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Tricyanovinylation of 2-aryl-1-vinylpyrroles: solvent- and substituent controlled chemo- and regioselectivity

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ABSTRACT

2-Aryl-1-vinylpyrroles in acetone, THF and benzene react with tetracyanoethene chemo- and regiospecifically across the vinyl group to give 3-(2-arylpyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitriles in 88–94% yield. The latter, upon recrystallization from EtOH, eliminates HCN and entirely rearranges to afford stereospecifically *trans*-(3*E*)-4-(2-arylpyrrol-1-yl)-1,3-butadiene-1,1,2-tricarbonitriles. In DMSO, along with the above [2+2]-cycloaddition, tricyanovinylation of the pyrrole ring occurs to form the corresponding 3- and 5-tricyanovinylpyrroles, the product ratio being dependent on the substituents in the pyrrole ring and the reaction conditions.

1. Introduction

Tricyanovinylation of *N*H-pyrroles with tetracyanoethene (TCNE) is known to proceed selectively at the annular α-position.[1] When both α-positions are substituted, the pyrroles are tricyanovinylated onto the free β-position.[1c] In the case of *N*-substituted pyrroles, both α- and β-tricyanovinylation has been reported to take place.[2–4]

With 1-vinylpyrroles, the [2+2]-cycloaddition of TCNE to the exocyclic double bond is also possible. Indeed, such a cycloaddition was observed as the only example in the pyrrole series for 1-vinyl-4,5,6,7-tetrahydroindole, which gave the corresponding 3-(4,5,6,7-tetrahydroindol-1-yl)-1,1,2,2-cyclobutanetetracarbonitrile.[5]

In contrast, 1-vinyl- and 1-isopropenyl-2-methyl-4,5,6,7-tetrahydroindoles reacted with TCNE exclusively at the free β-position to deliver the corresponding 3-tricyanovinyl derivatives with the vinyl (isopropenyl) group intact.[1c] The attempted [2+2]-cycloaddition of TCNE to 1-vinyl-4,5,6,7-tetrahydro-4,5,7-trimethylpyrrolo[3,2-*c*]pyridine led only to tricyanovinylation of the azine ring.[6]

Meanwhile, vinylpyrroles bearing the double bond conjugated to the pyrrole ring represent an important heterocyclic class. They are building blocks for the construction of indoles via Diels–Alder reaction,[7] as well as active bifunctional monomers for the design of conducting and NLO materials.[8]

Introduction of the tricyanovinyl substituent in the pyrrole ring provides compounds of interest both as molecules possessing high charge-transfer ability in the electronic ground state and as promising organic conductors. Due to their strong solvatochromic properties, which mainly originate from their donor-acceptor substitution, they can be utilized as dyes with strong NLO characteristics.[2]

Replacing the *N*H group of the pyrrole ring with another substituent prevents the formation of intra- and intermolecular hydrogen bonding, which influences the macroscopic structures and NLO properties. Some of these molecules, e.g., 3-, 4- or 5-tricyanovinyl-1-(alkyl)aryl-2-(2′-thienyl)pyrroles, have proven to be prospective monomers for manufacture of semi-conductors or materials with the pronounced NLO properties.[2]

The alternative products of the tricyanovinylation of 1-vinylpyrroles, the corresponding [2+2]-cycloadducts at the vinyl group, are also intriguing compounds (intermediates, monomers, and charge-transfer molecules).

2. Results and discussion

In this work, we have studied the direct tricyanovinylation of 1-vinyl-2-arylpyrroles **1a**–**e** with TCNE to gain a better understanding of both chemo- and regioselectivity of the reaction and to develop expedient syntheses of new building blocks and monomers of the pyrrole series.

As shown by the experiments in acetone, THF, and benzene, 1-vinylpyrroles **1a**–**e** reacted with TCNE (rt, 1 h) chemoselectively to form only the [2+2]-cycloadducts **2a**–**e**. We have failed to detect any side products (^{1}H NMR). The cycloadducts **2a**–**e** upon refluxing from EtOH (78 °C, 15 min) eliminated HCN and entirely stereospecifically rearranged to afford butadiene derivatives, *trans*-(3*E*)-4-(2-arylpyrrol-1-yl)-1,3-butadiene-1,1,2-tricarbonitriles **3a**–**e** (Table 1). In

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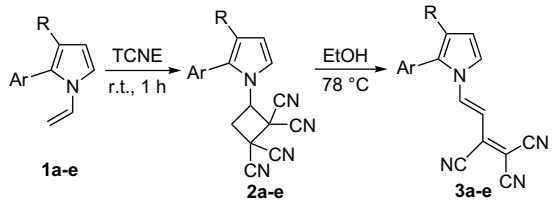
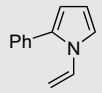
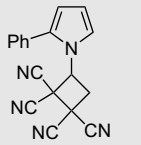
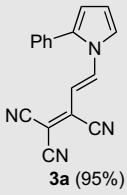
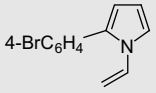
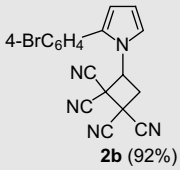
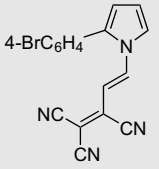
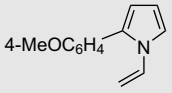
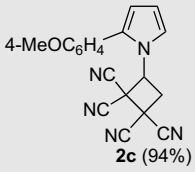
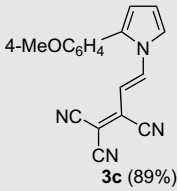
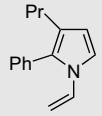
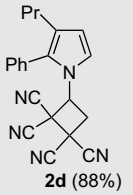
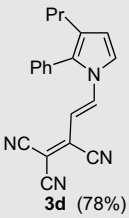
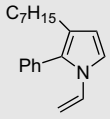
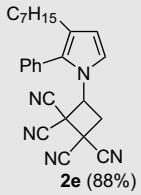
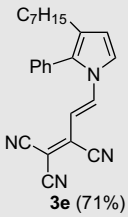
Table 1
Reaction of 2-aryl-1-vinylpyrroles **1a–e** with TCNE in acetone[a]

