

SYNTHESIS AND CHARACTERIZATIONS OF NEW 4-TRICYANOVINYLDENEPHENYLHYDRAZONES

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تم تحضير مجموعة من مركبات ثلاثي سيانو فينيل المشتقة من الهيدرازونات عن طريق مفاعلة رباعي سيانوايثيلين مع الهيدرازونات المطابقة. الأصباغ الجديدة أظهرت قمم امتصاص في مدى 500 nm في طيف الأشعة فوق البنفسجية والمرئية. الأصباغ المحضرة كذلك أظهرت اثر كبير للمذيب على قمم الامتصاص. بعض المركبات المحضرة لها خاصية التجمع في المحلول لتكوين دايمرات في المحلول بزيادة التركيز. وقد أظهرت الأصباغ المحضرة تغير في طيف الأشعة فوق البنفسجية والمرئية. كذلك درس الثبات الحراري للأصباغ المحضرة على شكل فلم من البولي ميثيل ميثا أكريليت عند 80 °م. والاستبدال على حلقات البترين قد أبدى زيادة في قمم الثبات الحراري للأصباغ.

Novel tricyanovinyl derived hydrazones have been prepared by the reaction of tetracyanoethylene and hydrazone, and these dyes showed absorption in the region of 500 nm. The dyes showed pronounced solvatochromic effects as the solvents polarity increased. Some of the new dyes were studied to show there aggregation properties in solution as the concentration changed. Most of the dyes studied showed change in the absorption spectrum and hence the position of the maximum absorption bands. The thermal stability of some of the prepared dyes were studied in polymethylmethacrylate film at 80 °C: the substitution on the aromatic aldehydes showed some improvement of the thermal stability of the dyes.

INTRODUCTION

The electronic and structural properties of donor-acceptor substituted π -conjugated organic compounds are of considerable interest because of their applicability to electro-optic devices and data storage [1,2]. A wide variety of structural modifications on the donor-acceptor and π -conjugated moieties have been carried out [3,4]. Major research efforts have focused on developing NLO chromospheres possessing large molecular nonliterary and good thermal stability as well as improved solubility and process ability. It is well known that the second order molecular nonlinear optical hyperpolarizability (β) increases with increasing donor and acceptor strengths and with increasing length of conjugation [5]. Many donor-acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzene, biphenyls, stilbenes, azobenzenes and schiff bases [6,7]. In all these classes, benzene rings with or without the π -bridges have been employed as the conjugated moieties to connect donor and acceptor functional

groups such as compounds 1, 2, 3, 4 and 5. However, optical studies on compounds containing more than two benzenoid rings are usually insoluble in most common organic solvents. We have recently [8], reported the synthesis of new NLO chromospheres based on pyrazoles as the donor groups for example compound 6. Also many new chromophores possessing the ferrocenyl moiety as a donor group have been reported [9]. In this paper, we report on the synthesis and spectroscopic data of novel push-pull system based on hydrazones as donor groups.

EXPERIMENTAL

General

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. ¹H NMR were recorded in CDCl₃ on a Bruker DPX 400 spectrometer using TMS as internal standard. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

2-{4-[2-(Benzylidenehydrazino)phenyl]ethylene-1,1,2-tricarbonitrile 8a. m.p. 285-288 °C, yield 76%, R_f 0.13 (Petroleum ether: ethyl acetate, 8:2); uv-vis(acetone): λ max(nm) 525, 333; IR $\nu(\text{cm}^{-1})$: 3272 (sec. NH), 2211(CN), 1613(C=N), 1345(C-N); ^1H NMR (CDCl_3): δ 7.42-8.13(m, 11H, Ar-H + CH + NH + Ph-H). ^{13}C NMR (CDCl_3): δ 111.85, 113.31, 114.14, 115.65, 117.5, 121.41, 127.14, 128.89, 130.21, 132.96, 136.54, 137.14, 144.19, 162.55.

2-{4-[2-(2-Chlorobenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8b. m.p. 244-245 °C, yield 96%, R_f 0.27 (Petroleum ether: ethyl acetate, 8:2); uv-vis(acetone): λ max(nm) 514; IR $\nu(\text{cm}^{-1})$: 3222 (sec.NH), 2218(CN), 1663 (C=N), 1339(C-N); ^1H NMR (CDCl_3): δ 7.16-7.41(m, 4H, Ar-H3,4,5,6), 8.0-8.16(m, 5H, CH + Ph-H2,3,5,6), 8.18(bs, 1H, NH). ^{13}C NMR (CDCl_3): δ 111.85, 113.45, 126.68, 127.0, 127.11, 127.23, 127.94, 129.66, 129.79, 130.0, 130.94, 132.90, 135.24, 140.39, 150.78, 162.61.

2-{4-[2-(3-Chlorobenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8c. m.p. 250-251 °C, yield 71%, R_f 0.20 (Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max(nm) 515, 339; IR $\nu(\text{cm}^{-1})$: 3266(sec.NH), 2213(CN), 1661(C=N), 1339(C-N); ^1H NMR (CDCl_3): δ 7.10-8.14 (m, 9H, Ph-H2,3,5,6 + Ar-H2,4,5,6 + CH), 8.42 (bs, 1H, NH). ^{13}C NMR (CDCl_3): δ 111.84, 113.0, 113.47, 124.58, 125.34, 125.77, 126.73, 127.96, 128.81, 129.10, 129.93, 130.18, 132.85, 137.10, 145.36, 162.54.

