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SYNTHESIS, ELECTRONIC ABSORPTION SPECTRA AND THERMAL STABILITY STUDIES OF SOME DONOR-CONJUGATED-ACCEPTORS 4-TRICYANOVINYLANILINE DYES

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عدد من اصباغ التراي سيانوفينيل **3-14** تم تشييدها بواسطة التفاعل بين مركب رباعي سيانو إيثيلين ومشتقات أنيلين في وجود مذيب ثنائي ميثيل فورمامايد عند درجة حرارة مابين ٧٠-٩٠° م. وقد وجد أنه عند تغيير مركب الأنيلين بحيث يحدث تغير في قوة المجموعة المعطية لوحظ إزاحة كبيرة في قمم الامتصاص في المجال المرئي. وقد تم دراسة أثر المذيب على الأصباغ المحضرة وقد وجد أن قمة الامتصاص في المجال المرئي للأصباغ المحضرة يحدث لها إزاحة حمراء في المذيبات القطبية. أيضا تم دراسة الثبات الحراري للأصباغ المحضرة في فيلم من البولي إيثلين عند ١٠٠° م وقد بينت الدراسة أن بعض الأصباغ المحضرة لها ثبات حراري عالي.

Several tricyanovinyl dyes were prepared via the interaction of tetracyanoethylene and the appropriate anilines with or without solvent. The solvent used is dimethylformamide, and the optimum temperature is in the range of 70-90 °C. Changing the aniline coupler causes change in the strength of the donor group and hence remarkable effect on the absorption maximum was observed. The solvatochromism of the synthesized dyes were investigated in different solvents, the maximum absorption of the dyes were found to be red shifted in more polar solvents. The thermal stability of the dyes was assessed on polyethylene film at 100 °C, and some of the dyes showed excellent thermal stability.

INTRODUCTION

Donor-acceptor chromophores are an important class of dyes owing to their potential applications in different fields such as photographic sensetiezer [1], or in the field of electrooptical devices [2]. Most organic non linear optical materials are based on

D-π-A systems [3-6]. Tricyanovinyl (TCV) group is one of the most known moieties as powerful electron acceptor. For example a comparison of the absorption maxima of dyes **2** and **3**, reveals the large effect of the (TCV) (λ_{max} 506 nm) over the dye **2**, which contains the dicyanomethylene as acceptor (λ_{max} 419 nm). In this paper, the effect of various electron donor groups on the colour, and constitution as well as the thermal stability is investigated.

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, NMR were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. UV-visible spectra were recorded on Shimadzu 260 spectrometer for solutions.

4-N,N-Dimethylaminobenzylidene malononitrile 2. To a refluxed solution of 4-N,N-dimethylaminobenzaldehyde (5.0g, 0.034 mol) and malononitrile (2.20g, 0.034 mole) in ethanol (50 ml), piperidene (1 ml) was added. After the addition, the solution became dark and reflux was continued for six hours, then the solution was left to cool to room temperature. The precipitated dye was filtered and washed with cold water and finally with coled ethanol, dried and recrystallized from ethanol. Shiny orange crystals (5.9g , 89 %), mp. 185 °C.

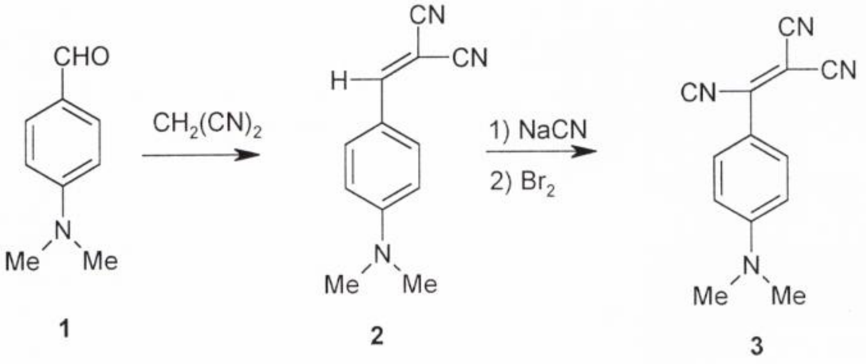
4-Tricyanovinyl-N,N-dimethylaniline 3 from 2. 4-N,N-Dimethylamino- benzylidene malononitrile **2** (4.0g, 0.02 mol) was dissolved in dimethylformamide (10 ml) and methanol (10ml). Then sodium cyanide (1.0g, 0.02 mole) in 0.6 ml of water is added at 60 °C and stirred for three hours and further one hour at room temperature. Bromine (3.2g, 0.02 mol) was added dropwise to the reaction mixture and left stirring for one hour . The solution mixture was poured into ice and the crude precipitated dye was filtered and washed with water and dried, affording the dye **3** as dark red powdered. Recrystallization from toluene gave dye **3** as dark red crystals (2.7 g, 60% overall), mp176-178 °C.