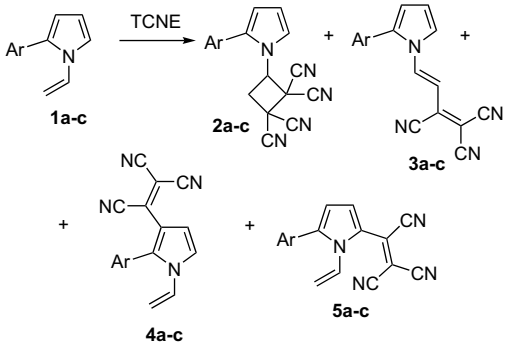


Entry	2-Aryl-1-vinylpyrrole **1**	Product **2** (yield, %)	Product **3** (yield, %)
1	 **1a**	 **2a** (89%)[b,c]	 **3a** (95%)
2	 **1b**	 **2b** (92%)	 **3b** (92%)
3	 **1c**	 **2c** (94%)	 **3c** (89%)
4	 **1d**	 **2d** (88%)	 **3d** (78%)
5	 **1e**	 **2e** (88%)	 **3e** (71%)

[a] All reactions were performed at rt for 1 h.
[b] Yield of **2a** in THF is 85%.
[c] Yield of **2a** in benzene is 42%.

contrast, recrystallization from $CHCl_3$ allowed the cyclobutanes **2a–e** to be recovered unchanged. Alcohols as proton donors seem to be essential for the ring cleavage reaction. This is also supported by the literature data. For example, the cyclobutane ring opening in 3-(indol-1-yl)[9] and 3-(isopropylpyrazol-4-yl)[10]-cyclobutane-1,1,2,2-tetracarbonitriles proceeds only in methanol[9,10] or aqueous acetonitrile.[9] 4-Anisyl-1,1,2-tricyano-1,3-butadiene is formed from

Table 2
Reaction of 2-aryl-1-vinylpyrroles **1a–c** with TCNE in DMSO[a]



Pyrrole	Ar	*T*, °C	Composition of reaction mixture, %				
			1	**2**	**3**	**4**	**5**
1a	Ph	20	14	43	1	22	20
		45	9	35	18	22	16
1b	4-BrC_6H_4	20	20	48	1	16	15
		45	19	33	15	18	15
1c	4-$MeOC_6H_4$	20	13	15	0	46	26
		45	0	0	9	63	29

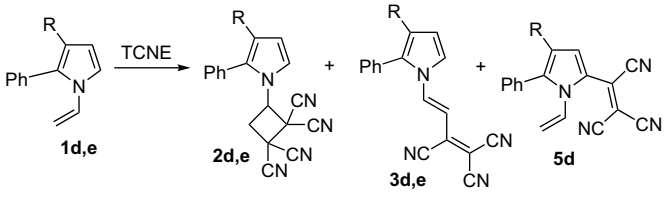
[a] The reactions time was 1 h.

3-anisyl-cyclobutane-1,1,2,2-tetracarbonitrile in methanol, but under heating in dioxane, acetonitrile, or benzene solution, the reaction does not occur.[11]

In DMSO, the chemo- and regioselectivity of the reaction was breached. As well as the [2+2]-cycloaddition products, cyclobutanes **2a–e**, and butadienes **3a–e**, the tricyanovinylation of the pyrrole ring on both α- and β-position occurred to give pyrroles **5a–d** and **4a–c** (Tables 2 and 3). In the case of 2-aryl-1-vinylpyrroles **1a–c**, 3- and 5-tricyanovinyl-1-vinylpyrroles **4a–c** and **5a–c** were simultaneously formed, the product ratio was determined by the substituents' (Ar) structure and the reaction conditions (Table 2). [2+2]-Cycloaddition at the vinyl group in tricyanovinylpyrroles **4** and **5** is not observed due to a very strong deactivating effect of the tricyanovinyl group.

As seen from Table 2, at room temperature pyrrole **1a** and pyrrole **1b** gave all four products in a close ratio; at 45 °C the content of butadienes **3a**,**b** increased (from 1% to 15–18%) due to the above cyclobutanes **2a**,**b** rearrangement. In the case of 2-(4-methoxyphenyl)-1-vinylpyrrole **1c**, tricyanovinylation of the 3-annular position turned out to be a major reaction (the content of

Table 3
Reaction of 2-aryl-1-vinylpyrroles **1d**,**e** with TCNE in DMSO[a]



Pyrrole	R	*T*, °C	Composition of reaction mixture, %			
			1	**2**	**3**	**5**
1d	*n*-Pr	20	2	76	19	4
		45	0	26	62	12
1e	*n*-C_7H_{15}	20	0	2	98	0

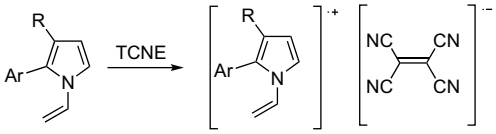
[a] The reactions time was 1 h.

3-tricyanovinylated product **4c** increased up to 46% at rt and 63% at 45 °C) and the tricyanovinylation position 5 became almost two times faster (the content of **5c** increased from 16 to 26%), consequently the content of the corresponding cyclobutane **2c** and butadiene **3c** dropped (Table 2).

