

SYNTHESIS AND ELECTRONIC ABSORPTION PROPERTIES OF SOME PYRAZOLES FUNCTIONALIZED WITH TRICYANOVINYL AND TRICYANO-P-QUINODIMETHANE CHROMOPHORES

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التفاعل بين كل من تيتراسيانوإيثيلين و تيتراسيانوكينونثائي الميثان مع مشتقات البيرازول 5a-d أعطى 1-(4-ثلاثي سيانو فينيل) و 1-(4-ثلاثي سيانو كينونثائي ميثان) فينيل 5, 3-ثنائي استبدال بيرازول 6a, 7a-d, 17a-c على التوالي. أصباغ البيرازول الجديدة أظهرت حزم امتصاص في المجال المرئي ومجال الأشعة تحت الحمراء القريبة من الطيف. ومن الملاحظ أيضا لهذه الأصباغ تأثير قمة الامتصاص بقطبية المذيب.

The reaction between tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane with pyrazoles **5a-d** gave 1-(4'-tricyanovinyl) and 1-(4'-tricyanoquinodimethane)phenyl-3,5-disubstituted pyrazoles **6a**, **7b-d** and **17a-c** respectively. The new pyrazole dyes showed absorption bands in the visible and near infrared region of the spectrum. The dyes showed remarkable solvatochromism.

Key Words: Pyrazole, Pyrazole dye, Tetracyanoethylene (TCNE), Pyrazolone Tetracyanoquinodimethane (TCNQ), Non-linear Optics

INTRODUCTION

In the past, dyes had found many applications in the field of textiles dying. Nowadays, dyes and pigments have found some new applications, for example, dyes based on conjugated donor-acceptors such as dyes **1a**, **2** and **3** [1,2] are used in the field of nonlinear optics for optical data storage and in the field of electrooptics for electrocommunications [3-5]. It has been reported that dyes containing heterocyclic systems such as thiophene as in dyes **2** and **3** showed improvement of both the polarizability and shifting the maxima to the desired longer wavelength. This can be illustrated by comparing the longest wavelength absorption bands of dye **1a**, which has λ_{max} at 515 nm and dyes **2** and **3** which have λ_{max} at 718 nm and 640 nm respectively. The thiophene moiety is more polarized than the normal benzene, and hence the excited state is more stable so that the maximum absorption is red shifted.

The heterocyclic systems containing pyrazoles are used as insecticides [6], acaricides [7] pesticides [8] and herbicides [9]. Although, the use of pyrazoles derivatives as intermediates in the synthesis of dyes is rare, some 5-pyrazolones were

used as coupling components in the synthesis of many yellows to orange azo dyes [10].

In this paper we wish to report on the synthesis of some new conjugated donor-acceptor chromogens using the pyrazole N-1 atom as the donor element.

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, ¹H NMR were recorded in CDCl₃ on a Bruker DPX 400 spectrometer using TMS as 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.

General procedure for the synthesis of pyrazoles **5a-d**

A solution of phenyl hydrazine hydrochloride (0.1 mol), the appropriate 1,3 diketone (0.1 mol) and sodium acetate (3.0 g) in absolute ethanol (50 ml) was refluxed for 6 hours. The reaction mixture was left to cool at room temperature, the

1-[4'-(7,8,8-Tricyanoquinodimethane)phenyl]-3,5-diphenylpyrazole 17c. Obtained as dark blue crystals (2.84 g, 60%), mp 122-124 °C; (Found: C, 80.98; H, 4.23; N, 14.61 C₃₂H₁₉N₅ requires C, 81.20; H, 4.01; N, 14.79%); *m/z* 433 (M) (2%), 296 (100), 268 (4), 245 (5), 192 (10), 165 (15), 147 (6), 122 (45), 105 (40); IR (KBr): 2190, 1597 cm⁻¹; δ_H (see Table 2).

Synthesis of pyrazole (7d) from (1b) and 1,3-diketone 4d. A mixture of dibenzoylmethane **4d** (0.50 g, 2.23 mmol) and the 4-tricyanovinylphenylhydrazine **1b** (0.47 g, 2.23 mmol) in DMF (20 ml) was heated at 90°C for 4 hrs. The solvent was removed and the residual was chromatographed on silica gel using ether as eluant. Evaporation of the ether (rotatory evaporator) gave compound **7d** as dark red crystals (0.58 g, 61%). All characterizations were identical to those obtained for compound **7d** prepared by the general procedure mentioned above.