General procedure for the reaction of TCNE with aromatic amines.- A solution of aromatic amine (10 mmol) was dissolved in DMF (20 ml) and cooled to 0 °C. Tetracyanoethylene (TCNE) (10 mmol) was dissolved in DMF (10 ml) and added dropwise to the aromatic amine solution with stirring at 0°C, after the addition was completed the solution was heated to 90 °C and left stirring at this temperature for 3 hrs. The solvent was removed under reduced pressure and the crude dyes was dissolved in chloroform and chromatographeied on silica gel using a mixture of chloroform ethyl acetate (3:7) as eluent. The dyes were recrystallized from toluene (Tables 1 and 2).

RESULTS AND DISCUSSION

Synthesis of dyes

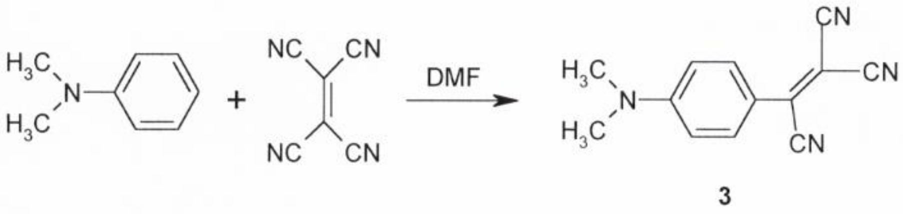
Two methods were used for the synthesis of dye **3**. In the first method, the aldehyde **1** was condensed with malononitrile to give the dicyanomethylene derivative **2**. The later was subjected to the addition of sodium cyanide, followed by oxidation using bromine to give the violet TCV dye **3** in 60% overall yield (Scheme 1).



Scheme 1

The second method implies a direct tricyanovinylation of aromatic amines using tetracyanoethylene (TCNE) in one pot reaction. Thus N,N-dimethylaniline was stirred at room temperature with (TCNE) in DMF, to afford in a very rapid reaction dye **3** in both high yield and purity (Scheme 2).

Dyes **3-14** exhibited a cyano stretching band in the region of 2202- 2221cm^{-1} and a second band in the region of 1607-1630 cm^{-1} in their IR spectrum. The dyes **4-14** were prepared using the direct tricyanovinylation described in scheme 2. Characterization data are given in Table 1. IR and ^{1}H-NMR data are summarized in Table 2. The most characteristic feature of H-NMR was the deshielding effects of the tricyanovinyl group on the two aromatic protons adjacent to it compared to the rest of the aromatic protons. For example dye **3** showed a doublet at 8.07 ppm for these two protons and a second doublet at 6.74 ppm for other two protons.