Even more dramatic was the effect of alkyl substituents in the 3-position of the pyrrole ring. 2-Phenyl-3-propyl-1-vinylpyrrole **1d** at rt was tricyanovinylated almost negligibly to afford just 4% of α-tricyanovinylated product **5d**; at 45 °C its content increased to 12% (Table 3). The main reaction in this case became [2+2]-cycloaddition delivering cyclobutane **2d** (76% at rt and 26% at 45 °C) together with its rearrangement product **3d** (19% at rt and 62% at 45 °C), Table 3.

Amazingly, in the case of 3-heptyl-2-phenyl-1-vinylpyrrole **1e** no products of tricyanovinylation of the pyrrole ring at rt were observed and the major product was almost exclusively butadiene **3e** (98%), Table 3.

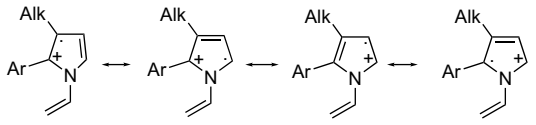
Thus, tricyanovinylation of 3-alkyl-2-aryl-1-vinylpyrroles was strongly controlled by the solvent and the substituent nature. To rationalize these phenomena, let us consider the primary intermediate of the reaction, the ion–radical pair **6** formed by the charge-transfer from the pyrrole moiety to TCNE (such a mechanism for the tricyanovinylation of the pyrrole ring has been established by the ESR spectroscopic study)[1a] (Scheme 1). For the [2+2]-cycloaddition of TCNE to the vinyl group, the above single electron transfer is less probable since a double bond is not as strong π-donor as a pyrrole moiety.



Scheme 1.

In DMSO, the pyrrole radical–cation is more stabilized than in less polar solvents such as acetone, THF, and benzene, and hence tricyanovinylation of the pyrrole ring in this solvent should be more feasible (as observed in experiment). Consequently thermodynamically favored tricyanovinylation of the pyrrole ring results from the solvent stabilization of the intermediate **6**. Conversely, the [2+2]-cycloaddition with the vinyl group is the kinetically preferred route in acetone.

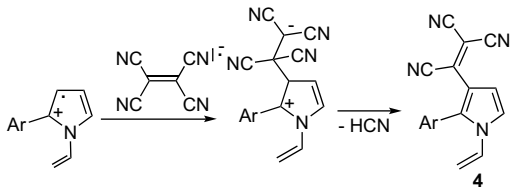
The positive charge of the pyrrole radical–cation was distributed between positions 2 and 5. The 2-position was preferable owing to the aryl substituents' participation in the positive charge distribution (a benzyl type cation), Scheme 2.



Scheme 2.

Consequently, positions 3 and 5, where a larger spin density was concentrated, were most favorable for the attack by the radical center of TCNE radical–anion, e.g., as is depicted in Scheme 3 for position 3 (Scheme 3).

The largest yield of the 3-tricyanovinylated **4c** (46–63%, Table 2) was due to the stronger stabilization of the positive charge in the 2-position of the radical–cation originated from the pyrrole



Scheme 3.

1c (the positive charge transfer onto the methoxy group). This approach explained why in DMSO tricyanovinylation of the pyrrole nucleus occurred and why the reaction was not chemo- and regioselective. When an alkyl substituent was located at the position 3, the coplanarity of the benzene and pyrrole rings was distorted and hence the stabilization of the pyrrole radical–cation was minimized. Consequently, the pyrrole ring lost its nucleophilicity and therefore the [2+2]-cycloaddition across the vinyl group remained more favorable reaction. The higher preference of the [2+2]-cycloaddition for R=C_7H_{15} having the greater steric hindrance than C_3H_7 was in agreement with this rationalization.

3. Conclusions

The reaction of 2-aryl- and 2-aryl-3-alkyl-1-vinylpyrroles with TCNE allows 3- and 5-tricyanovinyl-1-vinylpyrroles, pyrrol-1-yl-cyclobutanetetracarbonitriles, and pyrrol-1-ylbutadienetricarbonitriles to be synthesized. The latter two series can be prepared chemo-, regio-, and stereospecifically – (*E*-isomers for butadiene) in high yields. The chemo- and regioselectivity of the reaction (tricyanovinylation of pyrrole ring vs [2+2]-cycloaddition to the vinyl group) depends strongly on the solvent and the pyrrole substituents' nature and can be controlled by their variation. The novel series of functionalized pyrroles are promising precursors for design of conducting and NLO materials.

4. Experimental section

4.1. General information

IR spectra were obtained in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded at 400.13 MHz and 101.6 MHz, respectively. The concerted application of ^{1}H–^{1}H 2D homonuclear experiments COSY and NOESY and also ^{1}H–^{13}C 2D heteronuclear experiments HSQC and HMBC were used for the distinction of the carbon and proton resonances in all cases. The reaction was monitored by TLC on 'Silufol UV254' plates (hexane/diethyl ether, 2:1) and by ^{1}H NMR ($CDCl_3$). Fractionation of reaction mixtures was performed by column chromatography (silica, hexane/diethyl ether, 1:1 and 2:1).

2-Aryl-1-vinylpyrroles **1a–e** were prepared from oximes and acetylene by Trofimov reaction.[12]

4.2. Reaction of 2-aryl-1-vinylpyrroles 1a–e with TCNE in acetone (general procedure)

TCNE (128 mg, 1 mmol) was added to a solution of pyrroles **1a–e** (1.1 mmol) in acetone (5 mL) at room temperature. Instantly the solution turned blue and in 10 min it became red. The reaction mixture was stirred for 1 h, and then acetone was removed in vacuum. Grayish or light-beige powder, which was left after removing acetone, was washed with hexane to delete unreacted pyrroles **1a–e** and to give 3-(2-arylpyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitriles **2a–e**.

