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1-Cyanation of 2,2-Dicyanostyrenes under Anodic Oxidation and Their Absorption Spectra

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ABSTRACT

Electrochemical reactions of 2,2-dicyanostyrenes gave regioselectively 1-cyanated products in good yield using tetraethylammonium cyanide (TEAC) as the supporting electrolyte. The reaction proceeded via Michael addition followed by electrolytic oxidation of the adduct at the anode. 2,2-Dicyano- and 1,2,2-tricyanostyrenes showed a novel halochromism induced by the acid–base equilibrium affected by the concentration of the dyes in solution.

1 INTRODUCTION

1,2,2-Tricyanovinyl aromatic systems have been investigated by several methods from the interests of the dienophile component in Diels–Alder reactions and functional dyes with strong intramolecular charge-transfer chromophores.[1–3] The reaction of N,N-dialkylanilines with tetracyanoethylene (TCNE) gave the corresponding 1,2,2-tricyanovinyl-*N*,*N*-dialkylanilines[4] which are used as dyes for diffusion thermal transfer systems. The

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activated TCNE by aluminium chloride makes possible the tricyanovinylation of various aromatics.[5] Tricyanovinyl chloride also reacts with *N,N*-dialkylanilines to give 1,2,2-tricyanostyrenes.[6] Another process involves the condensation of aldehydes with malononitrile followed by the addition of hydrogen cyanide, and subsequent dehydrogenation by oxidation with *N*-bromosuccinimide.[4]

The spectral properties of 2,2-dicyano and 1,2,2-tricyano aromatics as styryl disperse dyes have been investigated from the interests of their solvatochromic properties.[7-9]

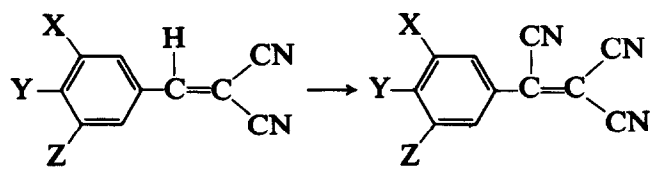
In this paper, an electrochemical one pot synthesis of 1,2,2-tricyanostyrenes is discussed in detail and the spectroscopic characteristics of the compounds are investigated.

2 RESULTS AND DISCUSSION

2.1 Electrochemical reaction of 2,2-dicyanostyrenes

Electrochemical reaction of 2,2-dicyanostyrene **1** gave the 1-cyanated product **2** in good yields using tetraethylammonium cyanide (TEAC) as the supporting electrolyte (Scheme 1). Cyclic voltammetry characteristics of dyes **1a–1e** were determined to elucidate the primary electrode process and to define the intermediate species. In the cases of **1a**, **1b** and **1c**, the electrode process were irreversible and their oxidation potentials were determined as 1·66 V (**1a**), 1·25 V (**1b**), and 0·56 and 1·66 V (**1c**), respectively. In the case of compounds **1d** and **1e**, their oxidation potentials were not detected within the range 0–2 V. The results of the reactions are summarized in Table 1, and the typical cyclic voltammogram of **1a** is shown in Fig. 1.

The electrochemical reaction of **1a** to give **2a** proceeded smoothly in 85% yield at the oxidation potential of **1a** (Run 1), but **2a** was also obtained in



1 **2**

a: X=Z=t-Bu, Y=OH
b: X=Z=H, Y=NMe_2
c: X=OMe, Y=OH, Z=H
d: X=Z=H, Y=OMe
e: X=Z=H, Y=Me