2-{4-[2-(4-Chlorobenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8d. m.p. 289-294 °C, yield 98%, R_f 0.09 (Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max(nm) 521; IR $\nu(\text{cm}^{-1})$: 3272 (NH), 2211(CN), 1613(C=N), 1345(C-N); ^1H NMR (CDCl_3): δ 7.15 (d, 2H, J = 8.60Hz, Ar-H2,6), 7.34-7.41(m, 4H, Ar-H3,5+ Ph-H2,6), 7.62(d, 2H, J =8.50, Ph-H3,5), 7.70(s, 1H, CH), 8.10(bs, 1H, NH). ^{13}C NMR (CDCl_3): δ 111.14, 113.34, 115.43, 127.48,

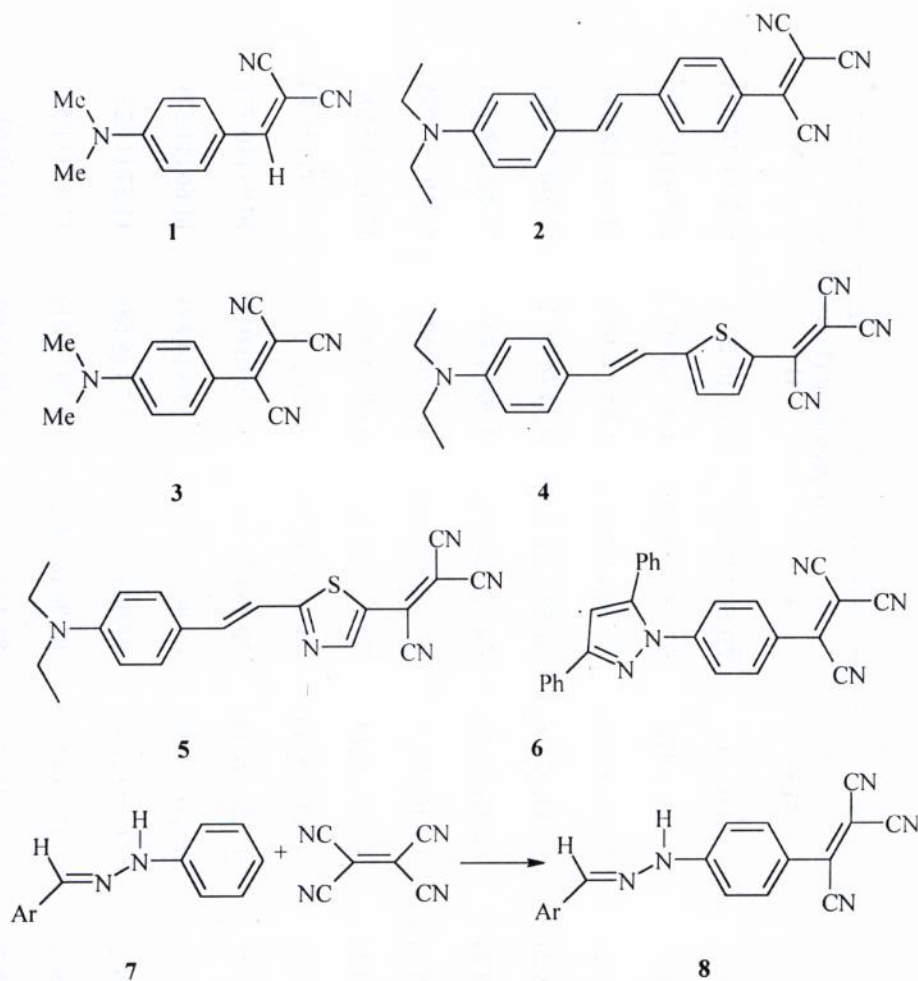
127.92, 128.75, 132.93, 134.53, 137.46, 145.63, 162.61.

2-{4-[2-(2-Nitrobenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8e; m.p. 275-278 °C, yield 80%, R_f 0.93 (Petroleum ether: ethyl acetate 6:4); uv-vis(acetone): λ max (nm) 508; IR $\nu(\text{cm}^{-1})$: 3301(sec.NH), 2217(CN), 1661(C=N), 1607, 1339(C-NO₂), 1298(C-N); ^1H NMR (CDCl_3): δ 6.92-8.32 (m, 10H, Ar-H + CH + NH + Ph-H). ^{13}C NMR (CDCl_3): δ 113.10, 113.72, 121.10, 124.87, 127.71, 127.87, 128.0, 128.17, 128.48, 129.41, 131.64, 133.11.

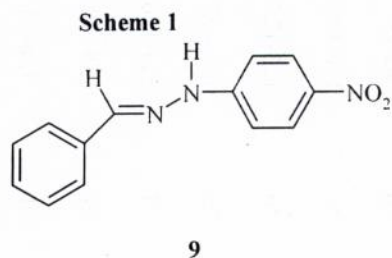
2-{4-[2-(3-Nitrobenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8f. m.p. 281- 283 °C, yield 90%, R_f 0.84 (Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max (nm) 507; IR $\nu(\text{cm}^{-1})$: 3292 (sec.NH), 2218(CN), 1665(C=N), 1293(CN), 1341+ 1605(C-NO₂); ^1H NMR (CDCl_3): δ 7.19-8.49 (m, 10H, Ar-H + CH + NH + Ph-H). ^{13}C NMR (CDCl_3): δ 112.97, 113.63, 115.30, 120.66, 120.96, 122.54, 123.10, 124.22, 125.27, 126.53, 127.99, 129.67, 131.58, 132.84, 135.67, 136.77, 140.55, 145.15, 148.71, 162.64.

