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An improved method for tricyanovinilation of aromatic amines under ultrasound irradiation

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ABSTRACT

A synthetic method for tricyanovinylation under ultrasound irradiation has been developed for preparation of tricyanovinyl aromatic amines. The method is reliable and can be applied to the synthesis of a variety of tricyanovinyl compounds, with high yields, purity and with short reaction times.

1. Introduction

The chemical applications of ultrasound, “sonochemistry”, have become an exciting new field of research in the past decade. The use of ultrasound in chemistry offers a convenient method of chemical activation which has broad applications and uses equipment which is relatively inexpensive. The advantages of ultrasonic irradiation include not only improving classical reactions, shortening reaction times, increasing yields, and suppressing by-product formation compared with conventional thermal heating but also ultrasound may offer cleaner reactions by improving selectivity, enhancing product recovery and purification processes [1,2]. It is widely used to improve traditional reactions which use expensive reagents, strongly acidic conditions, long reaction times, high temperatures and which are incompatible with other functional groups. Sonication allows the use of non-activated and crude reagents as well as an aqueous solvent system; therefore it is friendly and non-toxic [3].

The 4-tricyanovinylarylamines are a class of dyes used to colour synthetic polymer fibres [4], but their special optical and electrical properties also make them of considerable interest in applications in the field of nonlinear optics [5], in diode lasers in optical recording [6] to monitor polymerization reactions [7] and in the fabrication of hybrid organic–inorganic solar cells [8–10]. They act as cytotoxic agents against tumours [11], as X-ray protective agents [12] and as photostabilizers in plastics against UV radiation [13]. Electronic excitation on these compounds induces an initial intramolecular charge transfer (ICT) state with partial electron transfer, generally followed by molecular twisting to give a complete electron transfer in a twisted ICT (TICT) state, in which the donor orbital is perpendicular to the acceptor orbital. Depending on the molecule’s structure, both ICT and TICT states can be radiative, especially in fluid polar media [14]. Because these flexible fluorescent dye molecules are proven to be sensitive to both the local viscosity (rigidity) and local polarity, they provide a suitable means to study the relaxation processes in low density polyethylene films [15].

The reaction of tetracyanoethylene with secondary and tertiary aromatic amines in which hydrogen is bonded to the annular carbon in the 4-position and heterocyclic aromatic amines in which the ring is resonance stabilized, takes place via a condensation to give 4-tricyanovinylanilines or tricyanovinyl-substituted heterocyclic aromatic amines and hydrogen cyanide. The 4-tricyanovinylanilines absorb visible light very strongly and comprise a class of brilliant red and blue dyes [16].

Various methods to prepare tricyanovinylaryl compounds have been reported. These include condensations: the condensation of tetracyanoethylene with arylamines or phenols, carried in dry tetrahydrofuran, at boiling temperatures for between 0.5 and 18 h gives low to good yields [16]; good or excellent yields were obtained from the condensation in dimethylformamide at 50–90 °C [4,17–19]. Another method involves the tricyanovinylation of

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thiazoles and thiophenes carried in DMF for 12 h at room temperature, after refluxing for 1 h [20]. Two other widely used synthetic routes use stepwise conversions starting from arylaldehydes where the aldehydes are first converted to dicyanovinyl compounds via condensation with malonodinitrile, then to tricyanovinyl by nucleophilic substitution of dicyanovinyl with sodium cyanide, followed by oxidation with lead tetraacetate [21] or by lithiation followed by quenching with tetracyanoethylene [22,23].

We describe here a simple and convenient procedure to synthesize 4-tricyanovinylanilines and 5-tricyanovinyl-2-aminothiazoles by reaction of tetracyanoethylene with aromatic amines under mild conditions, generally at room or higher temperature and atmospheric pressure, using ultrasonic irradiation.

2. Experimental

All products were characterized and/or compared with reported data. Melting points were obtained on a Kofler apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra of the previously unreported compounds were recorded on a Bruker Avance DRX 600 MHz spectrometer in $CDCl_3$ as solvent. Mass spectra were obtained on a LC-HP1100 apparatus in methanol-water (3:1) as solvent. The experiments were performed in the positive ion mode. Visible absorption spectra were recorded on Unicam UV 500 (1×10^{-5} mol/l). The reactions were carried out in a Diamondback-UD50SH ultrasonic bath operating at frequency of 40 kHz, acoustic power 50 W, capacity 2 l, heating temperature up to 70 °C. The progress of the reactions was monitored by TLC (Merck F 254 silica gel; dichloromethane: n-heptane, 9:1). Starting compounds **1a**–**1e**, **1h**–**1k**, **1l**–**1p** are commercial products from Sigma–Aldrich. Tetracyanoethylene is a commercial product from TCI Europe. Compounds **1f**, **1g**, **1l**, **1q**, **2a** and **2b** were synthesized according to known procedures [24–30]. All of the solvents are also commercial products from Sigma–Aldrich and are used without further purification. Analytical samples of the reaction products were obtained by recrystallization from ethanol.