Scheme 1

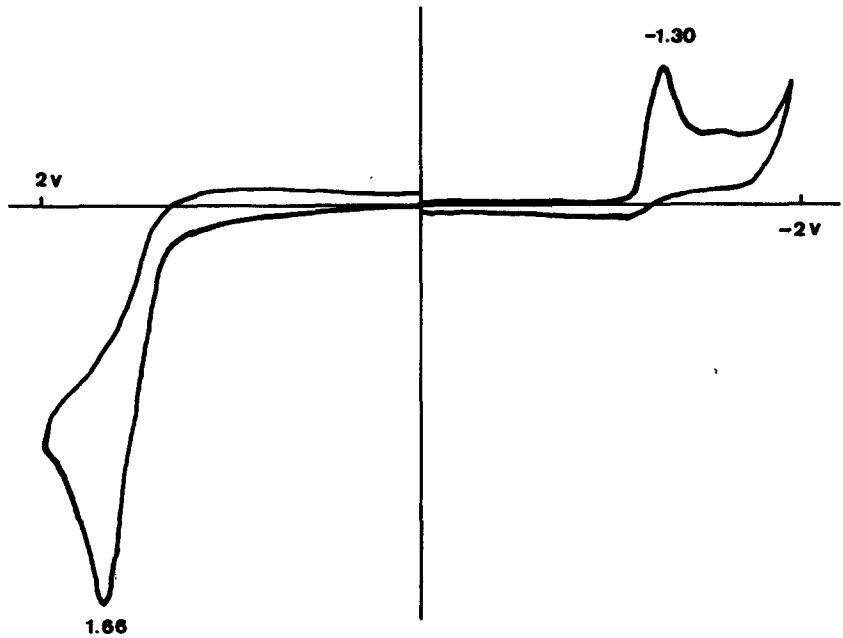
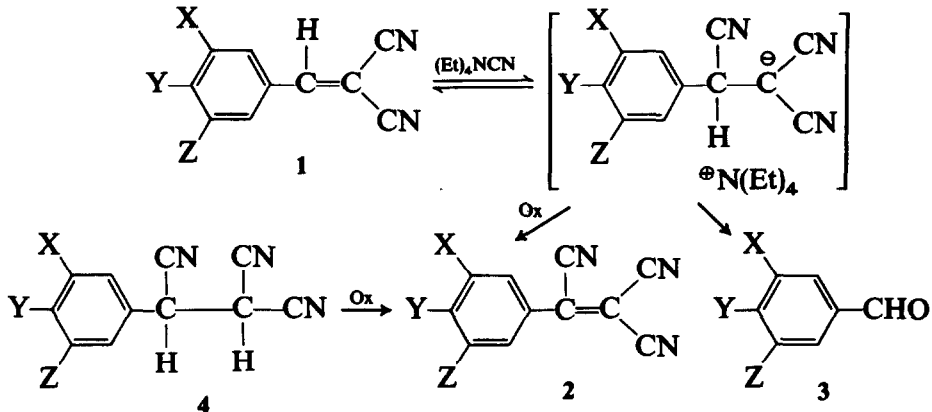


Fig. 1. Cyclic voltammogram of **1a**.

TABLE 1
Electrochemical Reaction of 2,2-Dicyanostyrenes

Run	*Reactant*	*Supporting electrolyte*[a]	*Potential (V)*	*Time (h)*	*Products*	*Yield (%)*	*Reactant recovered (%)*
1	**1a**	TEAC	1·66	0·5	**2a**	85	
2	**1a**	TEAC	0·5[b]	1·5	**2a**	74	
					3	18	
3	**1a**	TEAC	0	0·5	**1a**		88
					2a	8	
4	**1a**	TEAC	0	47	**1a**		22
					2a	68	
5[c]	**1a**	TEAC	0	23	**1a**		80
					2a	6	
6	**1a**	TEAB	1·66[b]	1·5	**1a**		100
7	**1b**	TEAC	1·24[b]	1·0	**2b**	61	
8	**4**	TEAB	0·4	1·5	**2b**	80	
9	**1c**	TEAC	0·5[b]	0·75	**2c**	75	
10	**1d**	TEAC	1·0[b]	1·5	**2d**	56	
11	**1e**	TEAC	1·0[b]	0·5	**2e**	50	

[a] TEAC: tetraethylammonium cyanide. TEAB: tetraethylammonium bromide.
[b] Oxidation potentials were not optimized.
[c] Reaction carried out under nitrogen atmosphere.



