 mmol) was added dropwise with stirring, after the addition was completed the reaction mixture was stirred for further 4 hours. THF was removed under reduced pressure and the residual was crystallized form appropriate solvent (Tables 1 and 2).

Method D [6]

A mixture of the aldehyde (10 mmol), the active methylene (10 mmol) in a mixture of acetic anhydride (50 ml), acetic acid (10 ml) and sodium acetate (0.5 g). The reaction mixture was refluxed for two hours. The reaction mixture was poured into water and the solid separated was collected and crystallized form the appropriate solvent (Tables 1 and 2).

Preparation of 4-(Dimethylamino)-α,β,–Tricyanostyrene 2b [7]

A solution of N,N-dimethylaniline (2 g, 16.5 mmol) and tetracyanoethylene (2.1 g, 16.5 mmol) in DMF (25 ml) was stirred at room temperature for 12 h. The solvent was removes and the residual solid was collected and recrystallized from hexane-chloroform mixture to give dark-blue needles (2.94 g, 80% yield), m.p. 177-197°C (lit.[7]: 173-175°C), for IR data, Table 2.

Preparation of the Salt B

To a solution of the benzoimidazol-2-yl derivative **2f** (1.0 g) in ethanol (15 ml) was added concentrated hydrochloric acid (5 ml). The solution was refluxed for 15 minuets then cooled and kept over night in refrigerator, the precipitated salt was collected by filtration washed with absolute ethanol and dried under vacuum to give purple crystals (Table 1).

Results and Discussion

Synthesis of Dyes

Apart from dye **1b**, all other dyes were prepared via knovenagel condensation of N,N-dimethylamino- benzaldehyde and the appropriate active methylene components according to the literatures[3,4].

Absorption Spectral Properties

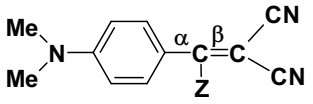
The relative strength of a certain electron acceptor can be estimated from the fact that it will give stabilization to the exited state of the chromophores and therefore a bathochromic shift. In the present paper, thirteen electron acceptors are selected.

Cyano Derivatives

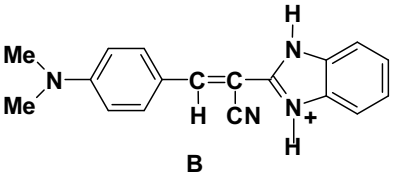
In this series six derivatives **2a-f** were selected. For the simplicity we selected the dicyanomethylene derivative **2a** (λmax = 430 nm) as a reference which has two cyano groups in position β (formula **A**). Replacement of one of the cyano groups by a group of less electron withdrawing character such as ethoxycarbonyl (*i.e.* **2c**) causes a hypsochromic shift of (c.a.9 nm) of the maximum absorption band. Moreover the replacement of both cyano groups by two ethoxy carbonyl (**2d**) causes a remarkable hypsochromic shift (*i.e.* 59 nm). The replacement of one of the cyano groups of the dicyanomethylene **2a** by *p*-FC_6H_4 (*e.g.* **2e**) and by 2-benzoimidazolyl **2f** resulted in hypsochromic shift of 36 nm and 3 nm respectively compared to **2a**, so that the strength of 2-benzoimidazol moiety is nearly similar to one cyano group. On the other hand, replacement of both cyano groups by hydrogen and one nitro group (**2g**) causes a small bathochromic shift. In addition to that, replacement of the α hydrogen (formula **A**) by a cyano group *e.g.* **2b** cusses a pronounced bathochromic shift of 88 nm compared to **2a**. Protonation of compound **2f** causes a bathochromic shift of some 80 nm, due to the formation of the cationic form (formula **B**). In this series the sequence **2b>2g>2f>2a>2c>2e** for the relative effectiveness as electron acceptor in producing a bathchromic shift was observed.

Barbituric Acid Derivatives 3a-c

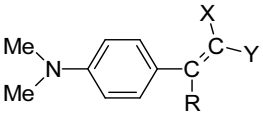
In this series of dyes the alkylation of the nitrogen (*e.g.* the replacement of the hydrogen by methyl dose not causes an appreciable bathochromic shift of the visible absorption band compared to the barbituric acid it self. However the use of thiobarbituric acid, *e.g.* **3c** does have noticeable bathochromic shift of 18 nm compared to its counterpart barbituric acid. The following order **3c>3a>3b** in producing a bathochromic shift was observed.



A



B



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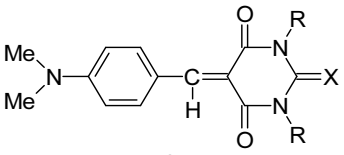


3

	X	Y	R
a	CN	CN	H
b	CN	CN	CN
c	CN	COOEt	H
d	COOEt	COOEt	H
e	CN	4-FC $_6$H$_5$	H
f	CN	2-benzoimidazolyl	H
g	H	NO $_2$	H

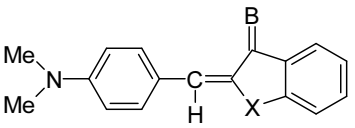
	R	X
a	H	O
b	Me	O
c	H	S

Indane Derivatives 4a-c

Chalcone **4a** has a visible absorption maximum at 428 nm. However the replacement of the oxygen atom of the indane carbonyl group by more powerful electron withdrawing group dicyanomethylene resulted in a large bathochromic shift (*e.g.* **4b** λmax = 516 nm). On the other hand Griffiths reported that the replacement of the methylene group in the indane moiety by another carbonyl *e.g.* chalcone **4c** gave more bathochromic shift[8]. It is also reported that the replacement of one or both carbonyl oxygen of the indane-1,3-dione by dicyanomethylene (*i.e.* dyes **4d** and **4e**) resulted in dyes absorbing at 557 nm and 602 nm respectively. In this series the order of the electron acceptors ability in producing a bathochromic shift of the visible absorption band **4e>4d>4b>4c>4a** was observed.

