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Novel dyes derived from hydrazones. Part 2: synthesis and characterizations of *N*-methyl-4-tricyanovinylidenephenyl-hydrazones

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Abstract

Novel tricyanovinyl derived from *N*-methylhydrazones have been prepared by the reaction of tetracyanoethylene and *N*-methylbenzylidenehydrazone, 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 their 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 was studied in poly(methyl methacrylate) film at 80 °C; the substitution on the aromatic aldehydes showed some improvement of the thermal stability of the dyes.

Keywords: Dyes; Tricyanovinyl; Hydrazones; NLO

1. Introduction

The electronic and structural properties of the 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 ferrocenyl and schiff bases [6–8]. 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**, **5** and **6**. However, optical studies on compounds containing more than two benzenoid rings are usually insoluble in most of the common organic solvents. We have recently [9], reported the synthesis of new NLO chromospheres based on pyrazoles as the donor groups for example compound **7**. We have also reported the synthesis of new tricyanovinyl based on hydrazones such as dye **8** [10]. In this paper, we report on the synthesis and spectroscopic investigations of the novel push–pull system based on hydrazones as donor groups.

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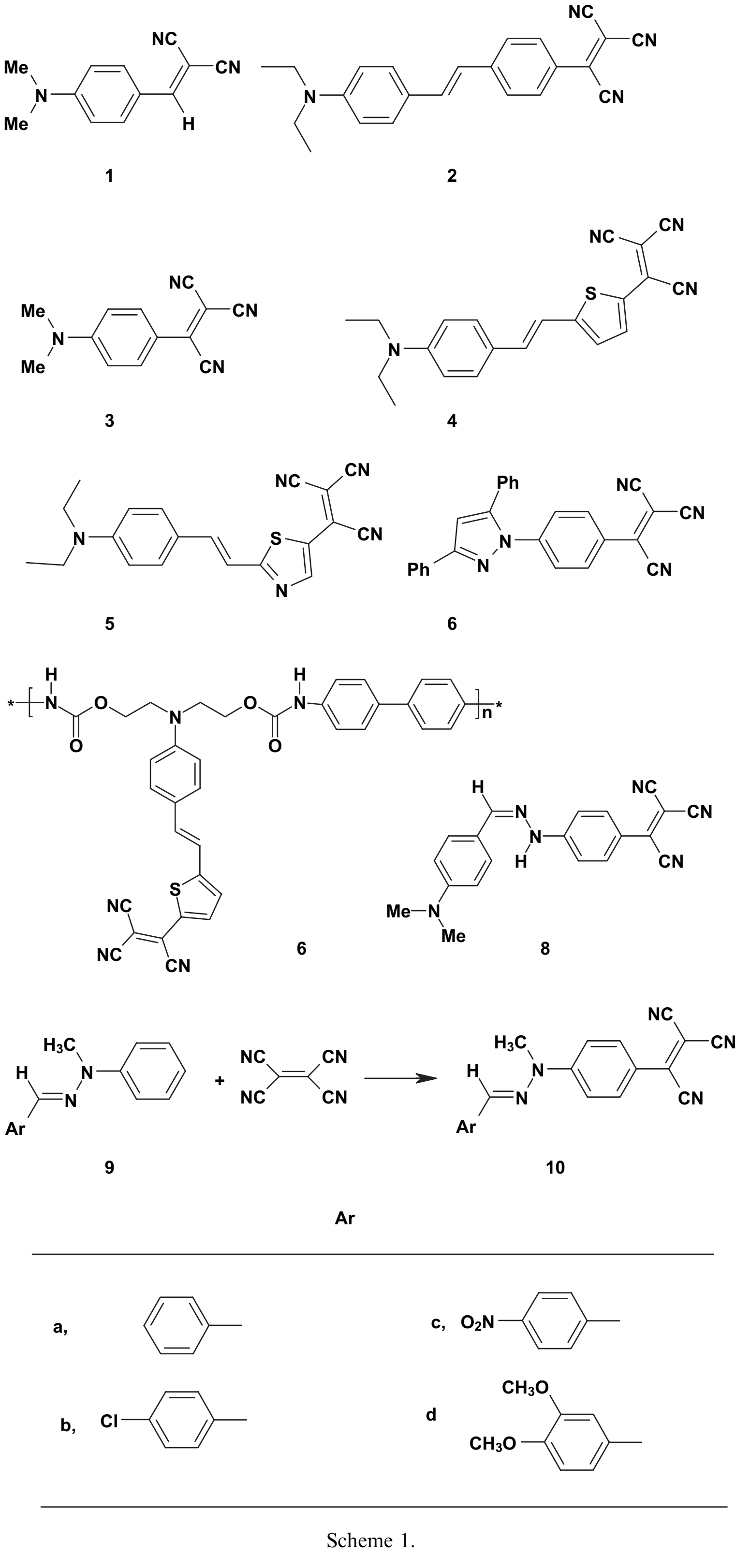