4-Dicyanomethylene-3-methyl-1-phenylpyrazol-5-one 9. A solution of 3-methyl-1-phenylpyrazol-5-one **8** (2.5 g, 14.36 mmol) and tetracyanoethylene (1.8 g, 14.36 mmol) in acetonitrile (25 ml), a rapid violet color was developed, then reaction mixture was stirred at room temperature for 20 minutes. The excess solvent was removed under reduced pressure and the violet solid residual was collected, washed with water and finally washed with ether to give compound **9** as dark red solid. (3.05 g, 90%), mp 144-146 °C; (Found: C, 66.04; H, 3.51; N, 23.51. C₁₃H₈N₄O requires C, 66.12; H, 3.39; N, 23.72%); IR (KBr): 2230, 2202, 1715, 1651, 1592 cm⁻¹; δ_H 7.82 (2H, d, *J* = 8 Hz, aromatic H-2, 6), 7.44, 7.22 (3H, m, aromatic H3, 4, 5), 2.56 (3H, s, CH₃).

4-Dicyanomethylene-3-methyl-5-(4-nitrophenyl)aza-1-phenylpyrazol 14. A solution of the dicyanomethylenepyrazolone derivative **9** (0.5 g, 2.11 mmol) and 4-nitroaniline (0.29 g, 2.11 mmol) in dry toluene (20 ml) was refluxed under dean stark azeotropic removal of water for 6 hours. Then the reaction mixture was left to cool to room temperature and dark red powder was precipitated, filtered and wash with ether (2x20ml) and dried. The aza compound **14** was

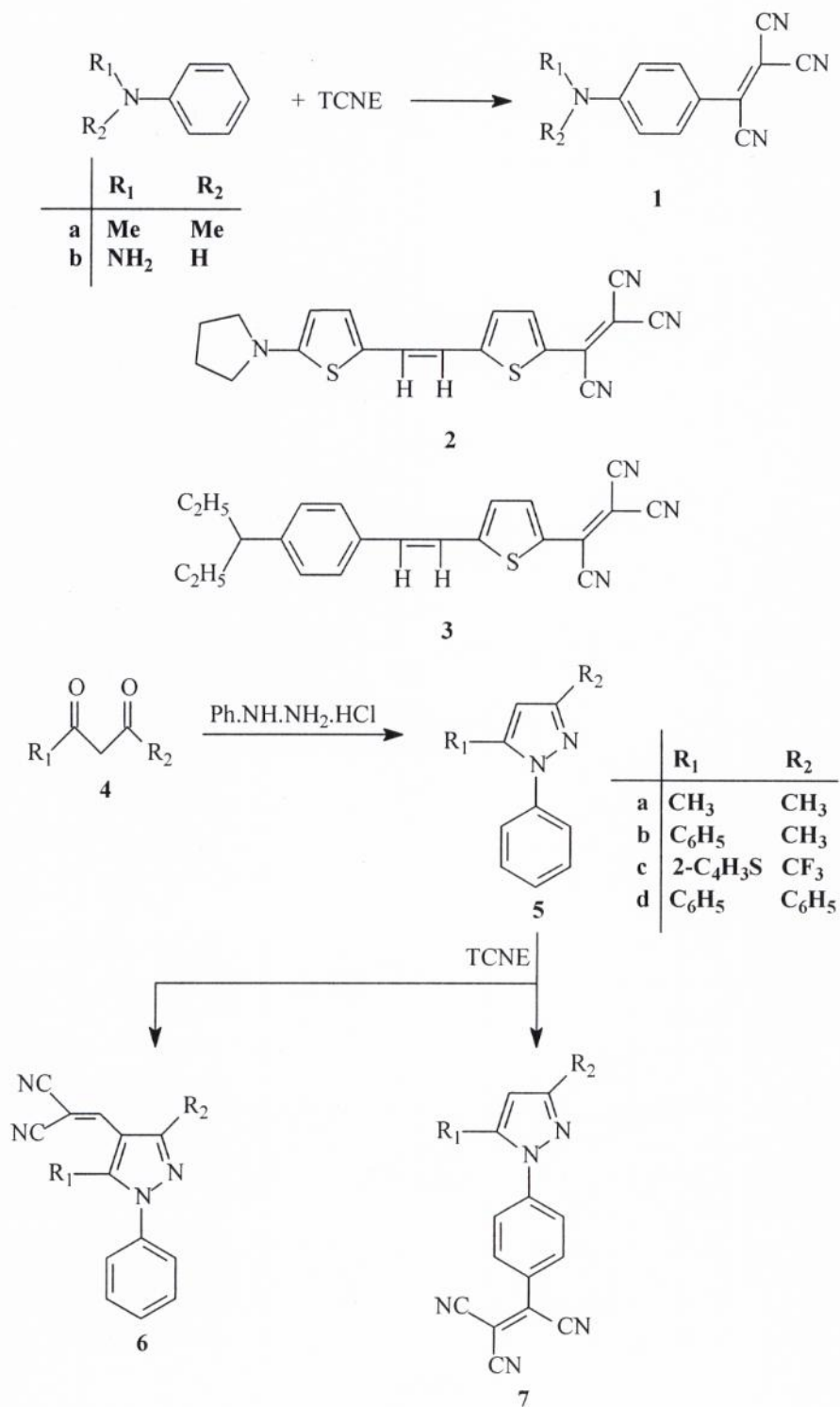
obtained as dark orange powder. (0.57 g, 76%), mp 85-87°C; (Found: C, 64.12; H, 3.41; N, 23.38. C₁₉H₁₂N₆O₂ requires C, 64.06; H, 3.37; N, 23.58%); IR (KBr): 2209, 1696, 1589, 1535, 1330 cm⁻¹; δ_H 7.94 (2H, d, *J* = 7.94 Hz, aromatic protons ortho to nitro group), 6.95 (2H, d, *J* = 7.97 Hz, aromatic protons meta to nitro group), 7.57, 6.83 (5H, m, aromatic protons), 2.53 (3H, s, CH₃).

