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Synthesis of 11-tricyanovinyl and 11-(7,8,8-tricyanoquino- dimethane)- 1,3,3-trimethyl-2-methyleneindoline

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ABSTRACT

The addition of tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane to 1,3,3-trimethyl-2-methyleneindoline **1** resulted in the formation of two novel compounds, **9** and **10** respectively, and not the expected products **5** and **6**. Compound **9** is dark brown, whereas **10** is deep blue-green. On increasing the solvent's polarity, compounds **10** showed remarkable red shift but compound **9** did not.

Keywords: Dyes; methyleneindoline; tetracyanoethylene; tetracyanoquinodimethane; tricyanovinyl.

INTRODUCTION

1,3,3-Trimethyl-2-methyleneindoline **1** is a major component in the synthesis of many organic colorants such as methine (Gordon & Gregory 1983), and it is also the key element in the synthesis of naphthopyran (**2**, X = CH) and naphthoxazine (**2**, X = N) (Brown 1971, Durr & Bouas-Laurent 1990).

Spironaphthopyran and spironaphthoxazine derivatives are the sole components in the production of photochromic sunglasses (Osterby *et al.* 1991, Crano *et al.* 1992).

On the other hand, tetracyanoethylene (TCNE) has played an important role in many organic reactions (Fatiadi 1987, Jacobson *et al.* 1988, Graziano & Chiosi 1989). For example, it interacts with simple aromatic amines to produce varieties of organic dyes such as **34** and **4** containing the powerful tricyanovinyl moiety, which has a remarkable effect on both the color and the stability of dyes.

Many other derivatives related to dyes **3** and **4** have found some application in the field of nonlinear optics and some other electro optics applications (Williams 1984, Boyd 1992, Marder *et al.* 1991, Rao *et al.* 1993).

As part of our interest in the synthesis of new photochromic molecules for

applications in the field of photoswitchable systems based on spironaphthopyran (**2**, X = CH) and spironaphthooxazine (**2**, X = N), we have performed an intensive literature search for derivatives of compound **2** containing tricyanovinyl moiety on the indoline part of the molecules and found no reported results.

In this report, we present the results of the reaction of two electron acceptor compounds (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with 1,3,3-trimethyl-2-methyleneindoline **1** in hopes of getting new indoline derivatives substituted at position - 4, as for example, compounds **5** and **6** respectively. Compounds **5** and **6** are expected then to react with 2-hydroxy-1-naphthaldehyde and 1-nitroso-2-hydroxynaphthalene in a similar manner to that used for the preparation of **2** to produce the photoswitchable derivatives ~~**7**~~ and **8** respectively.