2-{4-[2-(4-Nitrobenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8g; m.p > 350 °C, yield 85%, R_f 0.24 (Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max(nm) 511; IR $\nu(\text{cm}^{-1})$: 3283(sec.NH), 2215(CN), 1667(C=N), 1293(C-N), 1339+ 1611(C-NO₂); ^1H NMR (CDCl_3): δ 7.80 (s, 1H, CH), 7.90(d, 2H, J =8.60Hz, Ar-H3,5), 7.99-8.15(m, 4H, Ph-H), 8.25 (d, 2H, J =8.65Hz, Ar-H2,6), 11.81(bs, 1H, NH). ^{13}C NMR (DMSO, CDCl_3): δ 113.31, 113.39, 113.56, 114.32, 120.29, 123.88, 127.32, 132.65, 140.73, 141.18, 144.3, 147.61, 151.21.

2-{4-[2-(2-Methoxybenzylidene)hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8h. m.p. 254-257, yield 96%, R_f 0.25(Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max (nm) 531, 344; λ max/ cm^{-1} 2215 (CN), 1600 (C=N), 1300 (C-N); ^1H NMR (CDCl_3): δ 3.92 (s, 3H, O-CH₃),



7,8	Ar	7,8	Ar
a	C ₆ H ₅	g	4-NO ₂ C ₆ H ₄
b	2-ClC ₆ H ₄	h	2-MeOC ₆ H ₄
c	3-Cl-C ₆ H ₄	i	3,4-MeOC ₆ H ₄
d	4-Cl-C ₆ H ₄	j	3,4-OCH ₂ OC ₆ H ₃
e	2-NO ₂ C ₆ H ₄	k	1-Naphthyl
f	3-NO ₂ C ₆ H ₄	l	2-Naphthyl
		m	9-Anthryl



Electronic absorption properties

The electronic absorption spectra of the new chromospheres are characterized by an intense, low-energy band that is dependent on the nature and the position of the substituent on the aromatic aldehydes (Table 2). Dye 8a, which contains no substitution on the aldehyde phenyl, showed absorption band at 525 nm in acetone. A substitution by one chloro atom at positions 2, 3 or 4 of the aromatic aldehydes e.g. dyes 8b-d, generally showed a hypsochromic shift compared with the unsubstituted dye 8a. However, the most bathochromic shift was observed in the chloro derivative and in particular for 4-substituted dye 8d. In addition, a decrease in the

intensity of the absorption bands was observed for this series of dyes compared to the parent dye 8a. The same trends were observed when the substitution is nitro groups e.g. dyes 8e-g. Analation of benzaldehydes for instance, 1 and 2 naphthaldehydes dyes 8k and 8l respectively and anthracen-3-carboxaldehyde 8m, resulted generally in bathochromic shift compared to the parent dye 8a. Substitution with one or two methoxy groups has led to a pronounced bathochromic shift (Table 2). Figures 1-3, showed the visible absorption spectra of some representative examples of tricyanovinyl hydrazone dyes 8.

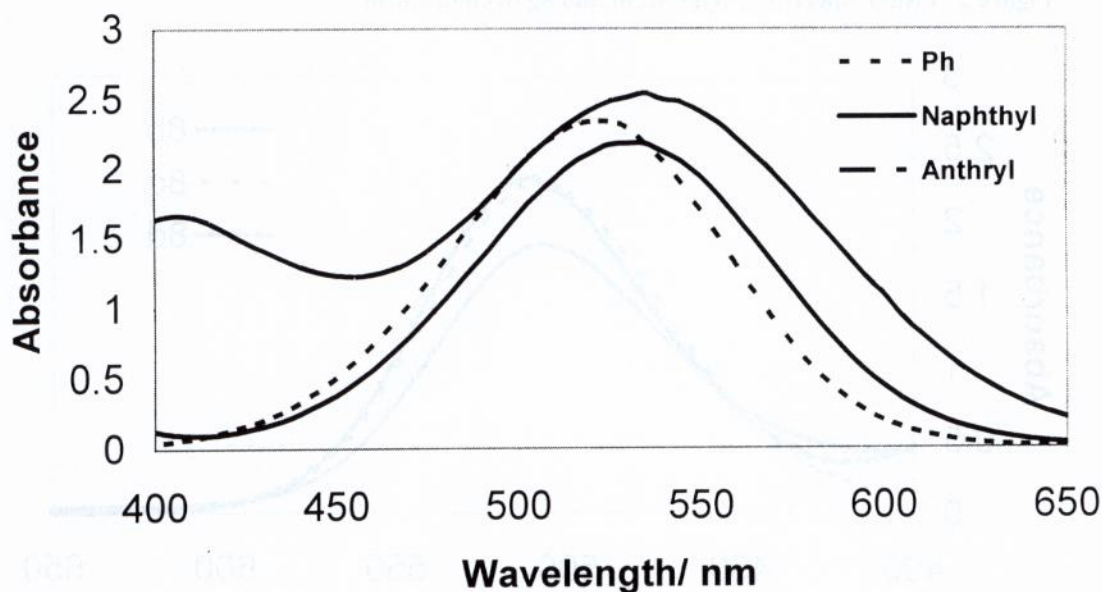


Figure 1: Visible Spectra of Dyes 8a, 8K and 8m in chloroform

hand in polar solvents such as DMF, the same dye showed the most bathochromic shift (λ_{\max} 593 nm) of the dyes series. The solvatochromic effect can be estimated from the difference between the absorption maxima in polar and non polar solvents e.g. $\Delta\lambda$ (Table 2).