Scheme 2

Table 1: Characterization of dyes 3-14

Dye no	Yield (%)	M.P. (°C)	Molecular Formula	Calculated (Found) C	H	N
3	95	177-179	$C_{13}H_{10}N_4$	70.27 (70.41)	4.50 (4.23)	25.23 (25.11)
4	85	110-112	$C_{15}H_{14}N_4$	72.00 (71.85)	5.60 (5.72)	22.40 (22.31)
5	98	190-192	$C_{14}H_{10}N_4$	71.79 (71.64)	4.27 (4.21)	23.9 (23.72)
6	80	240-242	$C_{13}H_{10}N_4$	74.18 (74.31)	5.45 (5.34)	20.36 (20.11)
7	73	170-175	$C_{17}H_{10}N_4$	75.55 (75.32)	3.70 (3.62)	20.74 (20.53)
8	50	110-112	$C_{17}H_{12}N_4$	75.00 (74.78)	4.41 (4.52)	20.59 (20.42)
9	75	120-122	$C_{12}H_8N_4$	69.24 (69.43)	3.84 (3.65)	26.92 (27.21)
10	85	128-130	$C_{15}H_{14}N_4O$	67.68 (67.81)	5.26 (5.43)	21.05 (20.84)
11	---	oil	$C_{16}H_{16}N_4O$	68.58 (68.21)	5.71 (5.83)	20.00 (19.82)
12	91	151-153	$C_{15}H_{14}N_4O_2$	63.79 (63.52)	4.96 (4.68)	19.85 (20.02)
13	83	112-114	$C_{19}H_{22}N_4$	74.52 (74.34)	7.18 (7.41)	18.31 (18.11)
14	---	oil	$C_{15}H_{14}N_4O$	67.68 (67.43)	5.26 (4.98)	21.05 (20.86)

Table 2: ^{1}H-NMR and IR data of Dyes 3-14

Dye No	δ		IR/cm^{-1}		
	Aromatic	**Other**	**CN**	**C=C**	**NH**
3	8.07 (d, *J* = 10 Hz, 2H), 6.74 (d, *J*= 10 Hz, 2H)	3.23 (s, 6H, CH_3)	2213	1609	
4	8.06 (d, 2H, *J*= 10 Hz), 6.73 (d, 2H, *J*= 10 Hz)	3.53 (q, 4H, *J*= 7Hz, CH_2), 1.29 (q, 6H, *J*=7 Hz, CH_3)	2213	1607	
5	7.83 (d, 2H, *J*= 9.0Hz), 6.74 (s, 1H), 6.64 (d, 1H, *J*= 9.1 Hz)	3.46 (t, 2H, CH_2N), 2.77 (m, 2H, CH_2), 1.98 (t, 2H, CH_2), 8.04 (1H,NH)	2211	1615	3368
6	7.68 (d, 1H, *J*= 10 Hz), 6.84 (d, 1H, *J*= 10 Hz)	3.45 (t, 1H, CH_2), 3.17 (t, 1H, CH_2), 2.77 (t, 1H, CH_2), 2.72 (t, 1H, CH_2), 2.02 (t, 1H, CH_2), 1.94 (m, 1H, CH_2), 1.6 (broad ,1H, CH_2)	2207	1613	
7	8.04 (d, 2H, *J*= 9.1 Hz), 7.41, 7.27 (m, 5H),7.10 (d, 2H, *J*= 9.1 Hz)	9.5 (1H, NH)	2216	1611	3312
8	7.68-6.93 (6H, m)	3.12-2.97 (6H, two singlets)	2208	1647	
9	8.06 (2H, d, *J*= 9.1 Hz), 6.65 (2H, d, *J*= 9.2 Hz),	3.04 (3H, s, CH_3N)	2213	1612	
10	8.05 (2H, d, *J*= 9.4 Hz), 6.81 (2H, d, *J*= 9.4 Hz),	3.67 (2H, t, CH_2N), 3.63 (2H, q, CH_2N), 1.29 (3H, q, CH_2N)	2209	1611	
11	7.55 (1H, d, *J*= 8.9 Hz), 7.13 (1H, s), 6.6 (1H, d, *J*= 9.3 Hz),	3.85 (2H, t, CH_2O), 3.77 (2H, t, CH_2N), 3.48 (2H, q, CH_3CH_2N), 1.23 (3H, t, CH_2)	2202	1610	3450 (OH)
12	8.02 (2H, d, *J*= 9.2 Hz), 6.91 (2H, d, *J*= 9.3 Hz),	3.84 (4H, t, 2xCH_2O), 3.75 (4H, t, 2xCH_2N)	2210	1615	3450 (OH)
13	8.05 (2H, d, *J*= 9.1 Hz), 6.69 (2H, d, J= 9.2 Hz),	3.43 (4H, t, 2xCH_2N), 1.63 (4H, m, 2xCH_2), 1.37 (4H, m, 2xCH_2), 0.95 (6H, t, 2xCH_2)	2215	1620	
14	7.53 (d, 2H, *J*= 9.2Hz), 6.59 (d, 2H, *J*=9.1Hz)	4.27 (s, 2H, CH_2O), 4.1 (q, 2H, CH_3CH_2), 3.78 (s, 3H, CH_3N), 1.12 (t, 3H, CH_3CH_2)	2221	1630	