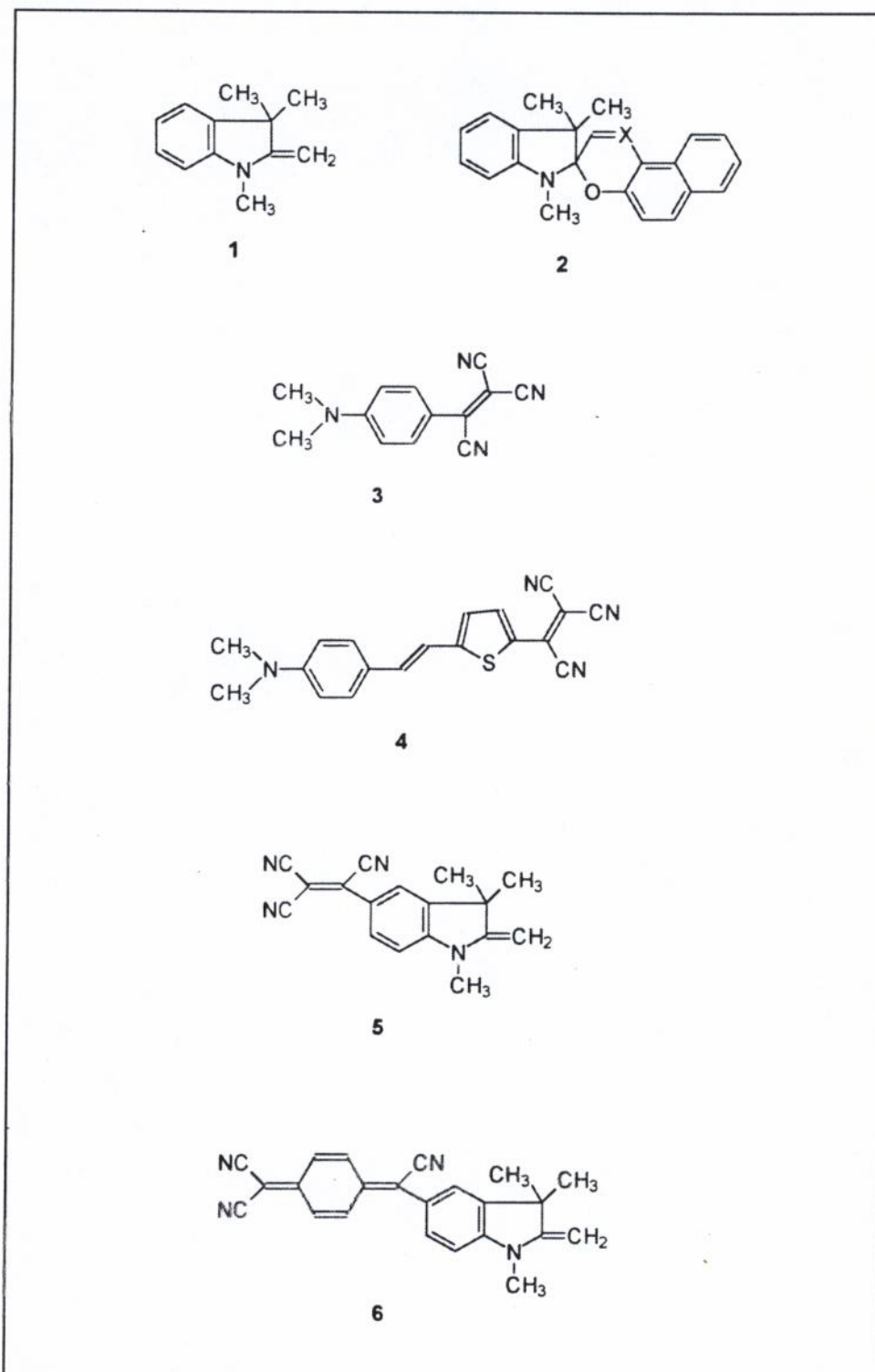
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RESULTS AND DISCUSSION