4-Pyrazolone Derivative 5

Pyrazolone **5** was obtained as wine-red crystals from acetic anhydride, however in ethanol the solution is deep orange (λmax = 463 nm).



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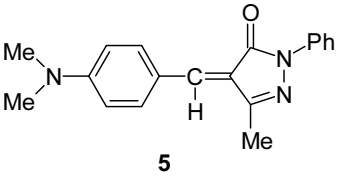

5

	X	B
a	CH_2	O
b	CH_2	$C(CN)_2$
c	C=O	O
d	C=O	$C(CN)_2$
e	$C=C(CN)_2$	$C(CN)_2$

Comparison between the Different series of Both the Maximum Absorption and the Intensity of the Visible Bands

Table 3 summarizes the visible absorption spectral data of the dyes prepared measured in acetonitrile and ethanol with molar extension coefficient measured in ethanol. From the value of the visible absorption bands of the prepared series, the following order of the relative strength of the different electron-acceptors studied in producing a bthochromic shift was observed: tricyanovinyl > 1-dicyanomethyleneindane > thiobarbituric acid > barbituric acid > N,N-dimethylbarbituric acid > 5-pyrazolone. On the other hand the cyanoderivative **2e** showed the greatest intensity then, come the barbituric acid derivatives. The brightness of a certain dye can be measured from the bandwidth of the visible band; this is presented in term of the half band width $\nu_{1/2}$ in cm^{-1}. The bigger the value the brighter the dye is. In the dyes series examined the brighter colour is obtained for dye **2a**, and the less bright dye is **4b** (Table 3).

Table 3. Electronic spectral data of synthesized dyes.

Dye no.	λmax (Ethanol)	Log ε (Ethanol)	$\nu_{1/2}$ (cm^{-s1}) (Ethanol)	λmax (Acetonitrile)
2a	430	4.1	25,0000	430
2b	518	4.0	9,0909	530
2c	421	3.92	17,8571	421
2d	371	3.98	20,8333	386
2e	394	4.37	19,2308	445
2f	420	3.82	18,2831	427
2g	438	3.94	11,1111	
3a	470	3.88	20,0000	460
3b	467	3.92	19,2350	458
3c	488	4.15	20,0000	489
4a	428	4.17	13,1579	417
4b	516a	3.53	8,3333	522
5	463	3.81	11,3636	449

References

[1] **Gerasimova, T.** and **Shelkovnikov, V.**, *Russian Chem. Review*, **61**(1): 55 (1992).
[2] **Prasad, P.N.** and **Williams, D.J.,** *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, Chichestr (1991).
[3] **Popp, E.D.** and **Catala, A.,** *J. Org. Chem*., **26**: 2738 (1961).
[4] **Prajapati, D.** and **Sandhu, J. S.,** *J. Chem. Soc. Perkin Trans*., **1**: 739 (1993).
[5] **Moore, J.A.** and **Kim, J.H**., *Tetrahedron Lett*., **32**: 3449 (1991).
[6] **Cope, A.C.,** *J. Am. Chem. Soc*., **59**: 2327 (1937).
[7] **McKusick, H., Coffman, C.** and **Mower**, *J. Am. Chem. Soc*., **80**: 2806 (1958).
[8] **Bello, K.A., Cheng, L.** and **Griffiths, J.,** *J. Chem.Soc. Perkin Trans.*, **2**: 815 (1987).

تحضير ودراسة أطياف الامتصاص الإلكتروني لمركبات ملونة لحاملات لون من النوع المعطي والمستقبل

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المستخلص. تم تحضير عدة حاملات لونية جديدة مقترن فيها المانح والمستقبل، المانح المقترن فيها عبارة عن المركب ثنائي ميثايل أمينو بنزين، وذلك مع عدة مستقبلات. وقد تمت دراسة الأطياف الإلكترونية لها في الإيثانول والأسيتونتريل بغية توضيح تأثير المذيب على خاصية اللون لهذه الأصباغ الجديدة. القوة النسبية للمستقبل لعمل انحياز باثوكرومي تم إيضاحها أيضا. وقد خلصت الدراسة إلى أن صبغة ثلاثي سيانو الفاينايل تعد من أفضل المستقبلات المستخدمة في هذه الدراسة، وذلك من خلال عملها لأكبر انحياز باثوكرومي في الامتصاص للطيف المرئي, في المقابل كانت صبغة داي إيثايل مالونات تعد الأقل في هذا الخصوص.