Copper(I)-Promoted Regioselective α-Tricyanoethenylation of *N*-Methylpyrroles

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Received 11 April 2008; revised 30 April 2008

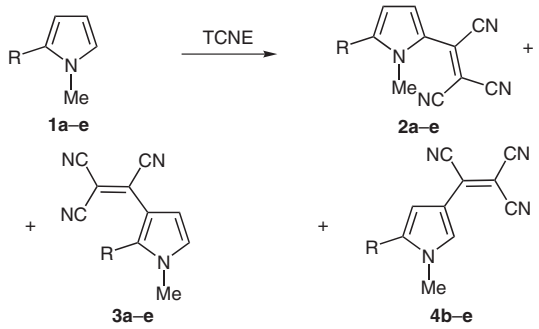
Abstract: The reaction of *N*-methylpyrroles with tetracyanoethylene (TCNE) has been studied in various solvents (DMSO, acetone, THF). A highly efficient protocol for the copper(I)-promoted regioselective α-tricyanoethenylation of *N*-methylpyrroles has been developed.

Key words: *N*-methylpyrroles, TCNE, tricyanoethenylation, copper(I) bromide, regioselectivity

Conjugated organic molecules containing simultaneously donor and acceptor moieties are important components of many electronic devices including nonlinear optical (NLO), photoelectric, and photo- and electroluminescent.[1] Among these systems, heterocyclic compounds such as pyrrole derivatives bearing electron-withdrawing groups (e.g. tricyanoethenyl) are considered to be especially promising.[2] Due to the strong solvatochromic properties caused by the donating–withdrawing interaction, these materials can be used as model compounds for the design of dyes possessing pronounced NLO characteristics, which are used for the preparation of novel materials with special electrooptical features such as frequency doubling or wave mixing.[3]

Tricyanoethenyl derivatives of NH-pyrroles show photosensitive effects and exhibit electroconductivity.[4] The substitution of hydrogen atom in the NH-pyrrole group for other substituents can dramatically change the properties of the compounds obtained, which is explained, firstly, by the absence of a hydrogen bond affecting the electronic and spatial structure of the molecules.

At the same time, substitution on the nitrogen atom of the pyrrole ring frequently influences the regioselectivity of tricyanoethenylation. For example, tricyanoethenylation of 1-propyl-2-(2-thienyl)-1*H*-pyrrole with tetracyanoethylene (TCNE) furnishes three compounds, 3-, 4-, and 5-(tricyanoethenyl)pyrroles, the former predominates.[2] It has been reported that selective tricyanoethenylation of *N*-methylpyrrole with TCNE in acetone proceeds through position 2 of the pyrrole ring.[5] However, as shown here, this reaction leads to a mixture of 2- and 3-(tricyanoethenyl)pyrroles, where the latter prevail.



R = H (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 4-ClC_6H_4 (**e**)

Scheme 1

The aim of this work is to investigate the reaction of *N*-methylpyrroles with TCNE as well as to develop a method for the selective introduction of the tricyanoethenyl moiety into the *N*-methylpyrrole ring.

Our experiments have shown that 1-methyl-1*H*-pyrrole (**1a**) reacts with TCNE in acetone and tetrahydrofuran (r.t., 1 h) to afford a mixture of 2- and 3-isomers **2a/3a** (ratio 30:70 in acetone, 17:83 in THF) (Scheme 1). However, in dimethyl sulfoxide the 2-isomer **2a** predominates, its content in the reaction mixture is 85% (Table 1).

Under analogous condition 2-aryl-*N*-methylpyrroles **1b–e** and pyrrole **1a** react with TCNE nonselectively to deliver mixtures of 5-, 3- and 4-(tricyanoethenyl)pyrroles (**2b–e**, **3b–e**, and **4b–e**, respectively) (Scheme 1).