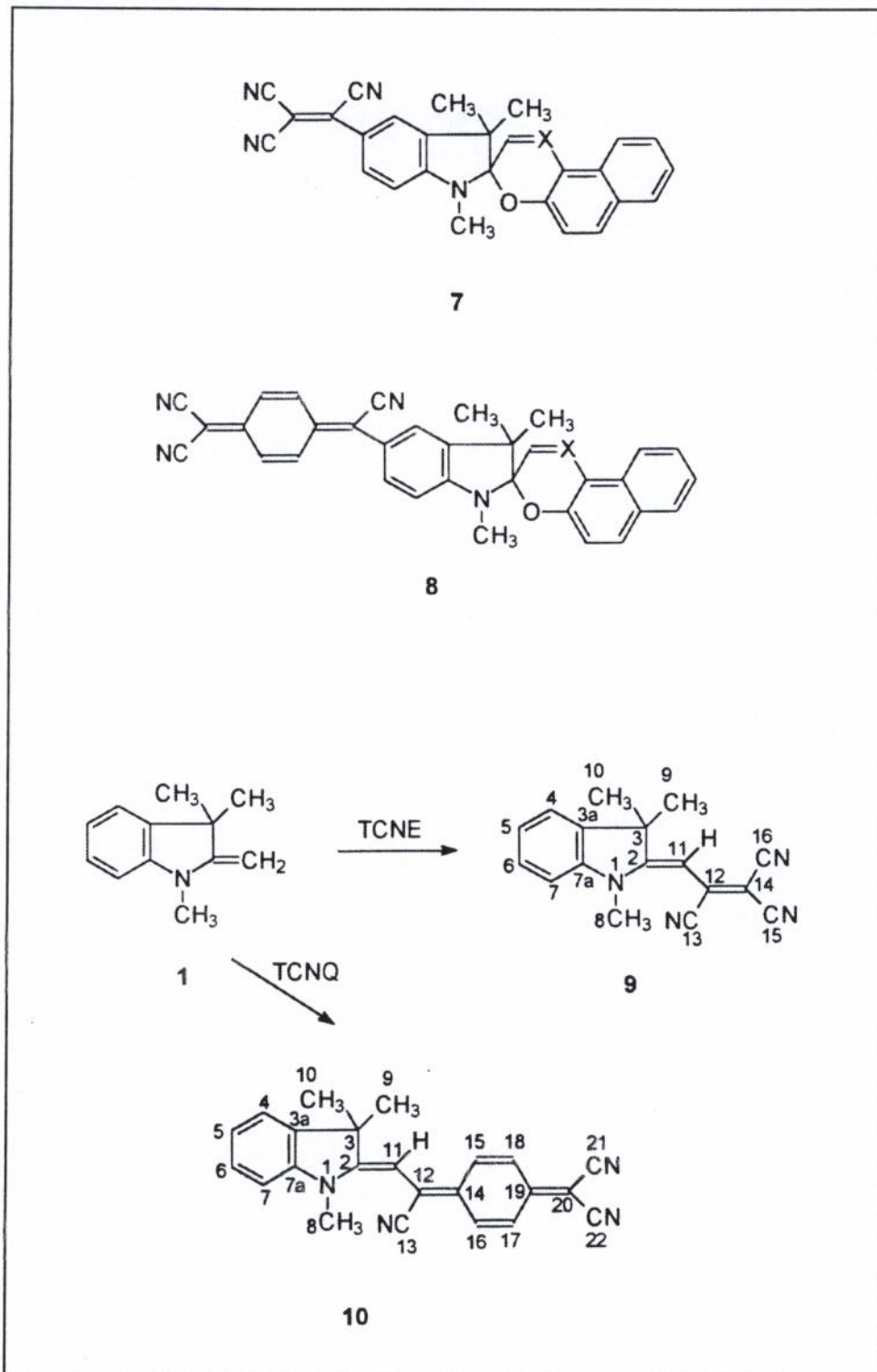
The reaction of (TCNE) with 1,3,3-trimethyl-2-methyleneindoline **1** under similar conditions used to prepare dye **3** gave compound **9** as dark brown crystals (Scheme 1). Unlike the reaction of (TCNE) with simple aromatic amine to get, for example, dye **3**, which contains tricyanovinyl (TCV) in para position with respect to the dimethylamino group, the attack took place on the methylene group.

The IR spectrum of compound **9** showed a sharp band at 2205 cm^{-1} for the cyano group and another band at 1611 cm^{-1} for C=C. These bands indicate the incorporation of the tricyanovinyl group. The $^1\text{H-NMR}$ spectrum showed a triplet (collapse of dd) at δ 6.88 with J value of 7.4 Hz, attributed to the H-5 of the indoline moiety. Another triplet appeared at δ 7.20 with J value of 7.5 Hz attributed to H-6, and two doublets at δ 7.11 and δ 6.68 attributed to H-4 and H-7 respectively. These $^1\text{H-NMR}$ results indicate that no electrophilic substitution had taken place on the aromatic part of the indoline and hence no (TCV) was introduced to the aromatic nucleus of **1**. Moreover, one of the two-methylene protons centered in the indoline **1** at δ 6.2 had disappeared and only one singlet integrated for one proton appeared at δ 5.92. This $^1\text{H-NMR}$ assignment which was based on both H, H-COSY and NOSY experiments lead us to conclude that the substitution reaction took place on the methylene carbon rather than on the aromatic carbon, and the dark brown crystals are proved to be compound **9**.