Electronic Absorption Spectroscopic Properties

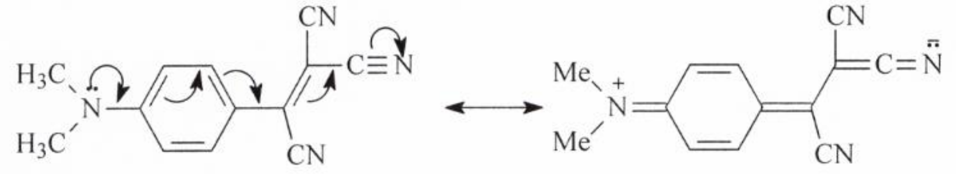
Absorption spectra were recorded in different solvents, with molar extension coefficients being measured in acetone; the results are summarized in Table 3.

Generally, the dyes showed a visible absorption bands in the region of 496-555 nm in acetone, with molar absorption coefficient in the range of 11,000- 95,000 dm^3. mol^{-1}. cm^{-1}.

Each dye showed two absorption bands. For example, the parent dye **3** showed an absorption band at 329 nm in acetone and a much more intense charge transfer band at 506nm. The visible absorption bands are assigned as a charge transfer bands arising from the resonance of the lone pair of nitrogen atom of the aniline to the tricyanovinyl substituents (Scheme 3).

Table 3 Electronic Spectral Data of Dyes 3-14

Dye No	λmax CH_3CN	λmax DMF	λmax AcOH	λmax $CHCl_3$	λmax C_7H_8	λmax Ether	Δλ	λmax $Me_2C{=}O$	εmax $Me_2C{=}O$
3	275 519	294 524	290 507	282 517	323 505	284 497	14	329 506	12500 11530
4	273 525	298 526	298 514	302 525	317 512	283 503	13	331 523	7700 16110
5	276 520	298 529	288 511	282 514	289 499	277 504	21	331 521	9200 14920
6	295 562	294 563	292 545	302 555	292 538	288 532	24	396 415 549	93500 95200 42600
7	421 475	280 521	282 501	284 504	290 493	283 495	18	332 515	6300 14110
8	395 414 560	317 397 562	394 411 543	401 418 561	288 539	217 524	21	331 555	18100 16730
9	289 498	291 509	288 491	289 491	288 481	280 485	18	310 474 505	31297 45643 40335
10	282 522	283 529	279 511	279 511	283 506	278 507	16	312 519	--- 26675
11	395 413 538	397 415 545	393 411 528	399 417 538	284 526	263 524	12	395 413 536	
12	298 520	280 532	295 506	284 506	288 502	203 506	18	280 314 518	38245 32324 33609
13	284 528	285 534	283 412 517	286 528	288 512	271 508	16	311 416 523	33819 1991 23931
14	267 499	273 512	265 491	267 491	297 481	317 486	18	335 496	



3 **3'**

Scheme 3

Dye **8**, which is derived from 1-N, N-dimethylaminonaphthylamine coupler, showed the most bathochromic shift (λ_{max} = 555 nm) in acetone. On the other hand dye **14** derived from N-methylaniline and N-ethoxymethyl-N-methyl aniline showed the most hypsochromic shift (λ_{max} = 496 nm) in acetone. In the fused coupler, the most bathocromic shift is produced by the Julolidine coupler e.g. dye **6** (λ_{max} = 549 nm) in acetone. This effect on λ_{max} is presumably as a result of an increasing electron release, or polarisability of the couplers. The extent of the shift can not be accounted for by the increase in molecular weight nor by steric effects of the coupler substituents. Increasing the length of the N-alkyl groups apparently has no effects on the value of λmax. However, the value of the εmax increases as the alkyl chain increased, this can be demonstrated when comparing dyes **4** and **13**. Addition of more donating groups to the aniline coupler causes extra bathochromic shift as can be seen for dye **11** (λmax = 536 nm) compare to dye **10** (λmax 519 nm) in acetone.