As can be seen from Table 1, the ratio of the tricyanoethenylation products depends on the solvent. In dimethyl sulfoxide, tricyanoethenylation of the pyrroles **1b–e** occurs mainly at positions 3 and 5 of the pyrrole nucleus to give 3- and 5-(tricyanoethenyl)pyrroles **3b–e** and **2b–e**, respectively. These compounds were separated by column chromatography and characterized.

4-(Tricyanoethenyl)pyrroles **4b–e** were formed in minor quantities and characterized only by NMR techniques. During the reaction of pyrroles **1b–e** with TCNE in tetrahydrofuran, the relative amount of 4-(tricyanoethenyl)pyrroles **4b–e** increases, while the content of 5-(tricyanoethenyl)pyrroles **2b–e** decreases. Noteworthy is that in this solvent under analogous conditions the tricyanoethenylation occurs slower than in dimethyl sulfoxide and is accompanied by a strong resinification making isolation of the reaction products difficult.

SYNTHESIS 2008, No. 16, pp 2631–2635
Advanced online publication: 17.07.2008
DOI: 10.1055/s-2008-1067178; Art ID: Z08708SS

Table 1 ^{1}H NMR Monitoring of the Reaction of Pyrroles **1a–e** with TCNE (r.t., 1 h)

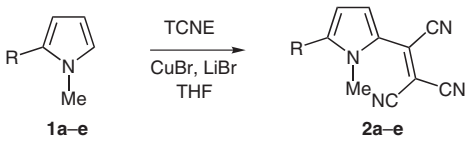
Entry	Pyrrole	Solvent	Product mix (%)			
			1	**2**	**3**	**4**
1	**1a**	acetone	0	30	70	–
2	**1a**	DMSO	0	85	15	–
3	**1a**	THF	0	17	83	–
4	**1b**	acetone	12	29	43	16
5	**1b**	DMSO	0	53	37	10
6	**1b**	THF	28	15	40	16
7	**1c**	DMSO	6	50	37	6
8	**1c**	THF	12	18	57	12
9	**1d**	DMSO	0	39	57	5
10	**1d**	THF	0	12	19	69
11	**1e**	DMSO	0	45	40	15
12	**1e**	THF	37	17	25	22

Thus, tricyanoethenylation of *N*-methylpyrroles represents a nonselective reaction. Particular emphasis is placed upon the unusually high sensitivity of the ratio of isomers to the nature of the solvent. This fact correlates well with a radical ion mechanism for the reaction,[6] i.e. with the formation of strongly and variously solvated radical cation of the pyrrole and radical anion of tetracyanoethylene. Since the solvents used are strong donors, they react primarily with the pyrrole radical cation, not only redistributing the electron density on the pyrrole ring, but also sterically shielding certain positions of the pyrrole ring.

We have assumed that the introduction of additional reducing agent (stronger than pyrrole) to the reaction mixture could prevent the formation of the pyrrole radical cation and, at the same time, retain the conditions for the generation of radical anion TCNE. In this case, one should expect the enhancement of the selectivity in the tricyanoethenylation, since the latter is dictated mainly by the attack of the tricyanoethenyl radical anion (or the product of its decyanation[7]) on the neutral molecule of pyrrole. Salts of copper(I) appear to be such reducing agents. This assumption is in good agreement with the known data that TCNE reacts with transition metal ions in a low valence state to provide the radical anion of TCNE.[7]

Indeed, *N*-methyl-substituted pyrroles react with TCNE in the presence of the tetrahydrofuran-soluble copper(I) bromide/lithium bromide system (LiBr is employed to increase the solubility of CuBr) regioselectively to afford exclusively the tricyanoethenylation products through the α-position of the pyrrole ring, *N*-methyl-5-(tricyanoethenyl)pyrroles **2a–e**, which were isolated in 88–91% yields (Table 2).