The structure of compound **9** was further verified from the $^{13}\text{C-NMR}$, which exhibited four hydrogen-bearing carbon-13 peaks in the aromatic region, i.e., peaks at 109.01 (C-7), 120.56 (C-5), 121.69 (C-4) and 128.55 (C-6).



Scheme 1



Scheme 1 (cont'd)

These four carbon signals correlated with the four protons connected to them as evidenced from the hetero-COSY experiment. A DEPT experiment was performed to help in the assignment of the carbon signals, and was further evidence for the absence of the two-methylene protons.

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a well known electron acceptor in charge transfer reactions. It has been reported that (TCNQ) can react in a similar manner to (TCNE) with aniline to form infrared active dyes (Boldt *et al.* 1996). It was thought that the use of (TCNQ) with indoline **1** would produce highly colored indoline derivative **6** if the substitution took place on C-6 of the aromatic part of the indoline moiety or it would proceed with an attack on the methylene as TCNE does.

When equimolar quantities of (TCNQ) and indoline **1** were reacted under similar reaction conditions as for (TCNE), compound **10** was obtained as dark blue-green powder (Scheme 1). The IR spectrum of this powder showed bands at 2220 cm^{-1} for cyano groups and at 1620 cm^{-1} for C=C. The $^1\text{H-NMR}$ spectrum of the blue-green powder exhibited the four aromatic protons of the indoline H-4, H-5, H-6 and H-7 at δ 7.05, 7.80, 7.13 and 6.67 respectively. Also the spectrum showed a singlet at δ 6.26 integrated for one proton assigned for the methylene proton. In addition to that, the $^1\text{H-NMR}$ showed four sets of doublets at δ 6.97, 7.68, 7.76 and 8.07 for quinoied protons. The deep color of the new indoline **9** and **10** is due to the conjugated donor-acceptor nature of this system, as the indoline nitrogen serves as the donor group and the (TCV) in **9** and 7,8,8-tricyanoquinodimethane in **10** as the acceptors.

Compound **9** showed a characteristic three bands in the region of 200-550 nm, whereas a compound **10** showed remarkable bathochromic shift and showed an absorption maximum in the near infra red region. This great bathochromic shift is due to the excellent accepting properties of the tricyanoquinodimethanyl group.

It is well known that conjugated donor-acceptor chromogens are characterized by remarkable solvatochromic effect (e.g. shifting the absorption maxima on changing the solvent polarity). Table 1 showed the UV-Visible spectral data of compounds **9** and **10** in various solvents. Increasing the solvent polarity causes no remarkable shift of the visible band of compound **9**, but showed remarkable effects on both the position and the shape of the visible absorption of compound **10**.

Table 1. UV-Visible Spectral Data of Compounds 9 and 10

Compd. No.	λ_{\max} (nm)/ ϵ (L/mol. cm)					
	Toulene	CHCl ₃	CH ₃ CN	EtOH	THF	EtOAc
9	330 (2300)	-	265 (7800)	-	-	292 (3200)
	384 (2700)	379 (6300)	368 (5300)	376 (14000)	378 (3000)	368 (7400)
	500 (1600)	504 (5000)	500 (4000)	501 (4400)	501 (5100)	498 (2400)
10	-	435 (1300)	-	547 (3000)	430 (1700)	415 (2100)
	-	725 (14000)	724 (16000)	728 (10000)	728 (14000)	722 (11200)
	705	797 (12000)	786 (16000)	787 (10000)	801 (14000)	795 (10100)

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 MHz spectrometer using TMS as internal standard. ¹³C NMR were recorded in CDCl₃ on a Bruker DPX 100 MHz. MS were recorded on a Shimadzu QP-5000 mass spectrometer. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