Furthermore, bathochromic shift was achieved by incorporating the alkyl group within the aniline coupler as can be illustrated by dye **5** which is derived from tetrahydroquinoline, and even greater bathochromic shift was obtained by fusion of the coupler aniline at position *2* and *4* such as 1-N,N-dimethylaminonaphthalene which used for the preparation of dye **8** .

Solvatochromism

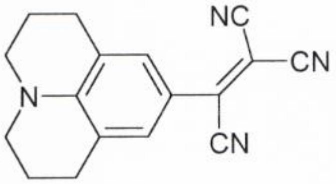
As expected for such highly polarized structures, the dyes showed a positive solvatochromism, and for example, the λmax values are displaced to longer wavelengths as the solvent polarity increased. The most solvatoochromic dye is **6,** which is derived from julolidine coupler ($\Delta\lambda_{max}$ = 24 nm) (Table 3).

Thermal Stability

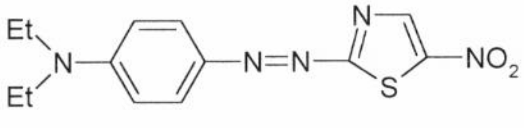
Non of the tricyanovinyl dyes synthesized were suitable for textile applications, and under typical aqueous dyeing conditions they tend to undergo decomposition and hence gradual loss of color. The potential of the dyes as colorants for plastics was also examined, as aqueous stability is unimportant for such applications to obtain information about photochemical stability in polymers. Transparent films of low density polyethylene polymer were prepared by dissolving sufficient amount of the dyes (to give absorpance values (at λmax in the range 0.5-2.0) and the polymer in benzene, and the solution was poured into glass watch and left to evaporate slowly. The dried film was peeled and the absorpance value were measured before and after heating (between two glass plates) the film for 6 hours at 100 °C. As a reference standard the blue azo dyes 2-(4-N,N-dethylaminophenylazo)-5-nitrothiazole **15** was used [7], which was similarly dissolved with polyethylene in benzene and its absorpance was measured before and after heating at 100 °C for 6 hours. The extent of thermal degradation in each case was determined, and the results are summarized in Table 4. In some cases the thermal stability of the dyes is excellent as in dyes **8, 11** and **14**. In addition, dyes **4**, **7**, **12** have a better thermal stability than the standard dye **15**, the later dye is not exceptionally thermally stable for coloration of plastic. In conclusion, dyes **4**, **7**, **8**, **11**, **12** and **14** are suitable for coloring plastic.

Table 4: Thermal Stability of Dyes 3-14

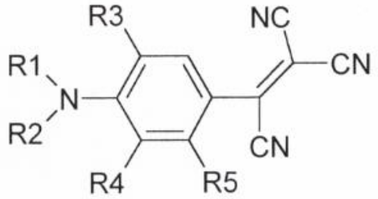
Dye No.	Thermal stability (% degradation)
Standard 15	10
3	68.6
4	4.54
5	35.4
6	18.9
7	5.4
8	14.7
9	27.9
10	0.61
11	38.4
12	9.5
13	0.66
14	0.00



6



15



Dye No.	R_1	R_2	R_3	R_4	R_5
3	Me	Me	H	H	H
4	Et	Et	H	H	H
5	H	-$(CH_2)_3$-		H	H
7	Ph	H	H	H	H
8	Me	Me	H	-CH=CH-CH=CH-	
9	Me	H	H	H	H
10	Et	-CH_2CH_2OH	H	H	H
11	Et	-CH_2CH_2OH	H	H	Me
12	-CH_2CH_2OH	-CH_2CH_2OH	H	H	H
13	n-Bu	n-Bu	H	H	H
14	Me	$EtOCH_2$	H	H	H

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