Scheme 2

74% yield even when the potential was lower than that of **1a** (Run 2). These facts indicate that the reaction does not proceed at the oxidation potential of the reactant. Furthermore, a formyl derivative (**3**) was obtained by oxidative cleavage of the vinyl bond under prolonged reaction conditions (Run 2). The yields of **2a** increased with the reaction time under atmospheric conditions at zero potential (Run 3 and 4). An oxidizing agent is required in this cyanation, because the reaction hardly proceeded under nitrogen atmosphere, and large amounts of **1a** was recovered (Run 5).

On the other hand, Compound **4**, 4-(1,2,2-tricyanoethyl)-*N*,*N*-dimethylaniline, gave **2b** in good yield at constant potential (0·4 V) even when tetraethylammonium bromide (TEAB) was used as an electrolyte (Run 8). The reactions of **1d** and **1e** at a constant potential (1·0 V) gave the corresponding **2d** and **2e**, respectively (Run 10 and 11).

This reaction proceeds by Michael addition of the electrolyte to **1** followed by anodic oxidation of the adduct to give the product **2** as shown in Scheme 2. Although this mechanism is the same as that when *N*-bromosuccinimide is used as an oxidizing agent, this new method has the advantage of a one pot process, excluding the isolation of Michael adducts. Furthermore, it is not necessary to employ an oxidizing agent and the 1-cyanations of **1d** and **1e** were also achieved in reasonable yields. They could not be synthesized by the direct tricyanovinylation using TCNE.

2.2 Spectroscopic properties

Solvent effects of the dyes are summarized in Table 2. The hydroxy dyes **1** and **2** showed remarkable solvatochromism. Dyes **1a**, **1c**, **2a** and **2c** showed one absorption maximum in chloroform but two absorption peaks in dimethylformamide, and both peaks were observed in ethanol. The λ_{max} of

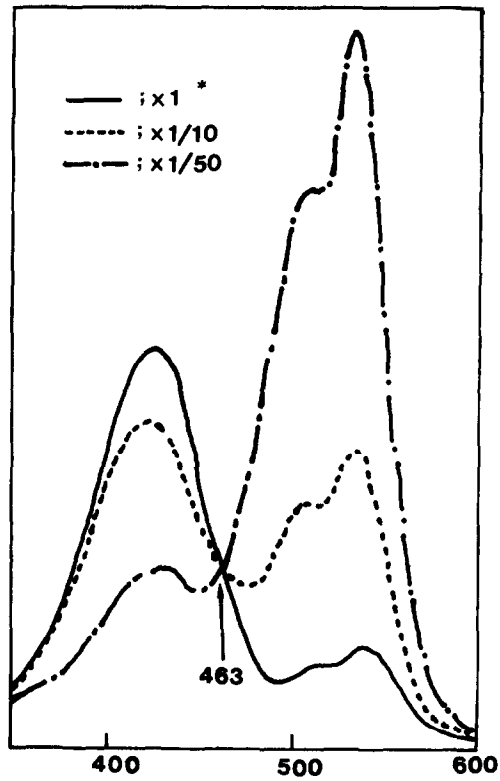
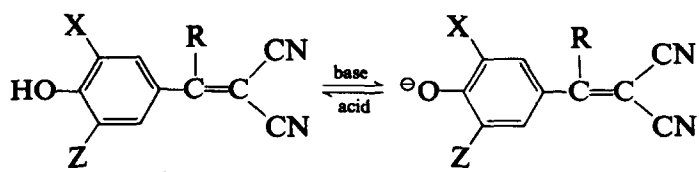


Fig. 2. Spectral changes depending on the concentration of **2a** in ethanol. *About 10^{-4} mol/l.