11-Tricyanovinyl-1,3,3-trimethyl-2-methyleneindoline 9 - A solution of 1,3,3-trimethyl-2-methyleneindoline **1** (1.0 g, 5.78 mmol) and TCNE (0.73 g, 5.78 mmol) in dry DMF (20 ml) was heated in an oil bath at 60°C for 6 hours. The reaction mixture was cooled to room temperature and poured into water (100 ml) with stirring then left to stand over night. Dark brown crystals were precipitated, filtered and washed with water (20 ml) and a small amount of ether (2x10 ml) to give compound **9** as dark brown crystals (1.26 g, 80%), m.p. 242-244°C; (Found: C, 74.21; H, 5.24; N, 20.29. C₁₇H₁₄N₄ requires C, 74.45; H, 5.10; N, 20.40%); $\nu_{\max}/\text{cm}^{-1}$ 2205 (CN), 1611 (C=C); δ_{H} 7.20 (1H, d, J = 7.5 Hz, H-6), 7.11 (1H, d, J = 7.3 Hz, H-4), 6.88 (1H, d, J = 7.4 Hz, H-5), 6.68 (1H, d, J = 7.73 Hz, H-7), 5.92 (1H, s, H-11), 2.80 (3H, s, CH₃N), 1.55 (3H, s, CH₃-9), 1.53 (3H, s, CH₃-10); δ_{C} 173.55 (C-12), 142.29 (C-7a), 140.35 (c-2), 128.55 (C-6), 125.99 (C-3a), 121.69 (C-4), 120.56 (C-5), 116.57 (C-16), 115.94 (C-13), 114.08 (C-15), 109.01 (C-7), 49.78 (C-3), 30.12 (C-8), 25.81 (C-10), 22.77 (C-9).

11-Tricyanoquinodimethane-1,3,3-trimethyl-2-methyleneindoline 10 - A solution of 1,3,3-trimethyl-2-methyleneindoline **1** (0.85 g, 4.91 mmol) and TCNQ (1.0 g, 4.91 mmol) in dry DMF (10 ml) was heated in an oil bath at 90°C for 12 hours. Work up as described for compound **9** gave compound **10** as blue-green powder (1.3 g, 75%), m.p. 145-147°C; (Found: C, 78.69; H, 5.31; N, 15.89. C₂₃H₁₈N₄ requires C, 78.87; H, 5.13; N, 16.00%; $\nu_{\max}/\text{cm}^{-1}$ 2220 (CN), 1621 (C=C); δ_{H} 8.07 (1H, d, J = 8.01Hz, H-18), 7.76 (1H, d, J = 8.90Hz, H-17), 7.68 (1H, d, J = 8.31Hz, H-15), 7.13 (1H, t, J = 7.33Hz, H-6), 7.05 (1H, d, J = 7.44Hz, H-4), 6.97 (1H, d, J = 8.86Hz, H-16), 6.80 (1H, t, J = 7.44 Hz, H-5), 6.67 (1H, d, J = 7.95Hz, H-7). 6.26 (1H, d, H-12), 2.74 (3H, s, CH3-8), 1.66 (6H, s, CH3-9 + CH3-10); δ_{C} 166.63 (C-12), 150.60 (C-14), 142.68 (C-7a), 141.20 (C-2), 130.86 (C-16), 130.32 (C-15), 127.59 (C-6), 126.98 (C-18), 125.84 (C-4), 122.90 (C-3a), 121.50 (C-19), 119.96 (C-52) (C-21), 118.79 (C-5), 117.02 (C-22), 114.81 (C-13), 96.77 (C-11), 46.71 (C-20), 30.68 (C-8), 23.74 (C9 + C-10).

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تحضير 11-ثلاثي سيانوفيناييل و11-(7,8,8)-ثلاثي
سيانوكينوثنائي ميثان)- 1,3,3-ثلاثي ميثايل-2-ميثيلين اندول

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خلاصة

إضافة رباعي سيانو الأيثان و 8,8,7,7-رباعي سيانوكينوثنائي الميثان إلى 1,3,3-ثلاثي ميثايل-2-ميثيلين اندان 1 نتج عنه تكوين مركبين 9 و 10 على التوالي وليس المركبين المتوقعين 5 و 6. المركب 9 بني غامق بينما المركب 10 أزرق - مخضر غامق. زيادة قطبية المذيب أدت إلى إزاحة حمراء للمركب 10 بينما لم تؤثر على المركب 9.