2.1. General procedure for tricyanovynilation of N,N-dialkylanilines and 2-aminosubstituted 4-phenylthiazoles by a sonochemical method

Caution! Because hydrogen cyanide is formed in this reaction, all operations up to the recrystallization of the product should be carried out in a good hood. Skin contact with tetracyanoethylene should be avoided.

Tetracyanoethylene (0.004 mol) and the corresponding N-alkyl or *N*,*N*-dialkylaniline or 2-aminothiazole (0.004 mol; for compound **2c** 0.002 mol) were dissolved in 2 ml *N*,*N*-dimethylformamide in a 25 ml Erlenmeyer flask. The reaction mixture was sonicated at a frequency of 40 kHz at room temperature or 60 °C for a time between 5 and 20 min (see Table 1). The mixture was poured into water (100 ml) and isolated by filtration. Compound **3q** was isolated as oil after addition of Et_2O. The oil was dissolved in methanol and a concentrated water solution of $NaClO_4$ was added to obtain the product as dark red solid.

2.1.1. 2-{4-[Methyl(phenethyl)amino]phenyl} ethene-1,1,2-tricarbonitrile (**3f**)

M.p.:116–118. ^{1}H-NMR (δ ppm): 2.87 t (2H, CH_2); 2.96 s (3H, CH_3); 3.69 t (2H, NCH_2); 6.65 d (2H, ArH); 7.10 d (2H, ArH); 7.19 t (2H, ArH); 7.24–7.26 m (3H, ArH). ^{13}C-NMR (δ ppm): 154.10, 148.11, 137.73, 137.46, 133.04, 128.99, 128.96, 128.92, 128.91, 128.75, 127.08, 117.56, 114.48, 114.03, 113.74, 112.26, 77.79, 54.70, 39.38, 33.59. MS (API-ES) *m*/*z*: 313 $[M+H]^+$. For $C_{20}H_{16}N_4$ (312.37) calcd: C, 76.90; H, 5.16; N, 17.94; found: C, 76.79; H, 5.16; N, 18.05.

2.1.2. 2-[4-(Diethylamino)-2-methoxyphenyl] ethene-1,1,2-tricarbonitrile (**3g**)

M.p.: 138–142. ^{1}H-NMR (δ ppm): 1.19 t (6H, $NCH_2\underline{CH_3}$); 3.42 q (4H, $N\underline{CH_2}CH_3$); 3.88 s (3H, OCH_3); 5.99 d (1H, ArH), 6.30 dd (1H, ArH); 7.55 d (1H, ArH). ^{13}C-NMR (δ ppm): 161.35, 154.65, 135.53, 133.65, 128.40, 118.73, 114.90, 113.96, 113.56, 108.41, 106.07, 98.33, 93.44, 55.03, 45.53, 12.60. MS (API-ES) *m*/*z*: 281 $[M+H]^+$. For $C_{16}H_{16}N_4O$ (280.32) calcd: C, 68.55; H, 5.75; N, 19.99; O, 5.71; found: C, 68.44; H, 5.90; N, 14.99; O, 13.71.

2.1.3. 2-{Benzyl[4-(1,2,2-tricyanovinyl)phenyl]amino}-N,N, N-trimethylethanaminium perchlorate (**3q**)

M.p.: 138–140. ^{1}H-NMR (δ ppm): 3.13 s (9H, $N(CH_3)_3$; 3.50–3.54 m (2H, CH_2); 3.74 t (2H, CH_2); 4.49 s (2H, CH_2); 6.89–6.93 m (2H, ArH); 7.29–7.39 (7H, ArH). ^{13}C-NMR (δ ppm): 148.66, 147.32, 138.82, 138.61, 137.92, 137.80, 129.06, 128.90, 127.73, 127.66, 127.03, 122.70, 118.25, 117.30, 112,63, 110.80, 91.81, 61.33, 59.54, 55.29, 54.61, 51.50, 48.13. MS (API-ES) *m*/*z*: 470 $[M+H]^+$. For $C_{23}H_{24}ClN_5O_4$ (469.92) calcd: C, 58.79; H, 5.15; N, 14.90; O, 13.62; found: C, 58.60; H, 5.20; N, 14.99; O, 13.71.