Scheme 1.

Table 1
The effects of solvents on the absorption maxima of dyes **10a–d**

Dye no	λ_{max}							ε_{max}	$\Delta\lambda$
	CH_3COCH_3 (20.7[a])	CH_3CN (37.5[a])	CH_3COOH (6.15[a])	$CHCl_3$ (4.8[a])	$(C_2H_3)_2O$ (4.33[a])	$C_6H_5CH_3$ (2.43[a])	$(CH_3)_2NCHO$ (36.7[a])		
10a	528	531	525	536	517	522	537	25,132	11
	337	323	334	321	330	337	326	13,062	
10b	522	527	521	535	514	519	535	22,072	8
	345	338	332	340	339	340	340	25,861	
10c	514	517	508	518	402	410	524	20,139	1
	410	409	408	416			414	19,566	
			262						
10d	550	552	544	556	540	541	570	31,904	11
	340	340	340	330	340	340	340	16,995	
			267						

λ_{max} CH_3CN–λ_{max} $CHCl_3$.
[a] Dielectric constant.

2. Results and discussion

2.1. Synthesis of dyes

The new chromospheres **10** were prepared by direct tricyanovinylation of hydrazones and this was achieved by mixing together the appropriate hydrazones **9** 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. The tricyanovinylation undoubtedly had taken place *para* to the hydrazine group as this was evidenced by the following observations.

2.2. 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 **10a**, which contains no substitution on the aldehyde phenyl, showed absorption band at 525 nm in acetone. A substitution by one chloro atom *para* to the aromatic aldehydes e.g. dyes **10b** generally showed a hypsochromic shift 522 nm compared with the unsubstituted dye **10a**. However, the most bathochromic shift was observed in the case of 3,4-dimethoxy derivative dye **10d**. In addition, a decrease in the intensity of the absorption bands was observed for the unsubstituted dye **10a** compared to the other dyes **10a–c** (Table 1).

Table 2
The extent of decomposition of dyes **10a–d**

Compound number	% Degradation
10a	60.0
10b	12.3
10c	20.8
10d	82.3

2.3. Solvatochromism

The dyes were measured in various solvents having different polarity. Generally increasing the solvent polarity gave a bathochromic shift of the maximum absorption bands of dyes **10a–d**. In non-polar solvents for instance in ether dye **10a** showed the most solvatochromic shift with absorption maxima at 517 nm while in the DMF the maxima was at 537 nm (Table 1). The solvatochromic effect can be estimated from the difference between the absorption maxima in polar and non-polar solvents e.g. $\Delta\lambda$ (Table 1). Figs. 1–4 show the visible absorption spectra of tricyanovinyl hydrazone dyes **10a–d** in various solvents. The solvent's effects can be rationalized on the basis of the dipole formed by charge migration from the nitrogen to the acceptor tricyanovinyl (Scheme 2).

