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New Push–Pull Chromophores. Synthesis of 2-[4-Aryl-3-cyano-5-hydroxy-5-methyl-1*H*-pyrrol-2(5*H*)-ylidene]malononitriles

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Abstract—2-Aminoprop-1-ene-1,1,3-tricarbonitrile (malononitrile dimer) reacted with 1-arylpropane-1,2-diones in ethanol in the presence of piperidine to give new donor–acceptor chromophores, 2-[4-aryl-3-cyano-5-hydroxy-5-methyl-1*H*-pyrrole-2(5*H*)-ylidene]malononitriles.

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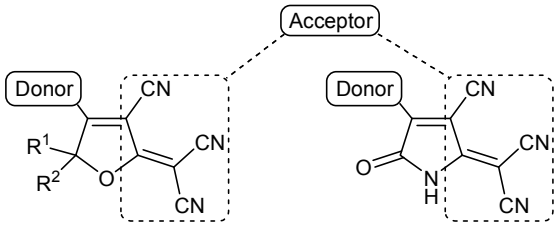
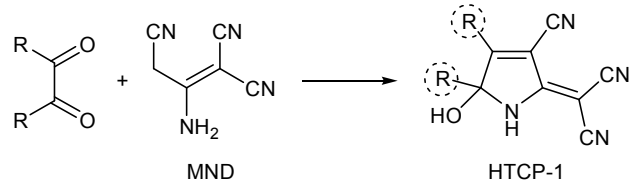
Donor–acceptor (push–pull) chromophores have attracted much attention over the past decades due to their potential applications in photovoltaics [1, 2] and optoelectronics [3–5], as well as in the design of nonlinear optical materials [6] and in other fields [7, 8]. Nowadays, the most promising push–pull chromophores are those based on tricyanofuran (TCF) and tricyanopyrrole (TCP) [9–13]. The main structural unit of their molecules is a conjugated system connecting the acceptor buta-1,3-diene-1,1,3-tricarbonitrile (BDTC) fragment and various electron-donating groups (Scheme 1).

Scheme 1.



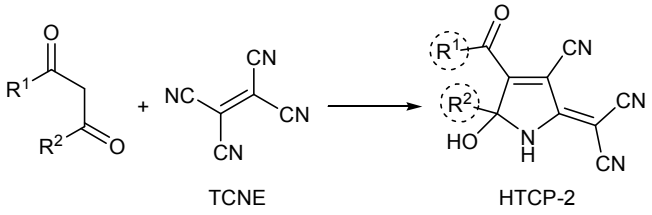
Taking into account practical importance of buta-1,3-diene-1,1,3-tricarbonitrile-based push–pull chromophores, in the present work we made an attempt to synthesize tricyanofuran and tricyanopyrrole analogs containing the above acceptor fragment and additional reaction centers. There are a few published data on hydroxytricyanopyrroles (HTCP) that are close analogs of TCF and TCP [14–17] (Schemes 2, 3). The presence of a hydroxy group in their molecules is expected to extend the ways of their further directed modifications with the goal of endowing them with desired properties. A synthetic approach to hydroxytricyanopyrroles is based on the reaction of malononitrile dimer (MND, 2-aminoprop-1-ene-1,1,3-tricarbonitrile) with 1,2-dicarbonyl compounds [14–16] (Scheme 2).

Scheme 2.

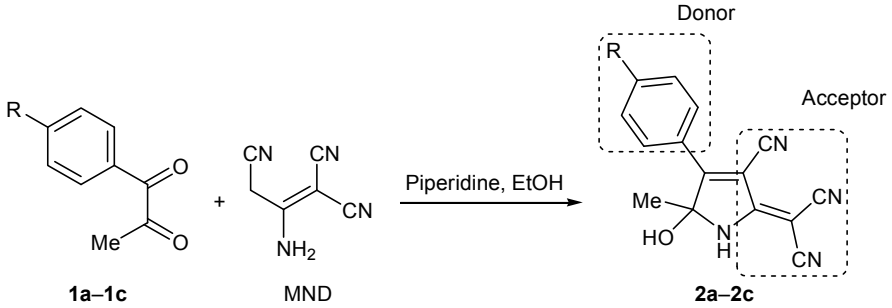


The reactions described in [14–16] were carried out mainly with 1,2-dicarbonyl compounds having similar substituents at the carbonyl groups. Therefore, the potential of this approach was not completely realized since it remained unclear how the nature of the R substituent affects the regioselectivity of the formation of hydroxytricyanopyrroles (HTCP-1). According to [17],

Scheme 3.



Scheme 4.



R = H (**a**), Me (**b**), MeO (**c**).

structures like hydroxytricyanopyrroles HTCP-2 can also be prepared from tetracyanoethylene and 1,3-dicarbonyl compounds (Scheme 3).