RESULTS AND DISCUSSION

The tricyanovinyl derivative **1a** was prepared for comparison between the simple aromatic ring and the heterocyclic pyrazole ring as the donor group. Compound **1a** was obtained in a very rapid reaction of N,N-dimethylaniline and tetracyanoethylene (TCNE) in DMF at room temperature as dark violet crystals (Scheme 1)[1].

The simplicity of the reaction of (TCNE) with aromatic amine encouraged us to investigate the reaction with different N-Ph derivatives such as pyrazoles **5a-d**. Thus reaction of (TCNE) and pyrazole **5a** under similar condition gave the 4-tricyanovinyl pyrazole derivative **6a** and not the expected derivative **7a** as deep yellow crystals. The structure of **6a** was elucidated from its spectral and analytical data. IR spectrum showed absorption band at 2230 cm⁻¹ for the cyano groups. The ¹H-NMR spectrum did not show the expected singlet of the pyrazole H-4, which appeared in the original pyrazole **5a** at δ 6.28 indicating that the pyrazole ring has been substituted.

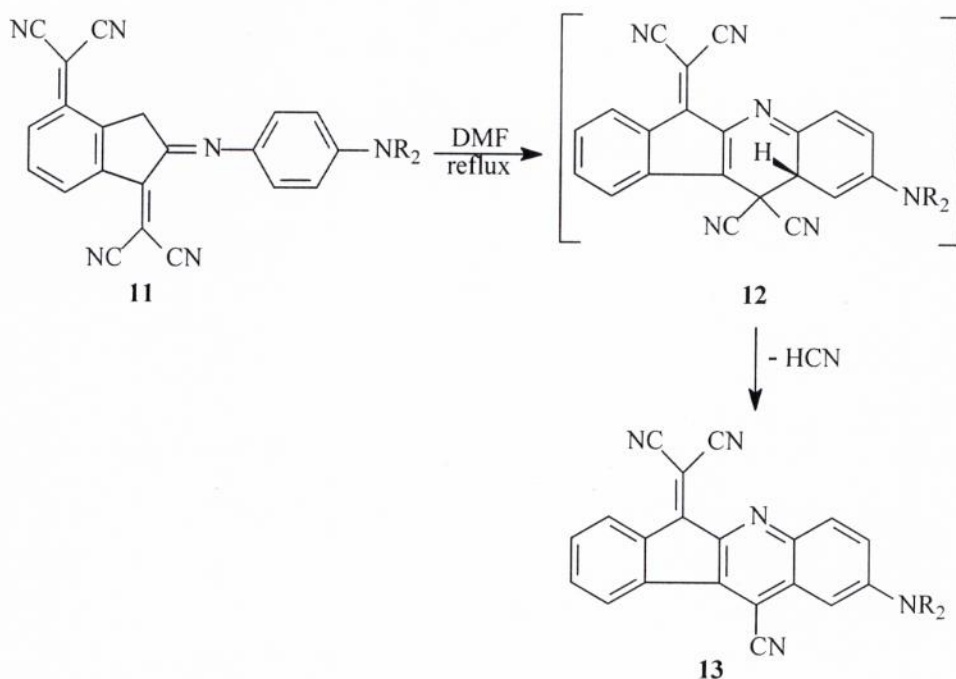
Unlike the reaction of pyrazole **5a** and (TCNE), when pyrazole **5b** reacted with (TCNE) under the same condition used with **5a**, compound **7b** was the only product obtained and not **6b**. This may be due to the less steric effect provided by the 5-methyl. The IR spectrum of the tricyanovinyl pyrazole derivative **7b** exhibited the cyano group band at 2211 cm⁻¹. The ¹H-NMR spectrum shows a singlet at δ 6.77 for the pyrazole H-4. The phenyl group of the pyrazole **7b** showed the normal AA'BB' system, and the two protons ortho to the nitrogen atom appeared as a doublet centered at δ 7.04 and the other two protons appeared as a doublet centered at δ 7.83 (see Table 1).



Scheme 1