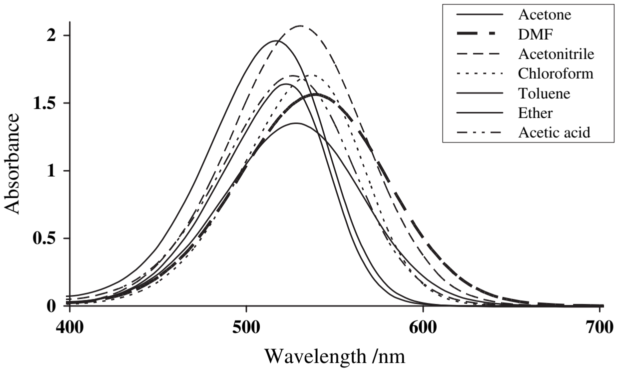


Fig. 1. Solvents' effects on electronic spectra of dye **10a**.

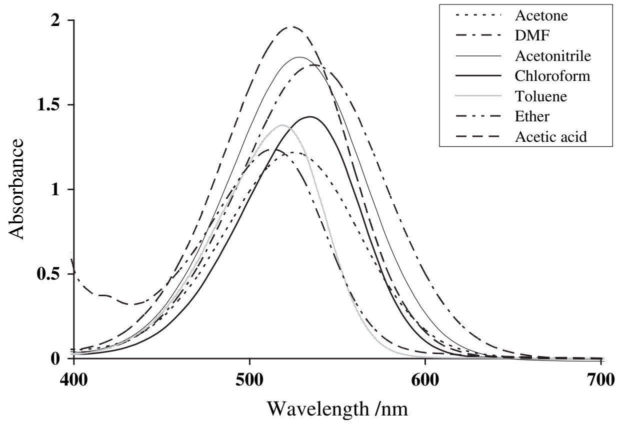


Fig. 2. Solvents' effects on electronic spectra of dye **10b**.

2.4. Thermal stability

The dyes were tested for their stability against the exposure to heat in poly(methyl methacrylate)s matrix at 80 °C. A thin film of poly(methyl methacrylate) (PMMA) doped with dyes **10a–b** and **10d** was prepared from a solution of the polymer and the dyes in chloroform (dye contents around 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 for which the absorption spectra were measured. The total heating period was 360 min.

Fig. 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 $(A^0 - At) \times 100/A^0$) of the dyes **10a–b** and **10d** were shown in Table 2. It is noteworthy to say that, the parent dye **10a** is the less stable dye on heating at 80 °C since 60% of the dye content was decomposed. On the other hand, dye **10c** is the most stable dye relative to the studied dyes. It is of great importance to notice that, the extent of the decomposition is measured after 360 min. However, most of the dyes are stable up to 60 min of heating at 80 °C.

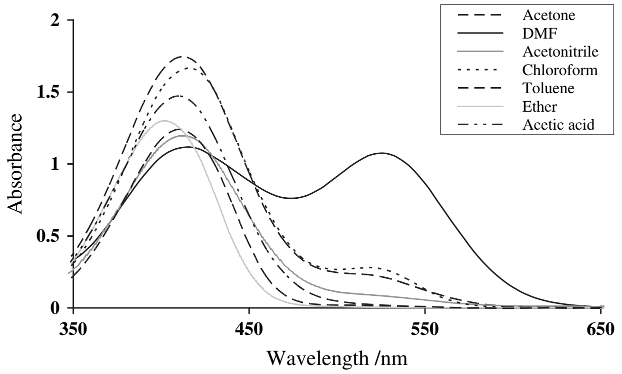


Fig. 3. Solvents' effects on electronic spectra of dye **10c**.

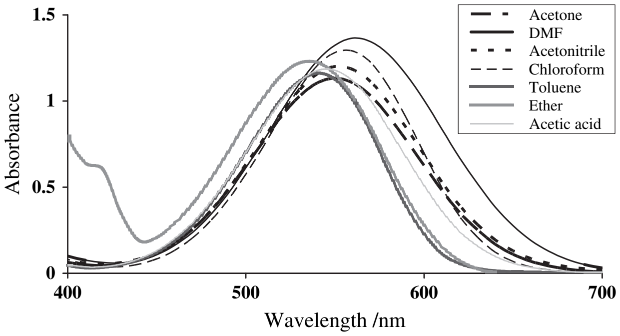


Fig. 4. Solvents' effects on electronic spectra of dye **10d**.