4.2.1. 3-(2-Phenyl-1H-pyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitrile, ***2a***

Yield 264 mg (89%) as light-beige solid, mp=159–160 °C (chloroform). [Found: C, 72.58; H, 3.64; N, 23.21. $C_{18}H_{11}N_5$ requires C, 72.72; H, 3.73; N, 23.56%.] ν_{max} (KBr) 2257 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 7.50 (m, 1H, CH^4 Ph), 7.48 (m, 2H, $CH^{3,5}$ Ph), 7.34 (m, 2H, $CH^{2,6}$ Ph), 7.06 (dd, *J*=3.3, 1.5 Hz, 1H, H^5), 6.43 (dd, *J*=3.8, 3.3 Hz, 1H, H^4), 6.34 (dd, *J*=3.8, 1.5 Hz, 1H, H^3), 5.48 (dd, *J*=11.1, 8.6 Hz, 1H, CH), 3.70 (dd, *J*=13.1, 11.1 Hz, 1H, CH_2), 3.48 (dd, *J*=13.1, 8.6 Hz, 1H, CH_2); δ_C (101.6 MHz, $CDCl_3$) 135.8 (C^2), 130.4 (C^1 Ph), 129.9 ($C^{2,6}$ Ph), 129.5 ($C^{3,5}$ Ph), 129.4 (C^4 Ph), 118.4 (C^5), 112.4 (C^4), 112.2 (C^3), 110.0 (CN), 109.5 (CN), 108.5 (CN), 107.8 (CN), 54.9 (CH), 47.0 [$CHC(CN)_2$], 39.3 (CH_2), 31.0 [$CH_2C(CN)_2$].

4.2.2. 3-(2-(4-Bromophenyl)-1H-pyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitrile, ***2b***

Yield 345 mg (92%) as beige crystals, mp=179–180 °C (chloroform). [Found: C, 57.11; H, 2.38; Br, 20.84; N, 18.26. $C_{18}H_{10}BrN_5$ requires C, 57.47; H, 2.68; Br, 21.24; N, 18.62%.] ν_{max} (KBr) 2258 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.49 (d, *J*=8.2 Hz, 2H, $CH^{3,5}$ Ar), 7.34 (d, *J*=8.2 Hz, 2H, $CH^{2,6}$ Ar), 7.06 (dd, *J*=3.3, 1.5 Hz, 1H, H^5), 6.43 (dd, *J*=3.8, 3.3 Hz, 1H, H^4), 6.33 (dd, *J*=3.8, 1.5 Hz, 1H, H^3), 5.48 (dd, *J*=11.1, 7.2 Hz, 1H, CH), 3.70 (dd, *J*=13.1, 11.1 Hz, 1H, CH_2), 3.48 (dd, *J*=13.1, 7.2 Hz, 1H, CH_2); δ_C (101.6 MHz, $CDCl_3$) 133.3 (C^2), 132.4 ($C^{2,6}$ Ar), 131.9 ($C^{3,5}$ Ar), 130.9 (C^1 Ar), 122.3 (C^4 Ar), 121.8 (C^5), 112.7 (C^3), 112.4 (CN), 112.2 (CN), 110.7 (C^4), 110.6 (CN), 109.4 (CN), 55.2 (CH), 46.3 [$CHC(CN)_2$], 37.1 (CH_2), 32.4 [$CH_2C(CN)_2$].

4.2.3. 3-[2-(4-Methoxyphenyl)-1H-pyrrol-1-yl]-1,1,2,2-cyclobutanetetracarbonitrile, ***2c***

Yield 307 mg (94%) as beige crystals, mp=144–145 °C (chloroform). [Found: C, 70.03; H, 3.79; N, 21.56. $C_{19}H_{13}N_5O$ requires C, 69.71; H, 4.00; Br, 21.24; N, 18.62%.] ν_{max} (KBr) 2255 cm^{-1} (CN); δ_H (400.13 MHz, acetone-d_6) 7.50 (dd, *J*=3.3, 1.5 Hz, 1H, H^5), 7.41 (d, *J*=8.4 Hz, 2H, $CH^{2,6}$ Ar), 7.07 (d, *J*=8.4 Hz, 2H, $CH^{3,5}$ Ar), 6.37 (dd, *J*=3.8, 3.3 Hz, 1H, H^4), 6.27 (dd, *J*=3.8, 1.5 Hz, 1H, H^3), 5.96 (dd, *J*=10.8, 9.3 Hz, 1H, CH), 4.33 (dd, *J*=13.7, 10.8 Hz, 1H, CH_2), 4.03 (dd, *J*=13.7, 9.3 Hz, 1H, CH_2), 3.88 (s, 3H, MeO); δ_C NMR (101.6 MHz, acetone-d_6) 161.1 (C^4 Ar), 135.7 (C^2), 132.1 ($C^{2,6}$ Ar), 124.4 (C^1 Ar), 120.2 (C^5), 115.2 ($C^{3,5}$ Ar), 112.3 (CN), 112.1 (CN, C^4), 111.3 (C^3), 110.7 (CN), 109.7 (CN), 56.2 (MeO), 55.7 (CH), 47.4 [$CHC(CN)_2$], 38.9 (CH_2), 32.8 [$CH_2C(CN)_2$].