Griffiths [12] reported some irreversible electrocyclization reaction of some 1,3-bis-dicyanomethylene-2-azaindan derivative such as **11** and found that, when **11** was heated in DMF at reflux derivatives **13** was obtained via the loss of one molecule of HCN from the intermediate **12** (Scheme 4). It was of interest to see whether we might be able to prepare some aza derivatives similar to compound **11** from **9** by its condensation with aromatic amine and to study the possibility of similar electrocyclization as those reported by Griffiths [12]. Thus, condensation of equimolar quantity of pyrazolone **9** and 4-nitroaniline in toluene with azeotropic

removal of water gave the 5-aza-4-dicyanomethylenepyrazole derivative **14** as an orange powder. The IR spectrum of compound **14** exhibited a band at 2209 cm^{-1} for the cyano and no carbonyl absorption was observed. The $^1\text{H-NMR}$ spectrum of compound **14** showed the AA'BB' characteristic spin system of para substituted benzene. When the 5-aza-4-dicyanomethylenepyrazole derivative **14** was refluxed in DMF for 3 hours, the expected electrocyclization product **15** was not detected and the starting compound **14** was recovered unchanged (Scheme 3).



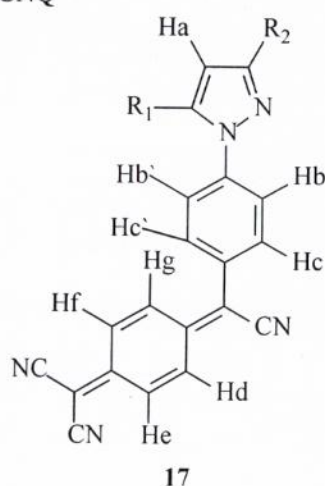
Scheme 4

Since the discovery of diode laser, which emits near 760 nm, interests have grown in dyes absorbing in the infrared region for applications in the field of optical data storage. For tricyanovinylpyrazoles derivatives **6a** and **7b-d** no absorption maxima in their visible spectra beyond 510 nm

was observed; and this make them unsuitable candidates for such application. On the other hand, it has been reported that 7,7,8,8-tetracyanoquinodimethane (TCNQ) can react smoothly with aromatic amine in a similar manner as that for (TCNE) to produce dyes absorbing in