Aggregation properties

The ability of certain dyes to form associates (aggregates) is called aggregation [10-11]. Until recently, the association of identical molecules of dyes (formation of homogeneous aggregates) was usually investigated using the absorption spectroscopy. The change of the position and the shape of the absorption maxima as the concentration of the dyes are usually appreciable. Table 3, showed the aggregation effects on the absorption properties as the concentration of the dyes change in DMF. From the data presented in Table 3, in general, decreasing the concentration of the dyes showed a bathochromic shift and hence the formation of new absorption band, due to the formation of dimmers of the dyes in solutions. The most aggregation of the series studied was observed for dye 8f, and the less one were for dyes 8e and 8g.

Thermal Stability

The dyes were tested for their stability against the exposure to heat in poly methylmetha acrylates matrix at 80 °C. A thin film of poly(methyl methacrylate) (PMMA) doped with some selected dyes was prepared from a solution of the polymer and the dyes in chloroform (dye contents 3%), and then the film was casted on a glass substrate. After drying at room temperature, the film was further dried under vacuum. The films were peeled from the glass and the absorption spectra were measured before heating, then the films were heated in an oven set at 80 °C, for intervals of each one the absorption spectra were measured. The total heating period was 360 minutes. Figures 4 and 5 showed the effects of heating for different time intervals on the degradations of some of the dyes prepared. Also the extents of the degradation (calculated from $(A^0 - A_t) \times 100 / A^0$) of the dyes studied were shown in Table 4. It is noteworthy to say that, the parent dyes 8a, 8i and 8j are the less stable dye on heating at 80 °C. On the other hand, dye such as 8d is the most stable compared to the other dyes. It is of great importance to notice that, the extent of the decomposition is measured after 360 minute. However, most of the dyes are stable up to 60 minuet of heating at 80 °C as can be seen in figures 4 and 5.

Table 2: Visible absorption spectral Data of dyes 8a-m in various solvents

Dye No.	$\lambda_{\max}/ \text{nm}$				$\Delta\lambda$	ϵ
	$(\text{CH}_3)_2\text{CO}$	AcOH	$\text{C}_6\text{H}_5\text{CH}_3$	DMF		
8a	525	520	507	558	51	45662
8b	514	514	503	554	51	22950
8c	515	513	501	557	56	25141
8d	521	519	506	559	53	32787
8e	508	507	391	527		16536
8f	507	506	492	553	61	27611
8g	511	510	495	627	132	23116
				541	46	24164
8h	531	351	518	562	44	29277
8i	693	696	-----	-----	-----	----
	537	535	552	559	7	1809
8j	700	695	---	---	---	----
	535	534	522	565	43	4455
8k	529	528	517	570	53	21145
8l	529	527	516	570	54	29249
8m	540	527	519	593	74	21062

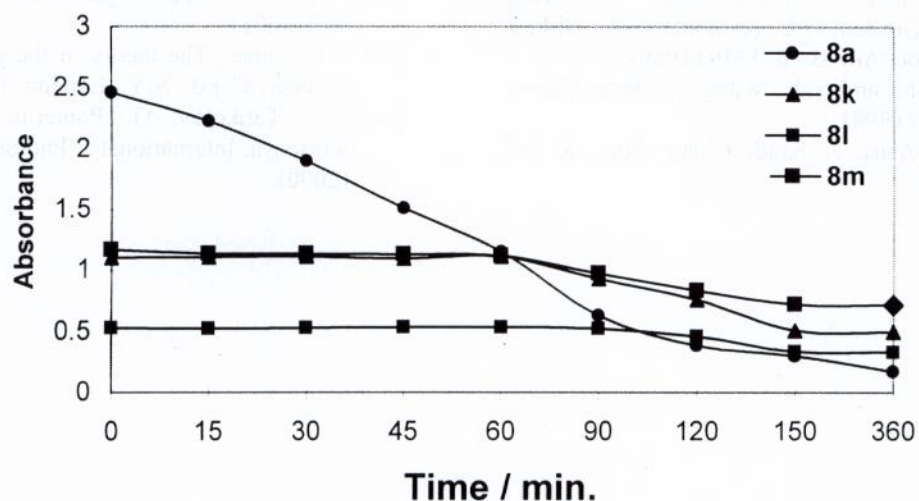


Figure 5: The effect of heat on polymethylmethacrylate thin film of dyes 8a, 8k, 8l and 8m.