4.2.4. 3-(2-Phenyl-3-propyl-1H-pyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitrile, ***2d***

Yield 299 mg (88%) as beige solid, mp=131–132 °C. [Found: C, 74.60; H, 5.30; N, 21.56. $C_{21}H_{17}N_5$ requires C, 74.32; H, 5.05; N, 20.63%.] ν_{max} (KBr) 2256 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.51 (m, 2H, $CH^{3,5}$ Ph), 7.52 (m, 1H, CH^4 Ph), 7.27 (m, 2H, $CH^{2,6}$ Ph), 6.94 (d, *J*=3.1 Hz, 1H, H^5), 6.32 (d, *J*=3.1 Hz, 1H, H^4), 5.28 (dd, *J*=11.7, 9.0 Hz, 1H, CH), 3.68 (dd, *J*=13.3, 11.7 Hz, 1H, CH_2), 3.42 (dd, *J*=13.3, 9.0 Hz, 1H, CH_2), 2.30 (m, 2H, CH_2Et), 1.51 (m, 2H, CH_2CH_3), 0.84 (t, *J*=6.6 Hz, 3H, CH_3); δ_C (101.6 MHz, $CDCl_3$) 131.7 (C^2), 131.1 (C^1, $C^{3,5}$ Ph), 130.0 (C^4 Ph), 129.4 ($C^{2,6}$ Ph), 126.1 (C^3), 117.2 (C^5), 112.6 (C^4), 110.3 (CN), 109.7 (CN), 108.6 (CN), 108.0 (CN), 55.4 [CH], 47.0 [$CHC(CN)_2$], 38.8 [CH_2], 31.0 [$CH_2C(CN)_2$], 28.1 ($EtCH_2$), 24.0 (CH_3CH_2), 14.0 (CH_3).

4.2.5. 3-(2-Phenyl-3-heptyl-1H-pyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitrile, ***2e***

Yield 348 mg (88%) as beige solids, mp=119–120 °C. [Found: C, 75.70; H, 6.30; N, 17.54. $C_{25}H_{25}N_5$ requires C, 75.92; H, 6.37; N, 17.71%.] ν_{max} (KBr) 2261 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.49 (m, 3H, $CH^{3,4,5}$ Ph), 7.26 (m, 2H, $CH^{2,6}$ Ph), 6.96 (d, *J*=3.0 Hz, 1H, H^5), 6.31 (d, *J*=3.0 Hz, 1H, H^4), 5.30 (dd, *J*=11.5, 8.8 Hz, 1H, CH), 3.71 (dd, *J*=12.8, 11.5 Hz, 1H, CH_2), 3.46 (dd, *J*=12.8, 8.8 Hz, 1H, CH_2), 2.32 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.19 (m, 8H, CH_2), 0.84 (t, *J*=6.6 Hz, 3H, CH_3); δ_C (101.6 MHz, $CDCl_3$) 132.0 (C^2), 131.4 (C^1 Ph), 131.1 ($C^{3,5}$ Ph), 129.9 (C^4 Ph), 129.4 ($C^{2,6}$ Ph), 126.3 (C^3), 117.1 (C^5), 112.6 (C^4), 110.1 (CN), 109.7 (CN), 108.5 (CN), 107.9 (CN), 55.3 [CH], 46.9 [$CHC(CN)_2$], 38.8 [$CH_2C(CN)_2$], 31.8 (CH_2), 30.8 [$CH_2C(CN)_2$], 29.3, 29.1, 25.9, 22.7 (CH_2), 14.1 (CH_3).

4.3. Synthesis of (3*E*)-4-(2-aryl-1*H*-pyrrol-1-yl)-1,3-butadiene-1,1,2-tricarbonitriles 3a–e

3-(2-Arylpyrrol-1-yl)-1,1,2,2-cyclobutanetetracarbonitriles **2a–e** (150 mg) were refluxed in ethanol (10 mL) for 15 min. After cooling to room temperature pyrroles **3a–e** were filtered off.

4.3.1. (3E)-4-(2-Phenyl-1H-pyrrol-1-yl)-1,3-butadiene-1,1,2-tricarbonitrile, ***3a***

Yield 129 mg (95%) as bright-yellow crystals, mp=236 °C. [Found: C, 75.37; H, 3.73; N, 20.56. $C_{17}H_{10}N_4$ requires C, 75.54; H, 3.73; N, 20.73%.] ν_{max} (KBr) 2218, 2231 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.98 (d, *J*=13.4 Hz, 1H, NCH=CH–), 7.50 (m, 3H, $CH^{3,4,5}$ Ph), 7.33 (m, 2H, $CH^{2,6}$ Ph), 7.25 (dd, *J*=3.3, 1.5 Hz, 1H, H^5), 6.72 (d, *J*=13.4 Hz, 1H, NCH=CH–), 6.56 (dd, *J*=3.8, 3.3 Hz, 1H, H^4), 6.44 (dd, *J*=3.8, 1.5 Hz, 1H, H^3); δ_C NMR (101.6 MHz, DMSO-d_6) 143.5 (NCH=), 139.8 [(CN)C=], 136.3 (C^2), 129.6 (C^1 Ph), 129.5 ($C^{2,6}$ Ph), 128.9 ($C^{3,5}$ Ph), 128.6 (C^4 Ph), 121.2 (C^5), 115.4 (C^3), 114.5 (C^4), 112.7 (CN), 112.2 (CN), 111.0 (CN), 106.8 (NCH=CH), 84.2 [$C(CN)_2$].

4.3.2. (3E)-4-[2-(4-Bromophenyl)-1H-pyrrol-1-yl]-1,3-butadiene-1,1,2-tricarbonitrile, ***3b***

Yield 128 mg (92%) as bright-yellow crystals, mp=252 °C. [Found C, 58.37; H, 2.54; Br, 22.48; N, 16.36. $C_{17}H_9BrN_4$ requires C, 58.47; H, 2.60; Br, 22.88; N, 16.05%.] ν_{max} (KBr) 2218, 2231 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.90 (d, *J*=13.4 Hz, 1H, NCH=CH–), 7.62 (d, *J*=8.0 Hz, 2H, $CH^{3,5}$ Ar), 7.25 (dd, *J*=3.3, 1.5 Hz, 1H, H^5), 7.19 (d, *J*=8.0 Hz, 2H, $CH^{2,6}$ Ar), 6.73 (d, *J*=13.4 Hz, 1H, NCH=CH–), 6.54 (dd, *J*=3.8, 3.3 Hz, 1H, H^4), 6.43 (dd, *J*=3.8, 1.5 Hz, 1H, H^3); δ_C (101.6 MHz, $CDCl_3$) 144.0 (NCH=), 140.3 [(CN)C=], 135.6 (C^2), 132.4 ($C^{3,5}$ Ar), 131.9 ($C^{2,6}$ Ar), 129.6 (C^1 Ar), 122.6 (C^4 Ar), 122.3 (C^5), 115.9 (C^3), 115.6 (C^4), 113.3 (CN), 112.8 (CN), 111.6 (CN), 107.6 (NCH=CH), 85.1 [$C(CN)_2$].