Table 2 Tricyanoethenylation Using TCNE with Copper(I) Bromide/Lithium Bromide in Tetrahydrofuran



1a–e **2a–e**

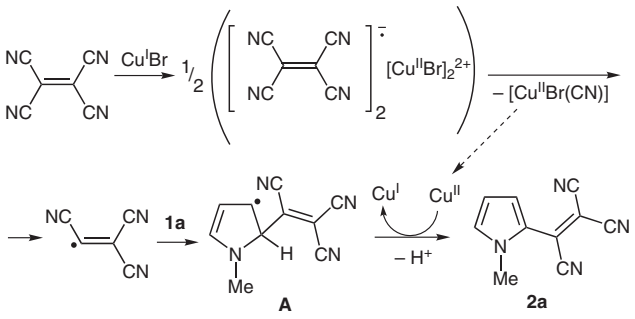
Product	R	Yield (%)
2a	H	91
2b	Ph	89
2c	4-MeC_6H_4	88
2d	4-MeOC_6H_4	91
2e	4-ClC_6H_4	89

To elucidate the reaction mechanism in the presence of the copper(I) bromide/lithium bromide system we carried out ESR studies, taking *N*-methylpyrrole **1a** as an example. It has been found that with the addition of copper(I) bromide and lithium bromide to a solution of TCNE in tetrahydrofuran the mixture turns brown and the ESR spectrum shows an unresolved singlet with a *g* factor of 2.0028 and width of 0.51 mT, the intensity of which increases over 30 minutes. The value of the *g* factor practically corresponds to the *g* factor of radical anion of TCNE, but the signal observed is not amenable to resolution, while its width is significantly lower than the total width of the signal assigned to the radical anion of TCNE.

The effects observed are likely to be interpreted as follows. When it is considered that the appearance of a narrow ESR signal in the system TCNE/CuBr/LiBr/THF is caused by electron transfer from copper(I) to TCNE, then one can conclude that the unresolved signal observed is assigned to the complex of TCNE radical anion with copper(II). The ESR spectrum of the studied system shows no typical signal for divalence copper that can be explained by the formation of the binuclear complex where antiferromagnetic interaction between copper ions can be realized.[8] Addition of the corresponding amount of *N*-methylpyrrole **1a** to this mixture leads to the rapid disappearance of the ESR signal.

It seems likely that in the reaction mixture exists an equilibrium between the $[TCNE^{-}]_2 \cdot [Cu^{II}Br]_2^{2+}$ complex and the very active tricyanoethenyl sp^2 radical formed due to its decyanation.[7] The addition of *N*-methylpyrrole to the system TCNE/CuBr/LiBr/THF involves the selective attack of this radical at the α-position of the pyrrole ring to furnish the more stable radical intermediate **A** (unlike the attack at the β-position). Then the hydrogen radical is cleaved from the α-position of the pyrrole ring to give pyrrole **2a** and reduce copper(II) to copper(I) (Scheme 2).

In conclusion, we have described a simple and efficient protocol for the copper(I)-promoted regioselective α-tricyanoethenylation of *N*-methylpyrroles to give *N*-methyl-



Scheme 2

2-(tricyanoethenyl)pyrroles in excellent yields. This represents a useful addition to the growing applications of donor–acceptor systems in preparative organic chemistry and the manufacture of materials for advanced technologies.

IR spectra were measured on a Bruker IFS-25 spectrophotometer (KBr pellets, 400–4000 cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument in $CDCl_3$ using HMDS as an internal standard. The concerted application of ^1H-^1H 2D homonuclear experiments COSY and NOESY and also ^1H-^{13}C 2D heteronuclear experiments HSQC and HMBC were used for the distinction of the carbon and proton resonances in all cases. ESR spectra were recorded on a Radiopan SE/X-2547 spectrometer, equipped with magnetometer and high frequency meter at r.t. in an argon atmosphere.