Compounds obtained by the above method possess an electron-withdrawing group (R^1CO) conjugated with the acceptor buta-1,3-diene-1,1,3-tricarbonitrile fragment, whereas donor–acceptor chromophores like TCF and TCP contain an electron-withdrawing substituent in that position (Scheme 1). Therefore, reactions of 1,3-dicarbonyl compounds with tetracyanoethylene seem hardly suitable for the synthesis of donor–acceptor hydroxytricyanopyrrole chromophores.

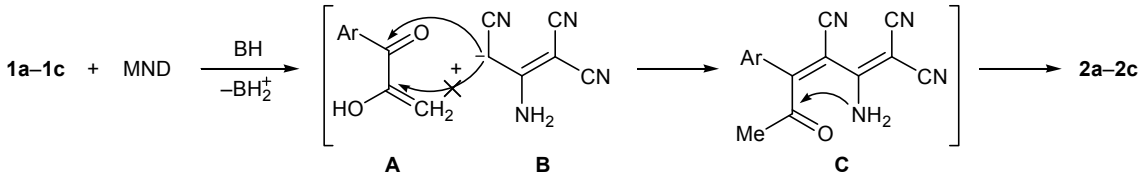
The above listed limitations intrinsic to known methods of synthesis of hydroxytricyanopyrroles, as well as increased interest in buta-1,3-diene-1,1,3-tricarbonitrile chromophores, prompted us to study the reaction of malononitrile dimer with unsymmetrical 1,2-diketones with substituents of different natures at the carbonyl groups. Our study was aimed at synthesizing new hydroxytricyanopyrroles in which the polyene chain is extended due to conjugation of the acceptor hydroxytricyanopyrrole fragment with an aromatic substituent on the pyrrole ring. The reaction of malononitrile dimer with 1-arylpropane-1,2-diones **1a**–**1c** in ethanol in the presence of piperidine afforded 2-[4-aryl-3-cyano-5-hydroxy-5-methyl-1*H*-pyrrole-2(5*H*)-ylidene]malononitriles **2a**–**2c** in 53–61% yield (Scheme 4).

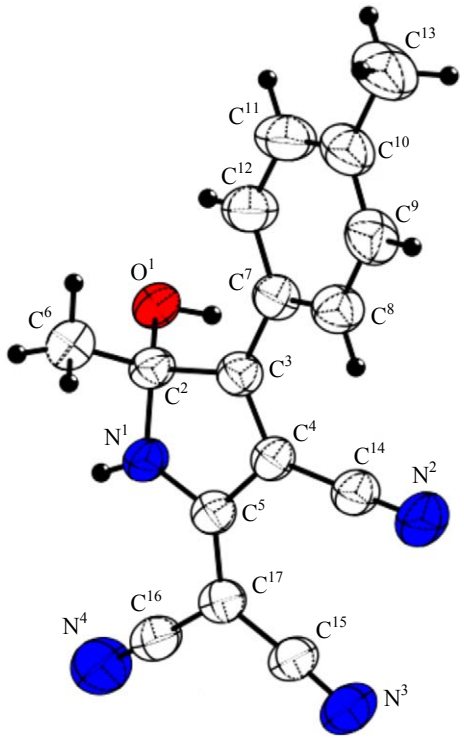
Variation of the aromatic substituent in initial diketone **1a**–**1c** ensures introduction of an electron-donating fragment into the 4-position of the pyrrole ring, so that donor–acceptor chromophore system can be obtained without further modification of the hydroxytricyanopyrrole structure. Analogous approach was applied to the synthesis of tricyanofuran derivatives as fluorescent probes for visualization of biological processes [18, 19].

The structure of **2a**–**2c** was confirmed by IR, ^{1}H NMR, and mass spectra. The IR spectra of **2a**–**2c** contained absorption bands due to stretching vibrations of the conjugated cyano groups (2225–2228 cm^{-1}) and primary amino group (3413–3375 cm^{-1}). In the ^{1}H NMR spectra of **2a**–**2c**, the NH proton signal was located at δ 10.64–10.77 ppm, the OH proton gave a broadened signal at δ 7.32–7.33 ppm, aromatic proton signals were observed in the region δ 7.19–8.16 ppm (*ortho*-protons resonated in a weaker field), and the 5-CH_3 protons resonated at δ 1.50–1.53 ppm. In addition, a signal from the substituent in the benzene ring was present (δ 2.41 and 3.84 ppm for Me and MeO group in **2b** and **2c**, respectively). Compounds **2a**–**2c** showed in the mass spectra the molecular ion peak $[M]^+$ with a relative intensity of 22–29% and $[M - CH_3]^+$ ion peak with an intensity of 45–77%. The structure of **2b** was unambiguously determined by X-ray analysis (see figure, CCDC entry no. 1476503).