Table 4: The Stability on poly methyl methacrylate of dyes 8a-m

Dye No.	Content of Decomposition (%)*
8a	93.1
8b	75.3
8c	43.3
8d	39.0
8i	100
8j	100
8k	53.7
8l	64.1
8m	72.3

* Calculated from $\% = (A^0 - A_t) \times 100 / A^0$

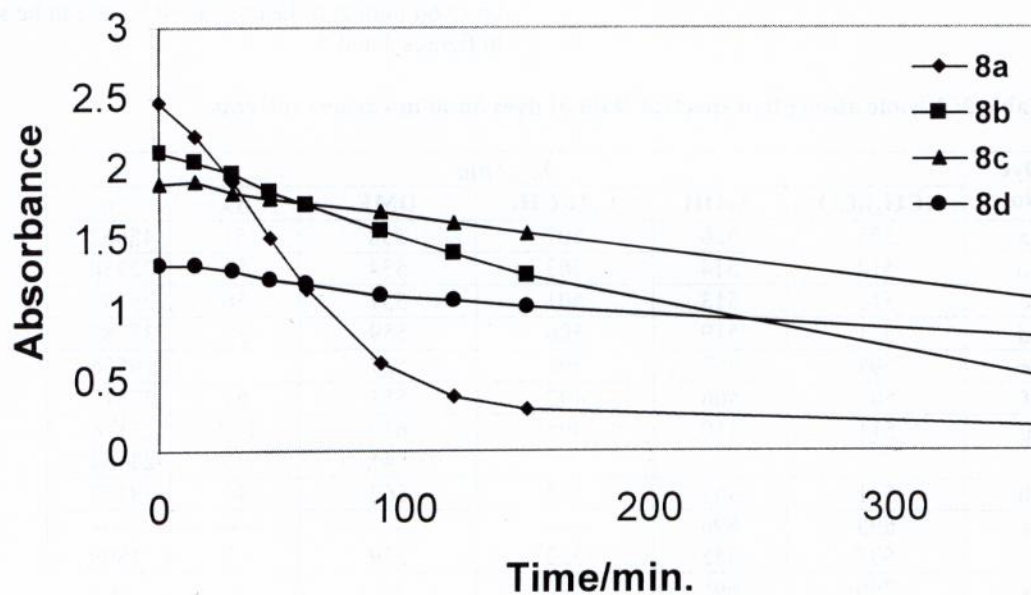
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Table 3: The effect of concentration on λ_{\max} of dyes 8a-m

Dye No.	λ_{\max} (nm)			
	1×10^{-4} M	4×10^{-5} M	2×10^{-5} M	1×10^{-5} M
8a	558 (4.57)	564 (1.83)	569 (0.96)	571 (0.48)
8b	570 (3.15)	580 (1.46)	585 (0.78)	586 (0.40)
8c	570 (3.28)	574 (1.50)	578 (0.80)	579 (0.42)
8d	570 (3.45)	573 (1.493)	576 (0.77)	578 (0.40)
8e	599 (1.56)	602 (0.77)	603 (0.42)	603 (0.23)
8f	554 (3.19)	582 (1.55)	585 (0.81)	587 (0.40)
8g	627 (2.73)	631 (1.48)	632 (0.79)	631 (0.41)
8k	570 (3.18)	580 (1.34)	583 (0.70)	583 (0.34)
8l	570 (2.93)	577 (1.24)	579 (0.63)	581 (0.32)
8m	579 (1.88)	602 (0.51)	602 (0.41)	603 (0.20)