Table 2: ¹H-NMR Data of Pyrazole Substituted TCNQ

17a: R₁ = R₂ = CH₃
17b: R₁ = Ph, R₂ = CH₃
17c: R₁ = R₂ = Ph



Compound			
δ	17a	17b	17c
Ha	6.01	6.77	6.86
Hb, Hb'	7.00 (2H, d, <i>J</i> _{bc} = 7.18 Hz)	7.19 (2H, d, <i>J</i> _{bc} = 7.36 Hz)	7.26 (2H, d, <i>J</i> _{bc} = 6.50 Hz)
Hc	8.15 (1H, d, <i>J</i> _{cb} = 7.34 Hz)	7.83 (1H, d, <i>J</i> _{cb} = 7.30 Hz)	7.92 (1H, d, <i>J</i> _{cb} = 6.60 Hz)
Hc'	8.07 (1H, dd, <i>J</i> _{b'c'} = 8.0 Hz, <i>J</i> _{c'g} = 4.5 Hz)	8.00 (1H, dd, <i>J</i> _{b'c'} = 8.5 Hz, <i>J</i> _{c'g} = 4.0 Hz)	7.93 (1H, dd, <i>J</i> _{b'c'} = 6.50 Hz, <i>J</i> _{c'g} = 4.4 Hz)
Hd	7.68 (1H, d, <i>J</i> _{de} = 9.8 Hz)	7.61 (1H, d, <i>J</i> _{de} = 7.2 Hz)	7.61 (1H, d, <i>J</i> _{de} = 7.5 Hz)
He	7.20 (1H, d, <i>J</i> _{de} = 9.5 Hz)	7.34 (1H, d, <i>J</i> _{de} = 7.3 Hz)	7.34 (1H, d, <i>J</i> _{de} = 7.5 Hz)
Hf	7.27 (1H, d, <i>J</i> _{fg} = 7.6 Hz)	7.44 (1H, d, <i>J</i> _{fg} = 8.1 Hz)	7.34 (1H, d, <i>J</i> _{fg} = 6.9 Hz)
Hg	7.82 (1H, dd, <i>J</i> _{fg} = 7.7 Hz, <i>J</i> _{c'g} = 4.5 Hz)	7.56 (1H, dd, <i>J</i> _{fg} = 8.1 Hz, <i>J</i> _{c'g} = 4.0 Hz)	7.56 (1H, dd, <i>J</i> _{fg} = 7.1 Hz, <i>J</i> _{c'g} = 4.7 Hz)
Other	2.59 (3H, s, 5-CH ₃ , 2.64 (3H, s, 3-CH ₃)	2.51 (3H, s, 3-CH ₃), 7.45-7.51 (5H, m, aromatic)	7.32-7.41 (10H, m, aromatic)

UV-Visible spectroscopic data

Table 3 summarizes the UV-Visible spectral data of the synthesized tricyanovinylpyrazole derivatives **6a**, **7b-d** and 7,8,8-tricyanoquinodimethanepyrazole derivatives **17a-c** in chloroform, ethyl acetate, acetone and acetonitrile. The molar extinction coefficient was measured in acetonitrile. In chloroform dye **6a** showed two absorption bands with equal intensity. The first band at 363 nm and the second band at 405 nm. On the other hand, tricyanovinyl derivatives **7b**, **7c** and **7d** showed similar absorption bands. The tricyanovinyl dye series **7b-d** absorb at shorter wavelength than that of dye **1a** indicating the poor electron donating character of the substituted pyrazole N-Ph. The relative increase in the

electron donating character of pyrazole derivatives can be assessed from λ_{max} values and in ethyl acetate the sequence **7d** > **7b** > **7c** was observed. In the tricyanoquinodimethane derivatives **17a-c**, all the dyes showed a strong charge transfer band in the visible region of the spectrum along with another absorption band in the range of 349-465 nm. The charge transfer band is not sensitive to the substituents on 3 and 5-position of the pyrazole moiety.

Solvatochromism and the non-linear optical properties

Solvatochromism is the change of the absorption bands with changing the solvent polarity. All the tricyanovinyl **7b-d** and the tricyanoquinodi-

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