the dyes thus changed significantly depending on the basicity of the solvent. An isosbestic point was observed at 463 nm for **2a** depending on changes in the ratio of mixed solvents. In addition, the λ_{max} was shifted to a shorter wavelength in acidic medium and to longer wavelength region in basic medium. The acid–base equilibrium of the hydroxy dyes is shown in Scheme 3. Additionally, changes in the concentration of dye **2a** showed also an isosbestic point in ethanol (Fig. 2). Thus, the absorbance at longer wavelength increases with a decrease of dye concentration. On the other



R(H, CN)
1, 2

Scheme 3

TABLE 2
Solvent Effects on λ_{max} (nm) of the Dyes

Dye no.	*$CHCl_3$* (*nm*)	*EtOH* (*nm*)	*DMF* (*nm*)
1a	359	362, 440[s], 461	444[s], 464
1b	432	428	437
1c	372	373, 465	432[s], 465
1d	352	346	352
1e	325	315	328
2a	422	427, 506, 532	506, 532
2b	518	514	507, 533
2c	438	441, 535	505[s], 530
2d	407	401	400
4e	369	356	359

[s] Shoulder.

hand, dyes **1b**, **1d**, **1e**, **2b**, **2d** and **2e** did not show any remarkable change of λ_{max} in ethanol.

Thus, it was found that the hydroxy dyes gave an acid–base equilibrium with changes of concentration of the dye in ethanol and showed remarkable halochromism. The absorption maximum were in accord with PPP-MO calculations and the large color changes from yellow to red were due to the chromophoric system having strong intramolecular charge-transfer character.

3 EXPERIMENTAL

2,2-Dicyanostyrenes were prepared by condensation of aldehydes with malononitrile, and were purified by chromatography over silica gel followed by recrystallization. 4-(1,2,2-Tricyanoethyl)-*N*,*N*-dimethylaniline (**4**) was prepared by the method described in the literature.[4] Acetonitrile was commercial grade and TEAC was prepared by the reported method.[10] Absorption spectra were measured using a Hitachi 200-20 spectrophotometer. Structural characterisations were identified with a JOEL JMS-302 (Mass) and JNM-FX60Q (NMR). Elemental analyses were recorded with a Yanaco CHN recorder MT-2.

3.1 Apparatus for electroanalytical studies

The cell used for cyclic voltammetry (Yanaco VMA-010) consisted of the working electrode, an auxiliary electrode of platinum wire and the reference

electrode of silver and silver chloride in one compartment. Acetonitrile solution (0·01 M) as reactant and tetrabutylammonium perchlorate as electrolyte were used.

3.2 Apparatus for synthesis

A cell of three compartments separated with sintered glass was used. The anode and cathode were constructed of platinum plate (1 cm × 1 cm) and the reference electrode consisted of silver and silver chloride. Constant electrode potential was maintained by using a Hokuto Denko HA301.

3.3 Cyanation under anodic oxidation

The general method was as follows. A solution of 0·28 g (0·001 mol) 2,6-di-tert-butyl-4-(2,2-dicyanovinyl)phenol (**1a**) and 0·78 g (0·005 mol) tetraethylammonium cyanide in 30 ml of acetonitrile was reacted in the cell at 1·66 V anode potential for 30 min. The acetonitrile was removed under vacuum and the resulting crude product was diluted with 100 ml of water, maintaining pH 4–5 with acetic acid. The liquor was extracted twice with 50 ml of chloroform and the combined chloroform layers were dried with anhydrous sodium sulfate. The filtrate was evaporated and chromatographed using chloroform. 2,6-Di-tert-butyl-4-(1,2,2-tricyanovinyl)phenol (**2a**) was obtained in 85·4% yield.

3.4 Characterization and identification of products

Compounds **1a**–**1e** were prepared by condensation of the appropriate aldehyde with malononitrile. Compounds **2b**,[4] **2d**[1] and **2e**[5] are known compounds. NMR spectra were measured in $CDCl_3$ using tetramethylsilane as an internal standard. The characteristics of dyes are as follows.