4.3.3. (3E)-4-[2-(4-Methoxyphenyl)-1H-pyrrol-1-yl]-1,3-butadiene-1,1,2-tricarbonitrile, ***3c***

Yield 122 mg (89%) as bright-yellow crystals, mp=238–239 °C. [Found: C, 71.67; H, 3.87; N, 18.44. $C_{18}H_{12}N_4O$ requires *C*, 71.99; H, 4.03; N, 18.66%.] ν_{max} (KBr) 2233, 2211 cm^{-1} (CN); δ_H NMR (400.13 MHz, $CDCl_3$) 7.94 (d, *J*=13.7 Hz, 1H, NCH=CH–), 7.23 (m, 3H, $CH^{2,6}$ Ar, H^5), 7.01 (d, *J*=8.4 Hz, 2H, $CH^{3,5}$ Ar), 6.71 (d, *J*=13.7 Hz, 1H, NCH=CH–), 6.52 (dd, *J*=3.8, 3.3 Hz, 1H, H^4), 6.36 (dd, *J*=3.8, 1.5 Hz, 1H, H^3), 3.85 (s, 3H, MeO). The ^{13}C NMR spectra of **3c** were failed to be recorded due to low solubility of the compound in $CDCl_3$ and acetone. In DMSO-d_6 compound **3c** was decomposed.

4.3.4. (3E)-4-(2-Phenyl-3-propyl-1H-pyrrol-1-yl)-1,3-butadiene-1,1,2-tricarbonitrile, ***3d***

Yield 107 mg (78%) as bright-red crystals, mp=137 °C. [Found: C, 76.58; H, 5.30; N, 17.56. $C_{20}H_{16}N_4$ requires C, 76.90; H, 5.16; N, 17.94%.] ν_{max} (KBr) 2228, 2220 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.94 (d, *J*=2.9 Hz, 1H, H^5), 7.70 (d, *J*=13.6 Hz, 1H, NCH=CH–), 7.53 (m, 3H, $CH^{3,4,5}$ Ph), 7.36 (m, 2H, $CH^{2,6}$ Ph), 6.98 (d, *J*=13.6 Hz, 1H, NCH=CH–), 6.57 (d, *J*=2.9 Hz, 1H, H^4), 2.31 (m, 2H, CH_2Et), 1.50 (m, 2H, CH_2CH_3), 0.81 (t, *J*=6.7 Hz, 3H, CH_3); δ_C (101.6 MHz, $CDCl_3$) 143.2 (NCH=), 139.0 [(CN)C=], 131.9 (C^2), 130.5 ($C^{2,6}$ Ph), 128.7 (C^3), 128.6 (C^4 Ph), 128.4 ($C^{3,5}$ Ph), 128.1 (C^1 Ph), 118.4 (C^5), 117.2 (C^4),

112.9 (CN), 112.2 (CN), 111.3 (CN), 105.0 (NCH=CH), 81.8 [$C(CN)_2$], 27.5, 22.7 (CH_2), 13.7 (CH_3).

4.3.5. (3E)-4-(2-Phenyl-3-heptyl-1H-pyrrol-1-yl)-1,3-butadiene-1,1,2-tricarbonitrile, ***3e***

Yield 99 mg (71%) as bright-red crystals, mp=137 °C. [Found: C, 78.29; H, 6.53; N, 15.04. $C_{24}H_{24}N_4$ requires C, 78.23; H, 6.57; N, 15.21%.] ν_{max} (KBr) 2226 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.73 (d, J=13.6 Hz, 1H, NCH=CH–), 7.49 (m, 2H, $CH^{2,6}$ Ph), 7.20 (m, 3H, $CH^{3,4,5}$ Ph), 7.16 (d, J=3.5 Hz, 1H, H^5), 6.60 (d, J=13.6 Hz, 1H, NCH=CH–), 6.47 (d, J=3.5 Hz, 1H, H^4), 2.36 (m, 2H, CH_2), 1.49 (m, 2H, CH_2), 1.20 (m, 8H, CH_2), 0.84 (t, J=6.6 Hz, 3H, CH_3); δ_C (101.6 MHz, $CDCl_3$) 143.5 (NCH=), 139.5 [(CN)C=], 132.8 (C^2), 131.1 ($C^{2,6}$ Ph), 129.8 (C^3), 129.5 (C^4 Ph), 129.2 ($C^{3,5}$ Ph), 128.7 (C^1 Ph), 118.1 (C^5, C^4), 111.8 (CN), 111.4 (CN), 111.1 (CN), 105.3 (NCH=CH), 83.1 [$C(CN)_2$], 31.8 (CH_2), 30.2, 29.2, 29.0, 26.0, 22.7 (CH_2), 14.1 (CH_3).

4.4. Reaction of pyrroles 1a–e with TCNE in DMSO

A. A solution of TCNE (12.8 mg, 0.1 mmol) in DMSO-d_6 (0.3 mL) was added to a solution of pyrroles **1a–e** (0.1 mmol) in DMSO-d_6 (0.2 mL) and the resulting mixture was stirred for 1 h at 20 °C or 45 °C. Then the sample was taken, diluted with $CDCl_3$, and analyzed by ^1H NMR.