**Figure 4: The effect of heat on polymethylmethacrylate thin film of dyes 8a, 8b, 8c and 8d**

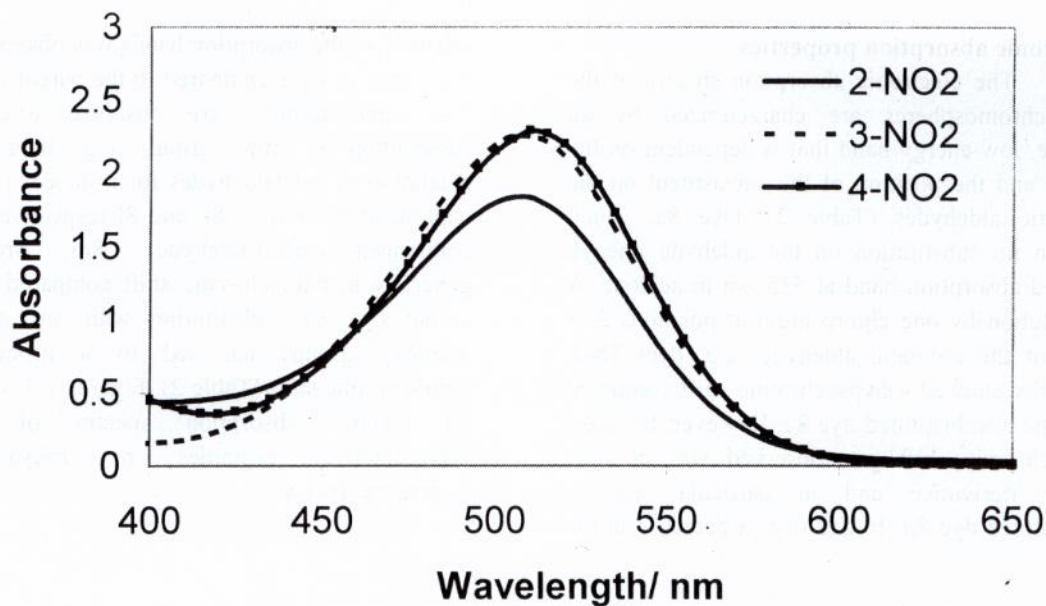


Figure 2: Visible Spectra of Dyes 8e, 8f and 8g in chloroform

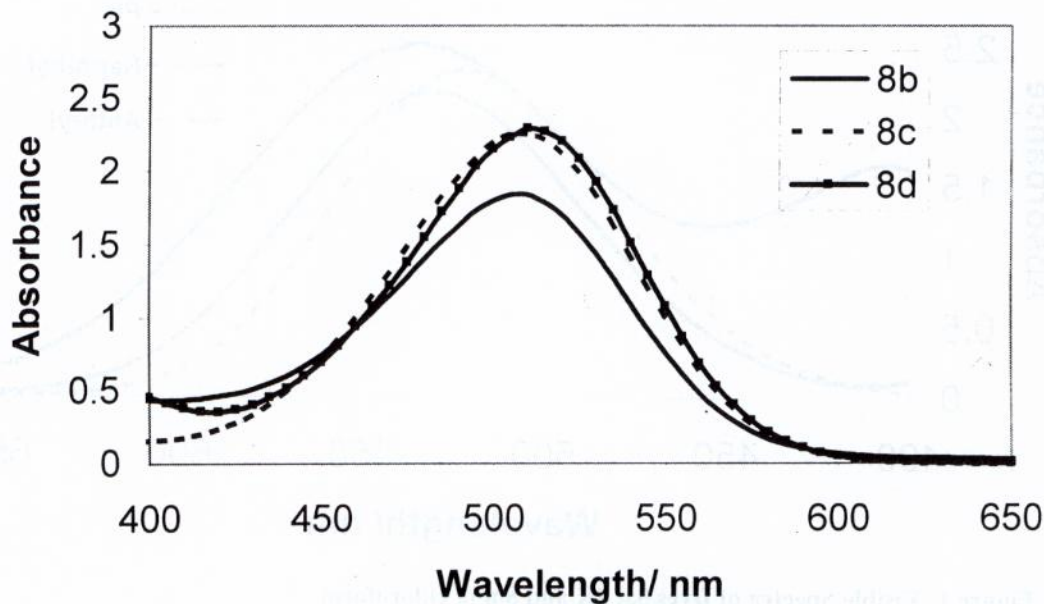


Figure 3: Visible Spectra of Dyes 8b, 8c and 8d in chloroform.

Solvatochromism

The dyes were measured in various solvents having different polarity (Table 2). Generally increasing the solvent polarity gave a

bathochromic shift of the maximum absorption bands of dyes 8a-m. In non-polar solvents for instance toluene dye 8e showed the most hypsochromic shift (λ_{\max} 391 nm). On the other

Table 1: Physical data of hydrazones 7 a-m and 9

Dye NO.	m.p (°C)	Yield (%)	R.f ^a	M.F	C	H	N
7a	150-152	92.46	0.61 (9:1)	C ₁₃ H ₁₂ N ₂	79.56 (79.23)	6.16 (6.02)	14.27 (14.11)
7b	87-89	57	0.76 (8:2)	C ₁₃ H ₁₁ ClN ₂	67.68 (67.53)	4.81 (4.95)	12.14 (11.91)
7c	130-132	79	0.27 (9:1)	C ₁₃ H ₁₁ ClN ₂	67.68 (67.48)	4.81 (4.91)	12.14 (12.01)
7d	123-125	65.28	0.44 (8:2)	C ₁₃ H ₁₁ ClN ₂	67.68 (67.52)	4.81 (4.96)	12.14 (11.96)
7e	155-157	92.18	0.36 (8:2)	C ₁₃ H ₁₁ N ₃ O ₂	64.72 (64.61)	4.60 (4.71)	17.42 (17.23)
7f	114-116	93.88	0.36 (8:2)	C ₁₃ H ₁₁ N ₃ O ₂	64.72 (64.58)	4.60 (4.68)	17.42 (17.22)
7g	158-160	86.1	0.08 (9:1)	C ₁₃ H ₁₁ N ₃ O ₂	64.72 (64.82)	4.60 (4.43)	17.42 (17.68)
7h	Liquid	93	0.75 (8:2)	C ₁₄ H ₁₄ N ₂ O	74.31 (74.22)	6.24 (6.01)	12.38 (12.53)
7i	99-101	71.6	0.5 (8:2)	C ₁₅ H ₁₆ N ₂ O ₂	70.29 (70.57)	6.29 (6.01)	10.93 (10.73)
7j	87-89	44.2	0.21 (8:2)	C ₁₄ H ₁₂ N ₂ O ₂	69.99 (70.21)	5.03 (4.87)	11.66 (11.57)
7k	130-133	32.53	0.61 (8:2)	C ₁₇ H ₁₄ N ₂	82.90 (83.12)	5.73 (5.68)	11.37 (11.23)
7l	135-136	90.66	0.36 (9:1)	C ₁₇ H ₁₄ N ₂	82.90 (81.98)	5.73 (5.61)	11.37 (11.54)
7m	222-224	87.95	0.58 (8:2)	C ₂₁ H ₁₆ N ₂	85.11 (84.87)	5.44 (5.66)	9.45 (9.61)
9	194-196	93.08	0.6 (7:3)	C ₁₃ H ₁₁ N ₃ O ₂	64.72 (64.53)	4.60 (4.82)	17.42 (17.25)

*Petroleum ether/Ethyl aceta

6.84-8.33 (m, 10H, Ar-H + CH + NH + Ph-H). ^{13}C NMR (CDCl_3): δ 55.55, 110.99, 113.19, 113.5, 120.98, 125.85, 127.87, 130.0, 134.99, 136.49, 144.17, 145.91, 154.52, 162.63.