3. Experimental

3.1. 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, ^{1}H NMR were recorded in $CDCl_3$ on a Bruker DPX 400 spectrometer using TMS as an internal standard. Mass spectra were obtained on a Varian MAT CH5 spectrometer using EI technique. UV–visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

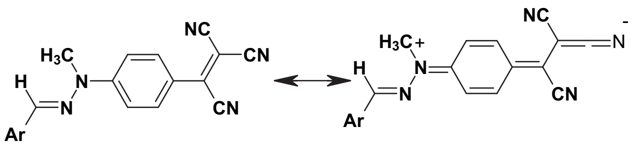
3.2. Synthesis of hydrazones

3.2.1. General procedure

Equimolar quantities of phenylhydrazine and the aldehydes were boiled in ethanol for 3–6 h. The precipitated hydrazones were filtered, washed and dried. The pure hydrazones were obtained after recrystallization from ethanol. The physical data are summarized in Table 1.

3.2.1.1. Benzaldehyde methyl(phenyl)hydrazone. M.p. 105–107 °C, yield 95%, ^{1}H NMR ($CDCl_3$) δ 7.78 (2H), 7.65 (1H), 7.61 (2H), 7.60 (2H), 7.52 (2H), 7.13 (2H), 6.97 (1H), 3.43 (3H).

3.2.1.2. 4-Chlorobenzaldehyde methyl(phenyl)hydrazone. M.p. 109–110 °C, yield 94%, ^{1}H NMR ($CDCl_3$)



Scheme 2.

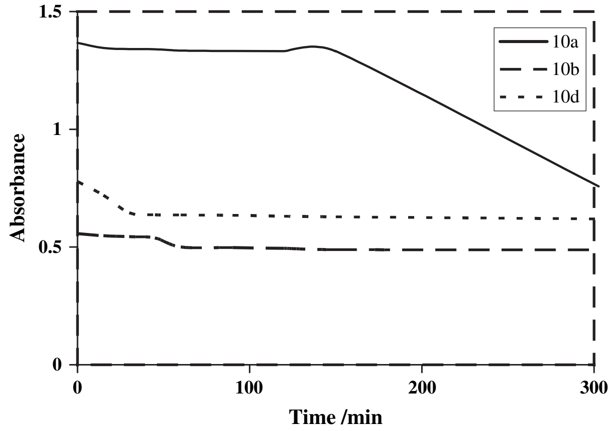


Fig. 5. Thermal stability of dyes **10a–b** and **10d**.

δ 7.64 (2H), 7.63 (1H), 7.61 (2H), 7.44 (2H), 7.13 (2H), 6.97 (1H), 3.45 (3H).

3.2.1.3. 4-Nitrobenzaldehyde methyl(phenyl)hydrazone. M.p. 135–136 °C, yield 91%, ^{1}H NMR ($CDCl_3$) δ 8.22 (2H), 7.96 (2H), 7.62 (1H), 7.61 (2H), 7.13 (2H), 6.95 (1H), 3.50 (3H).

3.2.1.4. 3,4-Dimethoxybenzaldehyde methyl(phenyl)hydrazone. M.p. 99–101 °C, yield 72%, ^{1}H NMR ($CDCl_3$) δ 7.61 (2H), 7.54 (1H), 7.40 (1H), 7.23(1H), 7.13 (2H), 6.97 (1H), 6.80 (1H), 3.64 (3H), 3.63 (3H), 3.33 (3H).