1a: MP, 136–138°C; PMR, $\delta = 1{\cdot}47$ (18H, s), 6·06 (1H, s), 7·65 (1H, s), 7·80 (2H, s).

1b: MP, 182–184°C; PMR, $\delta = 3{\cdot}14$ (6H, s), 6·68 (2H, d, J = 9·6 Hz), 7·43 (1H, s), 7·70 (2H, d, J = 9·6 Hz).

1c: MP, 117–119°C; PMR, $\delta = 3{\cdot}98$ (3H, s), 6·35 (1H, s), 7·00 (1H, d, J = 8·0 Hz), 7·24 (1H, s), 7·60 (1H, d, J = 8·0 Hz), 7·70 (1H, s).

1d: MP, 116–118°C; PMR, $\delta = 3{\cdot}91$ (3H, s), 7·00 (2H, d, J = 9·0 Hz), 7·64 (1H, s), 7·91 (2H, d, J = 9·0 Hz).

1e: MP, 137–139°C; PMR, $\delta = 2{\cdot}45$ (3H, s), 7·32 (2H, d, J = 8·4 Hz), 7·71 (1H, s), 7·81 (2H, d, J = 8·4 Hz).

2,6-Di-tert-butyl-4-(1,2,2-tricyanovinyl)phenol (**2a**)
MP, 149–150°C; PMR, $\delta = 1{\cdot}48$ (18H, s), 6·27 (1H, s), 7·98 (2H, s).

4-(1,2,2-Tricyanovinyl)-*N*,*N*-dimethylaniline (**2b**)
MP, 176–178°C; PMR ($CDCl_3$), $\delta = 3{\cdot}21$ (6H, s), 6·73 (2H, d, J = 9·6 Hz), 8·07 (2H, d, J = 9·6 Hz).

2-Methoxy-4-(1,2,2-tricyanovinyl)phenol (**2c**)
MP, 211–212°C; MS, 225 (M^+); PMR, $\delta = 4{\cdot}01$ (3H, s), 5·85 (1H, s), 7·10 (1H, d, J = 8·9 Hz), 7·70 (1H, s), 7·71 (1H, d, J = 8·9 Hz). Found: C, 63·25; H, 3·00; N, 17·95. $C_{12}H_7N_3O_2$ requires: C, 64·00; H, 3·13; N, 18·66%.

4-(1,2,2-Tricyanovinyl)anisole (**2d**)
MP, 113–115°C; MS, 209 (M^+); PMR, $\delta = 3{\cdot}95$ (3H, s), 7·07 (2H, d, J = 9·6 Hz), 8·10 (2H, d, J = 9·6 Hz). Found: C, 68·89; H, 2·97; N, 19·74. $C_{12}H_7N_3O$ requires: C, 68·90; H, 3·37; N, 20·09%.

4-(1,2,2-Tricyanovinyl)toluene (**2e**)
MP, 117–119°C; MS, 193 (M^+); PMR, $\delta = 2{\cdot}51$ (3H, s), 7·42 (2H, d, J = 8·1 Hz), 7·95 (2H, d, J = 8·1 Hz). Found: C, 74·95; H, 3·35; N, 21·85. $C_{12}H_7N_3$ requires: C, 74·60; H, 3·65; N, 21·75%.

4-(1,2,2-Tricyanoethyl)-*N*,*N*-dimethylaniline (**4**)
MP, 135–137°C; MS, 224 (M^+), 159 ($M^+ - 65$); PMR, $\delta = 3{\cdot}00$ (6H, s), 4·20 (1H, d, J = 13·7 Hz), 4·30 (1H, d, J = 13·7 Hz), 6·72 (2H, d, J = 8·4 Hz), 7·31 (2H, d, J = 8·4 Hz).

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