2-{4-[(3,4-Dimethoxybenzylidene)hydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile 8i. m.p. 130-132 °C, yield 81%, R_f 0.10 (Petroleum ether: ethyl acetate 7:3); uv-vis(acetone): λ max(nm) 693, 537, 354; IR $\nu(\text{cm}^{-1})$: 3250 (NH), 2217 (CN), 1665(C=N), 1267(C-N), 1024(C-O); ^1H NMR (CDCl_3): δ 3.97b(s, 3H, OCH_3), 3.99(s, 3H, OCH_3), 5.30(broad s, 1H, NH), 6.95-7.69 (m, 8H, Ar-H + CH + Ph-H). ^{13}C NMR (CDCl_3): δ 55.8, 56.10, 108.98, 110.43, 112.77, 121.50, 126.29, 126.94, 127.64, 128.28, 129.31, 129.37, 132.97, 141.0, 144.73, 159.19, 162.68.

2-{4-[(1,3-Benzodioxol-5-ylmethylene)-hydrazino]phenyl}ethylene-1,1,2-tricarbonitrile 8j. m.p. 152-153 °C, yield 99%, R_f 0.17 (Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max(nm) 700, 535, 331; IR $\nu(\text{cm}^{-1})$: 3240(NH), 2215(CN), 1665(C=N), 1337(C-N), 1254(C-O); ^1H NMR (CDCl_3): δ 5.91 (s, 3H, CH_2), 6.0-8.0 (m, 9H, Ar-H + CH + NH + Ph-H).

2-{4-[2-(1-Naphthylmethylene)hydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile 8k. m.p. 275-277 °C, yield 93%, R_f 0.32 (6:4); u.v-vis(acetone): λ max(nm) 529, 353; IR $\nu(\text{cm}^{-1})$: 3271(sec.NH), 2213(CN), 1655(C=N); ^1H NMR (CDCl_3): δ 7.22-8.0 (m, 13H, naph-H + Ph-H + CH + NH).

2-{4-[2-(2-Naphthylmethylene)hydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile 8l. m.p. > 300 °C, yield 89%, R_f 0.29 (Petroleum ether: ethyl acetate 8:2); uv-vis (acetone): λ max(nm) 529, 340; IR $\nu(\text{cm}^{-1})$: 3270 (sec.NH), 2210 (CN), 1628 (C=N), 1328(C-N); ^1H NMR (CDCl_3): δ 6.89 (bs, 1H, NH), 7.22-8.84(m, 11H, naph-H + Ph-H), 8.0(d, 1H, CH). ^{13}C NMR (CDCl_3): δ 111.85, 112.81, 113.39, 115.65, 117.5, 120.21, 122.86,

123.0, 123.57, 126.52, 127.13, 127.98, 128.10, 128.57, 129.35, 136.02, 137.21, 139.10, 144.29, 162.5.

2-{4-[(2-(9-Anthrylmethylene)hydrazino)-phenyl]ethylene-1,1,2-tricarbonitrile 8m. m.p. 248-250 °C, yield 64%, R_f 0.13 (Petroleum ether: ethyl acetate 8:2); uv-vis(acetone): λ max(nm) 540, 407; IR $\nu(\text{cm}^{-1})$: 3281(NH), 2215(CN), 1661(C=N), 1339(C-N); ^1H NMR (CDCl_3): δ 7.19-9.10(m, 14H, Ar-H + Ph-H + CH + NH).

RESULTS AND DISCUSSION

Synthesis of dyes

The new chromospheres 8 were prepared by direct tricyanovinilation of hydrazones and this was achieved by mixing together the appropriate hydrazones 7 and tetracyanoethylene (TCNE), as shown in scheme 1. All the prepared chromospheres were obtained as dark violet solids. The IR spectra of these new dyes exhibited three important absorption bands; the first band centered near 3200 cm^{-1} for the νNH absorption. The second band is a sharp absorption band in the region of 2220 cm^{-1} which was attributed to the cyano group absorption. The third is an absorption band in the region of 1610 cm^{-1} ascribed for the C=N absorption. On the other hand, the ^1H -NMR spectra showed a singlet signal centered around 8.2 ppm assign for the methine proton. The chemical shift of the benzene protons ortho with respect to the tricyanovinyl (TCV) moiety in 8 are shifted to lower magnetic field (doublet) as a result of the strong electron-withdrawing effect from the TCV groups. The tricyanovinilation undoubtedly taken place *Para* to the hydrazine group as this evidenced by the following observations. When the hydrazone 9 in which the *para* position of the hydrazone was blocked with a nitro group allowed reacting with TCNE in the same conditions as that used with hydrazones 7, no tricyanovinilation was taken place.

Synthesis of hydrazones:**General procedure.**

An equal molar quantities of phenylhydrazine and the aldehydes were boiled in ethanol for 3-6 hrs. The precipitated hydrazones were filtered, washed and dried. The pure hydrazones were obtained after recrystallization from ethanol. The physical data were summarized in Table 1.