2-Aryl-1-methyl-1*H*-pyrroles **1a–e** were prepared from 2-aryl-1*H*-pyrroles and MeI via a published procedure.[9]

Reaction of Pyrroles 1a–e with TCNE; General Procedures for Methods A–C

A soln of TCNE (128 mg, 1 mmol) in solvent [DMSO (method A), THF (method B), acetone (method C)] (2 mL) was added to a soln of pyrrole **1a–e** (1 mmol) in the corresponding solvent (3 mL) at r.t. The mixture was stirred for 1 h and then it was diluted with brine (50 mL), extracted with CH_2Cl_2 (5 × 20 mL), and the extract dried ($MgSO_4$). The residue after removing the solvent was analyzed (^1H, ^{13}C NMR) and purified by column chromatography (silica gel, Et_2O–hexane, 1:1) to give pure products **2a–e** and **3a–e**. Compounds **4b–e** were found in the reaction mixture and identified only by their NMR spectra. Their spectral characteristics are given below.

Selective Synthesis of Pyrroles 2a–e; General Procedure for Method D

CuBr (144 mg, 1 mmol) and LiBr (174 mg, 2 mmol) were added to a soln of TCNE (128 mg, 1 mmol) in THF (17 mL) and the resulting mixture was stirred until homogeneous (10 min). Then the soln was added to a soln of pyrrole **1a–e** (1 mmol) in THF (2 mL). The mixture was stirred for 1 h and then diluted with brine (100 mL). The precipitated residue was filtered off, dried, and washed with CH_2Cl_2 (40 mL). The solvent was removed under reduced pressure and residue was purified by flash chromatography (silica gel, CH_2Cl_2) to afford pure pyrroles **2a–e**.

1-Methyl-2-(tricyanoethenyl)-1*H*-pyrrole (2a)

Yield: 166 mg (91%, method D); 111 mg (61%, method A); mp 148 °C.

IR (KBr): 2216 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3 H, NMe), 6.42 (dd, *J* = 4.7, 2.5 Hz, 1 H, H4), 7.15 (dd, *J* = 2.5, 1.7 Hz, 1 H, H5), 7.58 (dd, *J* = 4.7, 1.7 Hz, 1 H, H3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.4 (NMe), 81.9 [=*C*$(CN)_2$], 112.6 (C4), 113.2 (2 CN), 113.3 (CN), 123.7 (C3), 125.0 (C2), 127.2 [(CN)*C*=], 137.2 (C5).

Anal. Calcd for $C_{10}H_6N_4$: C, 65.93; H, 3.32; N, 30.75. Found: C, 66.04; H, 3.42; N, 30.63.

1-Methyl-3-(tricyanoethenyl)-1*H*-pyrrole (3a)

Yield: 120 mg (66%, method C); mp 186–188 °C.

IR (KBr): 2216 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3 H, NMe), 6.76 (dd, *J* = 3.2, 1.7 Hz, 1 H, H4), 7.01 (dd, *J* = 3.2, 1.6 Hz, 1 H, H5), 7.61 (dd, *J* = 1.7, 1.6 Hz, 1 H, H2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.4 (NMe), 80.3 [=*C*$(CN)_2$], 110.8 (C4), 112.4 (CN), 112.9 (CN), 113.8 (CN), 117.1 (C3), 126.9 (C5), 131.4 (C2), 133.7 [(CN)*C*=].

Anal. Calcd for $C_{10}H_6N_4$: C, 65.93; H, 3.32; N, 30.75. Found: C, 65.71; H, 3.46; N, 30.89.

1-Methyl-2-phenyl-5-(tricyanoethenyl)-1*H*-pyrrole (2b)

Yield: 230 mg (89%, method D); 75 mg (29%, method A); mp 148 °C.

IR (KBr): 2212 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, NMe), 6.56 (d, *J* = 4.6 Hz, 1 H, H3), 7.43 (m, 2 H, CH_{Ar}-2,6), 7.51 (m, 3 H, CH_{Ar}-3,4,5), 7.61 (d, *J* = 4.6 Hz, 1 H, H4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.8 (NMe), 79.7 [=*C*$(CN)_2$], 113.0 (CN), 113.6 (CN), 113.7 (CN), 114.8 (C3), 124.1 (C4), 126.6 [(CN)*C*=], 128.2 (C5), 129.2 (C_{Ar}-3,5), 129.5 (C_{Ar}-2,6), 129.6 (C_{Ar}-1), 130.3 (CH_{Ar}-4), 150.4 (C2).

Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.69. Found: C, 74.22; H, 4.05; N, 21.51.

1-Methyl-2-phenyl-3-(tricyanoethenyl)-1*H*-pyrrole (3b)

Yield: 93 mg (36%, method A); mp 148 °C.

IR (KBr): 2217 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.50 (s, 3 H, NMe), 6.81 (d, *J* = 3.5 Hz, 1 H, H5), 7.17 (d, *J* = 3.5 Hz, 1 H, H4), 7.28 (m, 2 H, CH_{Ar}-2,6), 7.55 (m, 3 H, CH_{Ar}-3,4,5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.3 (NMe), 83.2 [=*C*$(CN)_2$], 109.2 (C4), 112.5 (CN), 112.8 (CN), 113.2 (CN), 115.4 (C3), 125.8 (C5), 128.1 (C_{Ar}-1), 128.7 (C_{Ar}-3,5), 130.6 (C_{Ar}-2,6), 130.9 (C_{Ar}-4), 135.0 [(CN)*C*=], 143.2 (C5).

Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.69. Found: C, 74.21; H, 3.72; N, 21.75.

1-Methyl-2-phenyl-4-(tricyanoethenyl)-1*H*-pyrrole (4b)

^1H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, NMe), 7.03 (d, *J* = 2.2 Hz, 1 H, H3), 7.36 (m, 2 H, CH_{Ar}-2,6), 7.54 (m, 3 H, CH_{Ar}-3,4,5), 7.71 (d, *J* = 2.2 Hz, 1 H, H5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0 (NMe), 79.2 [=*C*$(CN)_2$], 108.2 (C3), 112.5 (CN), 112.7 (CN), 113.5 (CN), 117.0 (C4), 128.7 (C_{Ar}-3,5), 129.3 (C_{Ar}-2,6), 129.4 (C_{Ar}-1), 130.6 (C_{Ar}-4), 133.7 (C5), 133.5 [(CN)*C*=], 139.9 (C2).

1-Methyl-2-(4-methylphenyl)-5-(tricyanoethenyl)-1*H*-pyrrole (2c)

Yield: 240 mg (88%, method D); 76 mg (28%, method A); mp 182 °C.

IR (KBr): 2218 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, C_{Ar}*Me*), 3.84 (s, 3 H, NMe), 6.55 (d, *J* = 4.7 Hz, 1 H, H3), 7.26–7.33 (m, 4 H, CH_{Ar}-2,3,5,6), 7.61 (d, *J* = 4.7 Hz, 1 H, H4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (C_{Ar}*Me*), 35.8 (NMe), 78.7 [=*C*$(CN)_2$], 113.1 (CN), 113.6 (CN), 113.8 (CN), 114.7 (C3), 124.2 (C4), 126.2 [(CN)*C*=], 126.6 (C_{Ar}-1), 128.3 (C5), 129.4 (C_{Ar}-3,5), 129.9 (C_{Ar}-2,6), 140.8 (C_{Ar}-4), 150.8 (C2).

Anal. Calcd for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44; N, 20.58. Found: C, 74.68; H, 4.62; N, 20.45.

1-Methyl-2-(4-methylphenyl)-3-(tricyanoethenyl)-1*H*-pyrrole (3c)

Yield: 87 mg (32%, method A); mp 167 °C.

IR (KBr): 2217 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, C_{Ar}*Me*), 3.49 (s, 3 H, NMe), 6.80 (d, *J* = 3.3 Hz, 1 H, H5), 7.16 (m, 3 H, H4, CH_{Ar}-2,6), 7.33 (m, 2 H, CH_{Ar}-3,5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (C_{Ar}*Me*), 35.2 (NMe), 83.0 [=*C*$(CN)_2$], 109.4 (C4), 112.4 (CN), 112.8 (CN), 113.2 (CN), 115.3 (C3), 125.0 (C_{Ar}-1), 125.6 (C5), 129.9 (C_{Ar}-3,5), 130.7 (C_{Ar}-2,6), 135.1 [(CN)*C*=], 141.2 (C_{Ar}-4), 143.5 (C2).