2.1.4. 2,2′-[2,2′-(piperazine-1,4-diyl)bis(4-phenylthiazole-5,2-diyl)] diethene-1,1,2-tricarbonitrile (**4b**)

M.p.: 220–222. ^{1}H-NMR (δ ppm): 3.72 s (4H, CH_2NCH_2); 3.93 s (4H, CH_2NCH_2); 7.19 s (2H, ArH); 7.24 t (1H, ArH); 7.33 t (2H, ArH); 7.44–7.48 m (4H, ArH); 7.53 t (1H, ArH). ^{13}C-NMR (δ ppm): 159.02, 158.72, 153.03, 152.81, 146.90, 146.01, 133.88, 133.45, 132.06, 130.45, 130.36, 130.31, 129.15, 129.10, 128.93, 128.88, 128.68, 128.24, 128.19, 126.28, 126.14, 112.09, 104.21, 102.73, 102.28, 60.51, 60.48, 50.92, 47.99, 47.82, 47.49, 47.27. MS (API-ES) *m*/*z*: 607 $[M+H]^+$. For $C_{32}H_{18}N_{10}S_2$ (606.68) calcd: C, 63.35; H, 2.99; N, 23.09; S, 10.57; found: C, 63.42; H, 2.95; N, 22.98; S, 10.55.

3. Results and discussion

The tricyanovinylation reaction of aromatic amines with tetracyanoethylene is a typical termal reaction involving the formation of charge-transfer (CT) complex. The reaction proceeds in two steps: formation of an accumulating intermediate, and slow formation of the final product. Rappoport [31] studied systematically the tetracyanovinylation reactions of *N*,*N*-dimethylaniline and *N*-methylaniline with tetracyanoethylene for the first time and found that the complex formed between reactants gradually disappears to form the intermediate zwitterionic σ-complex and thereafter the final tricyanovinyl compound is slowly produced.

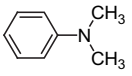
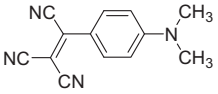
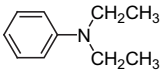
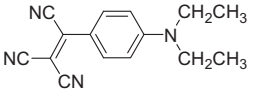
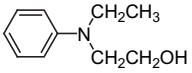
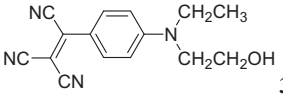
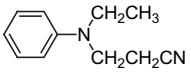
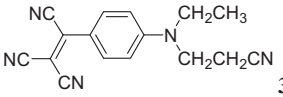
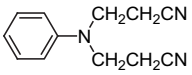
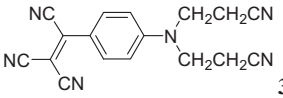
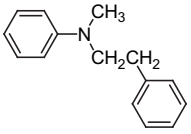
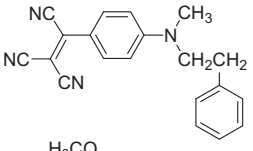
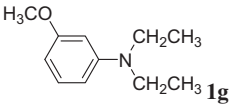
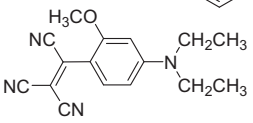
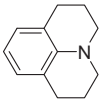
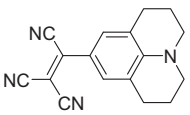
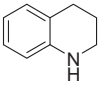
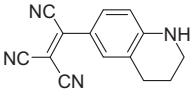
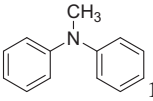
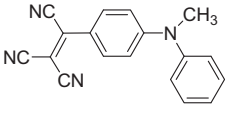
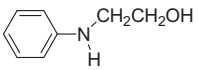
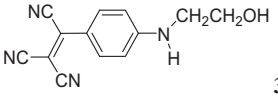
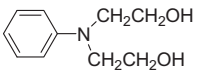
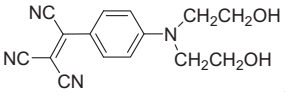
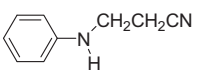
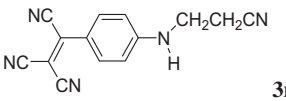
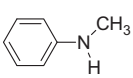
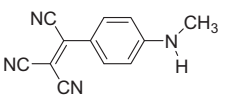
There is another proposed mechanism for this reaction where the zwitterionic σ-complex produce neutral intermediate by deprotonation from another donor molecule followed by back proton transfer from the quarternary amine to carbanion resulting from the zwitterionic complex [32].