Benzaldehyde phenylhydrazone 7a.

^1H NMR (CDCl_3): δ 6.82 (t, 1H), 7.13 (d, 2H), 7.27 (d, 2H), 7.40-7.67 (m, 5H), 8.17 (s, 1H).

2-Chlorobenzaldehyde phenylhydrazone 7b.

^1H NMR (CDCl_3): 6.85 (t, 1H), 7.11 (d, 2H), 7.26 (d, 2H), 7.34 (t, 1H), 7.57 (d, 2H), 8.96 (s, 1H).

3-Chlorobenzaldehyde phenylhydrazone 7c.

^1H NMR (CDCl_3): δ 6.80 (t, 1H), 7.10 (d, 2H), 7.19 (d, 2H), 7.78-6.75 (m, 5H), 8.10 (s, 1H).

4-Chlorobenzaldehyde phenylhydrazone 7d.

^1H NMR (CDCl_3): δ 6.88(t, 1H, $J=7.32\text{Hz}$, Ph-H4), 7.10(d, 2H, $J=7.58\text{Hz}$, Ph-H3,5), 7.26(d, 2H, $J=8.30\text{Hz}$, Ph-H2,6), 7.29-7.59(m, 6H, Ar-H + CHx + NH). ^{13}C NMR (CDCl_3): δ 112.76, 120.33, 127.25, 128.81, 129.10, 129.34, 133.84, 133.93, 135.79, 144.37.

4-Nitrobenzaldehyde phenylhydrazone 7g.

^1H NMR (CDCl_3): δ 6.95(t, 1H, $J=7.32\text{Hz}$, Ph-H4), 7.15(d, 2H, $J=7.60\text{Hz}$, Ph-H2,6), 7.30(t, 2H, $J=7.32\text{Hz}$, Ph-H3,5), 7.70(s, 1H, CH), 7.77(d, 2H, $J=5.48\text{Hz}$, Ar-H2,6), 7.99 (bs, 1H, NH), 8.22(d, 2H, $J=7.11\text{Hz}$, Ar-H3,5). ^{13}C NMR (CDCl_3): δ 111.84, 113.10, 121.26, 124.12, 126.22, 129.46, 133.76, 141.72, 143.55.

2-Methoxybenzaldehyde phenylhydrazone 7h.

^1H NMR (CDCl_3): δ 3.42(s, 3H, CH_3O), 6.87(d, 2H, $J=8.30\text{Hz}$, Ph-H2,6), 6.92(t, 1H, Ph-H4), 7.11(d, 2H, $J=8.21\text{Hz}$, Ph-H3,5), 7.30-7.40 (m, 3H, Ar-H2,5,6), 7.47(s, 1H, CHx).

3,4-Dimethoxybenzaldehyde phenylhydrazone 7i.

^1H NMR (CDCl_3): δ 3.88(s, 3H, $-\text{OCH}_3$), 3.93 (s, 3H, $-\text{OCH}_3$), 5.38 (bs, 1H, NH), 6.70-7.61(m, 9H, Ar-H + CH + Ph-H). ^{13}C NMR (CDCl_3): δ 55.82 ($2\text{CH}_3\text{O}$), 110.76, 112.27, 120.18, 121.34, 126.97, 128.52, 130.13, 136.12, 137.35, 143.18.

1,3-Benzodioxole-5-carbaldehyde phenylhydrazone 7j.

^1H NMR (CDCl_3): δ 5.91(s, 2H, CH_2), 5.97-7.61(m, 10H, Ar-H + CH + NH + Ph-H). ^{13}C NMR (CDCl_3): δ 100.84, 101.19, 102.12, 105.12, 106.93, 107.71, 107.87, 109.50, 112.58, 113.76, 119.92, 121.40, 122.33, 128.73, 130.10, 137.0, 143.11, 148.0.

1-Naphthaldehyde phenylhydrazone 7k

^1H NMR (CDCl_3): δ 6.89 (bs, 1H, NH), 7.16-7.82(m, 7H, naph-H), 7.84(s, 5H, Ph-H), 8.0(d, 1H, CH).

Anthracene-9-carbaldehyde phenylhydrazone 7m.

^1H NMR (CDCl_3): δ 7.31-7.63 (m, 14H, Ph-H), 9.13 (s, 1H, $\text{CH}=\text{N}$).

Benzaldehyde (4-nitrophenyl)hydrazone 9.

^1H NMR (CDCl_3): δ 7.14 (d, 2H, $J=9.14\text{Hz}$, Ar-H), 7.36-7.44 (m, 3H, Ar-H3,4,5), 7.70 (d, 2H, $J=6.58\text{Hz}$), 7.82 (s, 1H, CH), 8.10 (bs, 1H, NH), 8.20 (d, 2H, $J=9.20\text{Hz}$).

Synthesis of tricyanovinyl derivatives 8a-m:**General procedure for the reaction of TCNE with hydrazones.**

A solution of hydrazone (10 mmol) and TCNE (10 mmol) in DMF (25 ml) was stirred at 60-90 °C for 8 hrs. The solvent was removed and the residual solid was collected and recrystallized from toluene-chloroform mixture. UV data are measured in various solvents and summarized in Table 2.