B. A solution of TCNE (256 mg, 2 mmol) in DMSO (4 mL) was added to a solution of pyrroles **1a–e** (2 mmol) in DMSO (6 mL) at room temperature. The reaction mixture was stirred at 45 °C for 3 h and diluted with water. The products were isolated from the reaction mixture using the extraction by CH_2Cl_2. The extracts were washed with water and dried over $MgSO_4$. The residue after removing CH_2Cl_2 was purified by flash chromatography, eluted with hexane and then with diethyl ether. The ether extracts were concentrated and fractionated on column (SiO_2, l=60 cm, hexane/diethyl ether, 1:1) to isolate consequently pyrroles **5a–d**, pyrroles **4a–d** and pyrroles **3a–d**. Pyrroles **5a–d** in pure state were obtained after second chromatography of the first fraction (SiO_2, l=30 cm, hexane/diethyl ether, 2:1). Pyrroles **4a–d** and **3a–d** were purified additionally by washing with mixture of hexane and diethyl ether, 1:1.

4.4.1. 2-(2-Phenyl-1-vinyl-1H-pyrrol-3-yl)-1,1,2-ethylentricarbonitrile, ***4a***

Yield 48 mg (9%) as yellow crystals, mp=132–133 °C. [Found: C, 75.39; H, 3.58; N, 20.81. $C_{17}H_{10}N_4$ requires C, 75.54; H, 3.73; N, 20.73%.] ν_{max} (KBr) 2219 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.58–7.51 (m, 3H, $CH^{3,4,5}$ Ph), 7.30 (m, 2H, $CH^{2,6}$ Ph), 7.22 (m, 2H, $H^{4,5}$), 6.63 (dd, $J_{Hx,\ HA}$=15.9 Hz, $J_{Hx,\ HB}$=8.8 Hz, 1H, H^x), 5.39 (dd, $J_{HA,\ Hx}$=15.9 Hz, $J_{HA,\ HB}$=1.7 Hz, 1H, H^A), 4.96 (dd, $J_{HB,\ Hx}$=8.8 Hz, $J_{HB,\ HA}$=1.7 Hz, 1H, H^B); δ_C NMR (101.6 MHz, $CDCl_3$) 141.5 (C^2), 134.8 [(CN)C=], 131.4 ($C^{2,6}$ Ph), 131.2 (C^4 Ph), 129.7 (NCH=CH_2), 129.2 ($C^{3,5}$ Ph), 127.2 (C^1 Ph), 120.5 (C^5), 116.0 (C^3), 112.8 (CN), 112.5 (CN), 112.2 (CN), 110.4 (C^4), 104.7 (CH_2=C), 85.2 [=$C(CN)_2$].

4.4.2. 2-(2-Phenyl-1-vinyl-1H-pyrrol-5-yl)-1,1,2-ethylentricarbonitrile, ***5a***

Yield: 38 mg (7%) as red crystals, mp=101 °C. [Found: C, 75.20; H, 3.64; N, 20.41. $C_{17}H_{10}N_4$ requires C, 75.54; H, 3.73; N, 20.73%.] ν_{max} (KBr) 2220 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.56 (d, J=4.4 Hz, 1H, H^4), 7.45 (m, 5H, Ph), 7.07 (dd, $J_{Hx,\ HA}$=15.3 Hz, $J_{Hx,\ HB}$=7.9 Hz, 1H, H^x), 6.59 (d, J=4.4 Hz, 1H, H^3), 5.56 (dd, $J_{HB,\ Hx}$ 7.9 Hz, $J_{HB,\ HA}$=1.5 Hz, 1H, H^B), 5.18 (dd, $J_{HA,\ Hx}$=15.3 Hz, $J_{HA,\ HB}$=1.5 Hz, 1H, H^A); δ_C NMR (101.6 MHz, $CDCl_3$) 147.7 (C^2), 131.0 (NCH=CH_2), 130.0 (C^4 Ph), 129.6 (C^1 Ph), 129.3 ($C^{3,5}$ Ph), 129.0 ($C^{2,6}$ Ph), 128.4 [(CN)C=], 126.4 (C^5), 124.6 (C^4), 119.8 (CH_2=C), 114.7 (C^3), 113.2 (CN), 113.1 (CN), 112.6 (CN), 82.4 [=$C(CN)_2$].

4.4.3. 2-[2-(4-Bromophenyl)-1-vinyl-1H-pyrrol-3-yl]-1,1,2-ethylentricarbonitrile, ***4b***

Yield 49 mg (7%) as yellow crystals, mp=175 °C. [Found: C, 58.74; H, 2.81; Br, 22.53; N, 15.65. $C_{17}H_9BrN_4$ requires C, 58.47; H, 2.60; Br, 22.88; N, 16.05%.] ν_{max} (KBr) 2217 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.67 (d, J=8.4 Hz, 2H, $CH^{3,5}$ Ar), 7.23 (m, 2H, $H^{4,5}$), 7.19 (d, J=8.4 Hz, 2H, $CH^{2,6}$ Ar), 6.58 (dd, $J_{Hx,\ HA}$=15.6 Hz, $J_{Hx,\ HB}$=9.0 Hz, 1H, H^x), 5.38 (dd, $J_{Hx,\ HA}$=15.6 Hz, $J_{HA,\ HB}$=2.0 Hz, 1H, H^A), 4.97 (dd, $J_{HB,\ Hx}$=9.0 Hz, $J_{HB,\ HA}$=2.0 Hz, 1H, H^B); δ_C (101.6 MHz, $CDCl_3$) 139.8 (C^2), 134.5 [(CN)C=], 132.8 ($C^{3,5}$ Ar), 132.6 ($C^{2,6}$ Ar), 129.5 (NCH=CH_2), 126.1 ($C^{1,4}$ Ar), 120.9 (C^5), 116.0 (C^3), 112.6 (CN), 112.4 (CN), 112.3 (CN), 110.6 (C^4), 105.4 (CH_2=C), 85.9 [=$C(CN)_2$].