Anal. Calcd for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44; N, 20.58. Found: C, 75.15; H, 4.82; N, 20.44.

1-Methyl-2-(4-methylphenyl)-4-(tricyanoethenyl)-1*H*-pyrrole (4c)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, C_{Ar}*Me*), 3.70 (s, 3 H, NMe), 7.00 (d, *J* = 2.2 Hz, 1 H, H3), 7.29 (m, 2 H, CH_{Ar}-2,6), 7.31 (m, 2 H, CH_{Ar}-3,5), 7.69 (d, *J* = 2.2 Hz, 1 H, H5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (C_{Ar}*Me*), 36.4 (NMe), 79.3 [=*C*$(CN)_2$], 108.9 (C3), 112.6 (2 CN), 113.3 (CN), 117.2 (C4), 126.4 (C_{Ar}-1), 129.5 (CH_{Ar}-3,5), 130.0 (CH_{Ar}-2,6), 133.3 (C5), 133.4 [(CN)*C*=], 141.0 (C_{Ar}-4), 138.9 (C2).

2-(4-Methoxyphenyl)-1-methyl-5-(tricyanoethenyl)-1*H*-pyrrole (2d)

Yield: 262 mg (91%, method D); 58 mg (20%, method A); mp 209 °C.

IR (KBr): 2218 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, NMe), 3.86 (s, 3 H, OMe), 6.52 (d, *J* = 4.4 Hz, 1 H, H3), 7.01 (m, 2 H, CH_{Ar}-3,5), 7.37 (m, 2 H, CH_{Ar}-2,6), 7.60 (d, *J* = 4.4 Hz, 1 H, H4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0 (NMe), 55.6 (OMe), 78.1 [=*C*$(CN)_2$], 113.3 (CN), 113.7 (CN), 114.0 (CN), 114.7 (C3), 114.8 (C_{Ar}-3,5), 121.8 (C_{Ar}-1), 124.5 (C4), 126.0 [(CN)*C*=], 128.5 (C5), 131.1 (C_{Ar}-2,6), 150.9 (C2), 161.3 (C_{Ar}-4).

Anal. Calcd for $C_{17}H_{12}N_4O$: C, 70.82; H, 4.20; N, 19.43. Found: C, 71.14; H, 4.21; N, 19.23.

2-(4-Methoxyphenyl)-1-methyl-3-(tricyanoethenyl)-1*H*-pyrrole (3d)

Yield: 72 mg (25%, method A); mp 190 °C.

IR (KBr): 2216 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.49 (s, 3 H, NMe), 3.87 (s, 3 H, OMe), 6.79 (d, *J* = 3.2 Hz, 1 H, H5), 7.02 (m, 2 H, CH_{Ar}-3,5), 7.15 (d, *J* = 3.2 Hz, 1 H, H4), 7.20 (m, 2 H, CH_{Ar}-2,6).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.2 (NMe), 55.5 (OMe), 82.8 [=*C*$(CN)_2$], 109.1 (C4), 112.6 (CN), 112.9 (CN), 113.3 (CN), 114.7 (C_{Ar}-3,5), 115.6 (C3), 119.9 (C_{Ar}-1), 125.6 (C5), 132.3 (C_{Ar}-2,6), 135.1 [(CN)*C*=], 143.4 (C2), 161.7 (C_{Ar}-4).

Anal. Calcd for $C_{17}H_{12}N_4O$: C, 70.82; H, 4.20; N, 19.43. Found: C, 71.12; H, 4.38; N, 19.28.