A variety of *N*-alkyl-, *N*,*N*-dialkylanilines **1a**–**1q** and two 2-aminosubstituted 4-phenylthiazoles **2a**, **2b** were coupled with tetracyanoethylene for the first time under ultrasonic irradiation to form the corresponding 4-tricyanovynylarylamines **3a**–**3q** and 5-tricyanovynil thiazoles **4a**, **4b** according to Scheme 1.

We tried a variety of solvents, including THF, chloroform, dichloromethane, acetic acid, ethanol and others, but the best results were obtained in *N*, *N*-dimethylformamide. The reactions were carried for 5 to 20 min, at room temperature (20–25 °C) for compounds **3a**–**3d**, **3f**, **3g**, **3k**–**3q**, **4b**, and at 60 °C for compounds **3e**, **3h**–**3j**, and **4a**. In general, the desired products were isolated in good to excellent yields (Table 1).

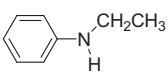
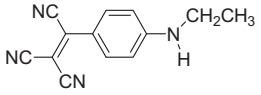
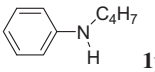
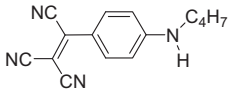
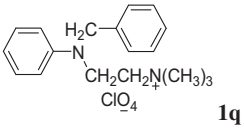
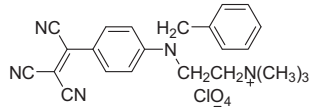
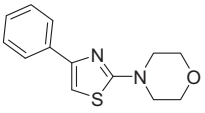
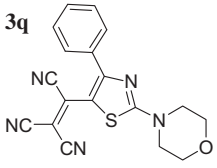
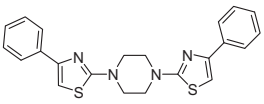
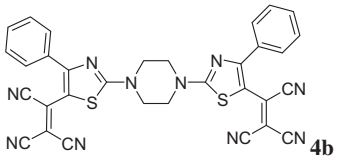
Initially we studied the reaction progress by conventional conditions for compounds **3b**, **3k** and **4a** – without using of

Table 1
Sonication times, reaction temperature, starting compounds (**1a**–**1q**, **2a**, **2b**), products (**3a**–**3q**, **4a**, **4b**) and yields (%).

Sonication time [min]	Temperature [°C]	Starting compound	Product structure	Yield %/Lit[a]
5	r.t.		 **3a**	99/83 [21]
5	r.t.		 **3b**	91/80 [21]/51[c]
10	r.t.		 **3c**	90/66 [33]
15	r.t.		 **3d**	73/63 [21]
20	60		 **3e**	82/50 [21]
10	r.t.		 **3f**	99
10	r.t.	 **1g**	 **3g**	79
15	60	 **1h**	 **3h**	70/59 [21]
10	60	 **1i**	 **3i**	88/37 [21]
15	60	 **1j**	 **3j**	77/65 [21]
5	r.t.	 **1k**	 **3k**	82/47 [21]/35[c]
5	r.t.	 **1l**	 **3l**	92/63 [34]
15	r.t.	 **1m**	 **3m**	71/35 [16]
5	r.t.	 **1n**	 **3n**	82/70 [21]

(*continued on next page*)

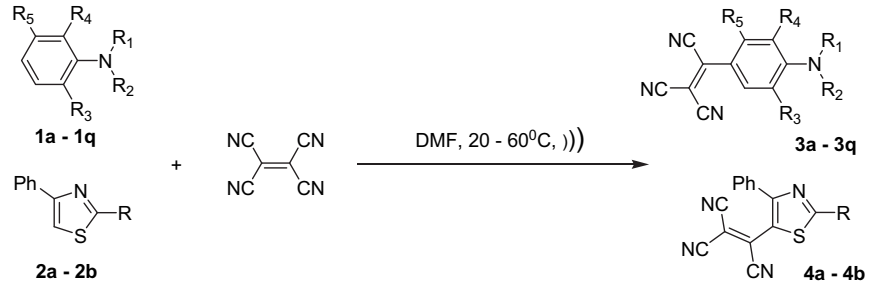
Table 1 (*continued*)

Sonication time [min]	Temperature [°C]	Starting compound	Product structure	Yield %/Lit[a]
10	r.t.	 **1o**	 **3o**	70/[b] [35]
15	r.t.	 **1p**	 **3p**	78/42 [21]
10	r.t.	 **1q**	 **3q**	40
20	60	 **2a**	 **4a**	89/22 [20]/7[c]
10	r.t.	 **2b**	 **4b**	82

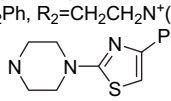
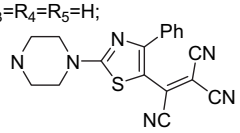
[a] Literature data.
[b] No yield reported.
[c] Blank reaction: same reaction conditions with stirring, without ultrasound irradiation.

ultrasound (see Table 1, note c). The desire product was isolated with significantly lower yield in comparison with the same reaction carried out by sonication (Table 1).