4.4.4. 2-[2-(4-Bromophenyl)-1-vinyl-1H-pyrrol-5-yl]-1,1,2-ethylentricarbonitrile, ***5b***

Yield 42 mg (6%) as red crystals, mp=163 °C. [Found: C, 58.62; H, 2.71; Br, 23.09; N, 16.15. $C_{17}H_9BrN_4$ requires C, 58.47; H, 2.60; Br, 22.88; N, 16.05%.] ν_{max} (KBr) 2219 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.58 (d, J=8.8 Hz, 2H, $CH^{3,5}$ Ar), 7.54 (d, J=4.5 Hz, 1H, H^4), 7.31 (d, J=8.8 Hz, 2H, $CH^{2,6}$ Ar), 7.02 (dd, $J_{Hx,\ HA}$=15.4 Hz, $J_{Hx,\ HB}$=8.1 Hz, 1H, H^x), 6.58 (d, J=4.5 Hz, 1H, H^3), 5.58 (dd, $J_{HB,\ Hx}$=8.1 Hz, $J_{HB,\ HA}$=1.2 Hz, 1H, H^B), 5.20 (dd, $J_{HA,\ Hx}$=15.4 Hz, $J_{HA,\ HB}$=1.2 Hz, 1H, H^A); δ_C (101.6 MHz, $CDCl_3$) 146.0 (C^2), 132.4 ($C^{3,5}$ Ar), 130.8 (NCH=CH_2), 130.7 ($C^{2,6}$ Ar), 128.6 (C^1 Ar), 128.5 [(CN)C=], 126.6 (C^5), 124.6 (C^4 Ar), 124.3 (C^4), 120.3 (CH_2=C), 114.7 (C^3), 113.01 (CN), 112.98 (CN), 112.4 (CN), 83.4 [=$C(CN)_2$].

4.4.5. 2-[2-(4-Methoxyphenyl)-1-vinyl-1H-pyrrol-3-yl]-1,1,2-ethylentricarbonitrile, ***4c***

Yield 48 mg (8%) as yellow crystals, mp=160 °C. [Found: C, 72.18; H, 3.85; N, 18.54. $C_{18}H_{12}N_4O$ requires C, 71.99; H, 4.03; N, 18.66%.] ν_{max} (KBr) 2220 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$): 7.24–7.19 (m, 4H, $CH^{2,6}$ Ar, $H^{4,5}$), 7.01 (m, 2H, $CH^{3,5}$ Ar), 6.65 (dd, $J_{Hx,\ HA}$=15.7 Hz, $J_{Hx,\ HB}$=9.0 Hz, 1H, H^x), 5.35 (dd, $J_{HA,\ Hx}$=15.7 Hz, $J_{HA,\ HB}$=1.8 Hz, 1H, H^A), 4.95 (dd, $J_{HB,\ Hx}$=9.0 Hz, $J_{HB,\ HA}$=1.8 Hz, 1H, H^B), 3.86 (s, 3H, MeO); δ_C (101.6 MHz, $CDCl_3$) 162.0 (C^4 Ar), 141.8 (C^2), 135.0 [(CN)C=], 132.9 ($C^{2,6}$ Ar), 129.9 (NCH=CH_2), 120.4 (C^5), 119.0 (C^1 Ar), 116.2 (C^3), 114.8 ($C^{3,5}$ Ar), 113.0 (CN), 112.6 (CN), 112.5 (CN), 110.4 (C_4), 104.4 (CH_2=C), 84.9 [=$C(CN)_2$], 55.5 (OMe).

4.4.6. 2-[2-(4-Methoxyphenyl)-1-vinyl-1H-pyrrol-5-yl]-1,1,2-ethylentricarbonitrile, ***5c***

Yield 42 mg (7%) as red crystals, mp=155 °C. [Found: C, 72.18; H, 3.85; N, 18.54. $C_{18}H_{12}N_4O$ requires C, 71.99; H, 4.03; N, 18.66%.] ν_{max} (KBr): 2214 cm^{-1} (CN); δ_H (400.13 MHz, $CDCl_3$) 7.58 (d, J=4.4 Hz, 1H, H^4), 7.39 (d, J=8.8 Hz, 2H, $CH^{2,6}$ Ar), 7.08 (dd, $J_{Hx,\ HA}$=15.2 Hz, $J_{Hx,\ HB}$=7.9 Hz, 1H, H^x), 6.97 (d, J=8.8 Hz, 2H, $CH^{3,5}$ Ar), 6.55 (d, 1H, J=4.4 Hz, H^3), 5.55 (dd, $J_{HB,\ Hx}$=7.9 Hz, $J_{HB,\ HA}$=1.5 Hz, 1H, H^B), 5.18 (dd, $J_{HA,\ Hx}$=15.2 Hz, $J_{HA,\ HB}$=1.5 Hz, 1H, H^A), 3.85 (s, 3H, MeO); δ_C (101.6 MHz, $CDCl_3$) 161.0 (C^4 Ar), 148.1 (C^2), 131.2 (NCH=CH_2), 130.7 ($C^{2,6}$ Ar), 127.7 (C^5), 126.6 [(CN)C=], 124.9 (C^4), 121.8 (C^1 Ar), 119.8 (CH_2=C), 114.6 ($C^{3,5}$ Ar), 114.5 (C^3), 113.4 (CN), 113.2 (CN), 112.8 (CN), 80.8 [=$C(CN)_2$], 55.5 (OMe).

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References and notes

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