2-(4-Methoxyphenyl)-1-methyl-4-(tricyanoethenyl)-1*H*-pyrrole (4d)

^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3 H, NMe), 3.85 (s, 3 H, OMe), 6.98 (m, 3 H, H3, CH_{Ar}-3,5), 7.28 (m, 2 H, CH_{Ar}-2,6), 7.65 (d, *J* = 2.0 Hz, 1 H, H5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.2 (NMe), 55.5 (OMe), 79.7 [=*C*$(CN)_2$], 108.3 (C3), 112.7 (CN), 113.1 (CN), 113.9 (CN), 114.4 (C_{Ar}-3,5), 117.4 (C4), 122.0 (C_{Ar}-1), 130.5 (C_{Ar}-2,6), 133.1 [(CN)*C*=], 134.0 (C5), 140.1 (C2), 160.4 (C_{Ar}-4).

2-(4-Chlorophenyl)-1-methyl-5-(tricyanoethenyl)-1*H*-pyrrole (2e)

Yield: 261 mg (89%, method D); 94 mg (32%, method A); mp 170–172 °C.

IR (KBr): 2216 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, NMe), 6.54 (d, *J* = 4.6 Hz, 1 H, H3), 7.38 (m, 2 H, CH_{Ar}-2,6), 7.61 (m, 2 H, CH_{Ar}-3,5), 7.59 (d, *J* = 4.6 Hz, 1 H, H4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.8 (NMe), 80.8 [=*C*$(CN)_2$], 112.8 (CN), 113.5 (2 CN), 114.5 (C3), 123.9 (C4), 126.8 [(CN)*C*=], 128.1 (C_{Ar}-1), 128.2 (C5), 129.6 (C_{Ar}-3,5), 130.7 (C_{Ar}-2,6), 136.7 (C_{Ar}-4), 148.8 (C2).

Anal. Calcd for $C_{16}H_9ClN_4$: C, 65.65; H, 3.10; Cl, 12.11; N, 19.14. Found: C, 65.28; H, 3.17; Cl, 12.04; N, 19.37.

2-(4-Chlorophenyl)-1-methyl-3-(tricyanoethenyl)-1*H*-pyrrole (3e)

Yield: 82 mg (28%, method A); mp 191 °C.

IR (KBr): 2219 cm^{-1} (CN).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H, NMe), 6.82 (d, *J* = 3.4 Hz, 1 H, H5), 7.16 (d, *J* = 3.4 Hz, 1 H, H4), 7.27 (m, 2 H, CH_{Ar}-2,6), 7.52 (m, 2 H, CH_{Ar}-3,5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.7 (NMe), 83.9 [=*C*$(CN)_2$], 109.4 (C4), 112.6 (CN), 112.7 (CN), 113.0 (CN), 115.4 (C3), 126.0 (C5), 126.5 (C_{Ar}-1), 129.6 (C_{Ar}-3,5), 132.2 (C_{Ar}-2,6), 134.7 [(CN)*C*=], 137.4 (C_{Ar}-4), 141.5 (C2).

Anal. Calcd for $C_{16}H_9ClN_4$: C, 65.65; H, 3.10; Cl, 12.11; N, 19.14. Found: C, 65.44; H, 3.27; Cl, 12.24; N, 19.31.

2-(4-Chlorophenyl)-1-methyl-4-(tricyanoethenyl)-1*H*-pyrrole (4e)

^1H NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 3 H, NMe), 7.03 (d, *J* = 2.2 Hz, 1 H, H3), 7.30 (m, 2 H, CH_{Ar}-2,6), 7.44 (m, 2 H, CH_{Ar}-3,5), 7.71 (d, *J* = 2.20 Hz, 1 H, H5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.8 (NMe), 79.8 [=*C*$(CN)_2$], 109.2 (C3), 112.4 (2 CN), 113.2 (CN), 117.4 (C4), 128.3 (C_{Ar}-1), 129.4 (C_{Ar}-3,5), 130.4 (C_{Ar}-2,6), 133.3 (C5), 134.1 [(CN)*C*=], 135.7 (C_{Ar}-4), 138.8 (C2).

Acknowledgment

This work was supported by the Innovation Agency of the Russian Federation (grant no. NSH-263.2008.3).

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