A number of the compounds have not been previously reported, specifically **3f**, **3g**, **3q** and **4b**. These were fully characterized by ^{1}H-NMR, ^{13}C-NMR, mass spectra and by elemental analyses. The longest wavelength absorption maxima of the structures are in the region 484–520 nm. The corresponding molar absorptivities are in the range 27 900–85 900 l mol^{-1} cm^{-1}. The absorption spectra of the new chromophores are characterized by an intense, low energy band. The most bathochromic shift was observed for 3-methoxy-*N*,*N*-diethyl derivative dye **3g**. Dye **3q**, which contains a positive charge, showed the highest molar absorptivity compared to the other dyes. Table 2 summarizes the visible absorption spectral data for the four new dyes measured in methanol.



1a, 3a: R_1=R_2=CH_3, R_3,R_4, R_5=H; **1b, 3b:** R_1=R_2=C_2H_5, R_3=R_4=R_5=H; **1c, 3c:** R_1=CH_3, R_2=C_2H_4OH, R_3=R_4=R_5=H; **1d, 3d:** R_1=C_2H_5, R_2=C_2H_4CN, R_3=R_4=R_5=H; **1e, 3e:** R_1=R_2=C_2H_4CN, R_3=R_4=R_5=H; **1f, 3f:** R_1=CH_3, R_2=CH_2CH_2Ph, R_3=R_4=R_5=H; **1g, 3g:** R_1=R_2=C_2H_5, R_3=R_4=H, R_5=OCH_3; **1h, 3h:** R_1,R_4 and R_2, R_3=$CH_2CH_2CH_2$, R_5=H; **1i, 3i:** R_1=H, R_2,R_3=$CH_2CH_2CH_2$, R_4=R_5=H; **1j, 3j:** R_1=CH_3, R_2=Ph, R_3=R_4=R_5=H; **1k, 3k:** R_1=C_2H_4OH, R_2=R_3=R_4=R_5=H; **1l,3l:** R_1=R_2=C_2H_4OH, R_3=R_4=R_5=H; **1m, 3m:** R_1=C_2H_4CN, R_2=R_3=R_4=R_5=H; **1n, 3n:** R_1=CH_3, R_2=R_3=R_4=R_5=H; **1o, 3o:** R_1=C_2H_5, R_2=R_3=R_4=R_5=H; **1p, 3p:** R_1=C_4H_7, R_2=R_3=R_4=R_5=H; **1q, 3q:** R_1=CH_2Ph, R_2=$CH_2CH_2N^+(CH_3)_3$, R_3=R_4=R_5=H;

2a, 4a: R=  ; **2b:** R=  ; **4b:** R= 

Scheme 1.

Table 2
Absorption maxima and molar absorptivities for compounds **3a**–**3q** and **4a**, **4b**.

Compound	λ_{max} [nm]	ϵ [l mol^{-1} cm^{-1}][a]
3a	514	41,500 [21]
3b	521	46,500 [21]
3c	518	44,000 [7]
3d	507	42,300[21]
3e	488	37,200 [21]
3f	517	47,800
3g	520	79,000
3h	555	47,200 [21]
3i	519	43,800 [21]
3j	509	40,900 [21]
3k	503	32,600 [21]
3l	515	38,400[b] [29]
3m	487	32,900 [21]
3n	498	41,400 [21]
3o	504	41,400[b] [30]
3p	504	44,000 [21]
3q	484	85,900
4a	504	23,000 [20]
4b	502	27,900

[a] Reported data.
[b] No molar absorptivities reported, measured by us.

4. Conclusion

In summary we developed an effective and reliable method for tricyanovinylation of a variety of *N*-alkyl-, *N*,*N*-dialkylanilines and 2-aminosubstituted-4-phenylthiazoles under ultrasound irradiation. The reaction is completed in very short times (5–20 min) and provides higher yields (from 10 to 67%) and purer products than the previously known procedures.

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