*3.3. Synthesis of tricyanovinyl derivatives **10a–d***

3.3.1. General procedure for the reaction of TCNE with hydrazones

A solution of aromatic amine (10 mmol) and TCNE in DMF (25 ml) was stirred at 60–90 °C for 8 h. The solvent was removed and the residual solid collected and recrystallized from toluene–chloroform mixture.

3.3.1.1. 2-{4-[2-Benzylidene-1-methylhydrazino]phenyl}-ethylene-1,1,2-tricarbonitrile ***10a***. M.p. 222–224 °C, yield 85%; UV–vis (acetone): λ_{max} (nm) 528, 337; IR ν (cm^{-1}): 2212(C'N), 1608(C=N), 1341(C–N); ^{1}H NMR ($CDCl_3$) δ 3.58(s, 3H, CH_3), 7.38–8.18(m, 10H, Ar-H + CH_x + Ph-H); ^{13}C NMR ($CDCl_3$) δ 32.34, 98.05, 114.64, 115.25, 115.37, 120.57, 126.10, 126.33, 127.57, 127.71, 128.57, 128.68, 128.96, 129.0, 129.97, 132.39, 133.39, 150.18.

3.3.1.2. 2-{4-[2-(4-Chlorobenzylidene)-1-methylhydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile ***10b***. M.p. 258–261 °C, yield 74%; UV–vis (acetone): λ_{max} (nm) 522, 345; IR ν (cm^{-1}): 2208(C'N), 1608(C=N), 1338(C–N); ^{1}H NMR ($CDCl_3$) δ 3.40(s, 3H, CH_3), 7.28–7.75(m, 9H, Ar-H + CH_x + Ph-H). ^{13}C NMR (DMSO) δ 32.93, 97.56, 112.57, 114.75, 115.25, 120.28, 127.34, 128.69, 128.93, 129.0, 131.25, 131.99, 133.42, 135.35, 150.8

3.3.1.3. 2-{4-[2-(4-Nitrobenzylidene)-1-methylhydrazino]-phenyl}ethylene-1,1,2-tricarbonitrile ***10c***. M.p. 292–295 °C, yield 74%; UV–vis(acetone): λ_{max} (nm) 514, 410; IR ν (cm^{-1}): 2214(C'N), 1594(C=N), 1328(C–N); ^{1}H NMR (DMSO, $CDCl_3$) δ 2.97(s, 3H, CH_3), 7.37–7.40(m, 4H, Ph-H), 7.47(s, 1H, CH_x), 7.80(d, 2H, $J = 8.10$ Hz, Ar-H2,6), 8.20(d, 2H, $J = 8.10$ Hz, Ar-H3,5); ^{13}C NMR (DMSO, $CDCl_3$) δ 34.60, 101.2, 115.28, 121.21, 123.44, 125.50, 128.31, 128.56, 142.77, 145.72, 146.59, 150.3.

3.3.1.4. 2-{4-[2-(3,4-Dimethoxybenzylidene)-1-methylhydrazino]phenyl} ethylene-1,1,2-tricarbonitrile ***10d***. M.p. 266–268 °C, yield 93%; UV–vis (acetone): λ_{max} (nm) 550, 340; IR ν (cm^{-1}): 2213(C'N), 1596(C=N), 1343(C–N); ^{1}H NMR ($CDCl_3$) δ 3.57(s, 3H, CH_3), 3.95(s, 3H, *m*-OCH_3), 4.0 (s, 3H, *p*-OCH_3), 6.92(d, 2H, $J = 8.30$ Hz, Ph-H2,6), 7.20(d, 2H, $J = 8.25$ Hz, Ph-H3,5), 7.42–7.51(m, 2H, Ar-H2,6), 7.80(s, 1H, CH_x), 8.15(d, 2H, $J = 9.30$ Hz, Ar-H3,5); ^{13}C NMR ($CDCl_3$) δ 34.6, 55.8, 56.0, 107.69, 108.10, 110.93, 114.41, 115.18, 122.10, 127.61, 129.0, 132.47, 139.84, 151.4, 152.01.

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