Scheme 5 shows a probable mechanism of the formation of compounds **2**. Basic conditions, on the one hand, force the keto–enol equilibrium of 1,2-diketone to shift toward intermediate **A** and, on the other hand, favor formation of carbanion **B** from malononitrile dimer. Presumably, the acetyl carbonyl group in

Scheme 5.





ORTEP representation of the molecule of 2-[3-cyano-5-hydroxy-5-methyl-4-(4-methylphenyl)-1*H*-pyrrol-2(5*H*)-ylidene]malononitrile (**2b**).

diketone **1** is deactivated due to enolization, and nucleophilic attack by carbanion **B** is directed at the aroyl carbonyl group with formation of amino ketone **C**. The subsequent intramolecular heterocyclization involving the amino group and acetyl fragment yields final product **2**.

Thus, the reaction of unsymmetrical 1-arylpropane-1,2-diones **1a**–**1c** with malononitrile dimer gives new donor–acceptor chromophores, 2-[4-aryl-3-cyano-5-hydroxy-5-methyl-1*H*-pyrrol-2(5*H*)-ylidene]malononitriles **2a**–**2c** in which the conjugation system comprises the aryl and buta-1,3-diene-1,1,3-tricarbonitrile fragments.

EXPERIMENTAL

The purity of the isolated compounds was checked by TLC on Sorbfil PTSKh-AF-A-UF plates; spots were visualized by UV irradiation, treatment with iodine vapor, or thermal decomposition. The melting points were measured on an OptiMelt MPA100 melting point apparatus. The IR spectra were recorded from samples dispersed in mineral oil on an FSM-1202 spectrometer with Fourier transform. The ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer at 500.13 MHz using tetramethylsilane as internal standard. The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP 2010 SE instrument. The elemental compositions were determined using a Vario Micro cube CHN analyzer. The X-ray diffraction data for a single crystal of **2b** were acquired on a STOE StadiVari Pilatus 100K diffractometer (MoK_α radiation) using STOE X-Area software for data collection and processing. The structure was solved by the direct method (SHELXS-97) [20], and the molecular structure was plotted using DIAMOND [21]. The X-ray diffraction study was carried out at the General Chemistry Department, Faculty of Chemistry, Moscow State University.

Initial 1-arylpropane-1,2-diones **1a**–**1c** were synthesized by oxidation of the corresponding propiophenones with selenium dioxide in dioxane [22].

2-[3-Cyano-5-hydroxy-5-methyl-4-phenyl-1*H*-pyrrol-2(5*H*)-ylidene]malononitrile (2a). Malononitrile dimer, 0.396 g (3 mmol), was dissolved in 5 mL of ethanol, and 0.592 g (4 mmol) of 1-phenylpropane-1,2-dione (**1a**) and three drops of piperidine were added. When the reaction was complete (TLC), the mixture was diluted with water and extracted with ethyl acetate (5×2 mL), the extract was dried over anhydrous sodium sulfate and evaporated to a volume of 3 mL, and the residue was purified by column chromatography using ethyl acetate as eluent; a yellow fraction was collected. The eluate was evaporated to dryness, the residue was treated with carbon tetrachloride, and the precipitate was filtered off. If necessary, the product was additionally recrystallized from propan-2-ol–water (3:1 by volume). The product was dried in a vacuum desiccator over $CaCl_2$. Yield 0.480 g (61%), mp 167–168°C. IR spectrum, ν, cm^{-1}: 3402 (NH), 2225 (C≡N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.50 s (3H, CH_3), 7.33 br.s (1H, OH), 7.60–7.69 m (3H, *m*-H, *p*-H), 8.02–8.05 m (2H, *o*-H), 10.77 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 262 (29) $[M]^+$, 247 (77) $[M - 15]^+$. Found, %: C 68.43; H 3.95; N 21.22. $C_{15}H_{10}N_4O$. Calculated, %: C 68.69; H 3.84; N 21.36. *M* 262.27.

Compounds **2b** and **2c** were synthesized in a similar way.

2-[3-Cyano-5-hydroxy-5-methyl-4-(4-methylphenyl)-1*H*-pyrrol-2(5*H*)-ylidene]malononitrile (2b). Yield 0.480 g (58%), mp 144–145°C. IR spectrum, ν, cm^{-1}: 3413 (NH), 2228 (C≡N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.50 s (3H, CH_3), 2.41 s (3H, $C_6H_4C\mathbf{H}_3$), 7.32 br.s (1H, OH), 7.43–7.46 m (2H,

m-H), 7.97–8.00 m (2H, *o*-H), 10.71 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 276 (22) $[M]^+$, 277 (62) $[M - 15]^+$. Found, %: C 69.68; H 4.46; N 20.14. $C_{16}H_{12}N_4O$. Calculated, %: C 69.55; H 4.38; N 20.28. *M* 276.29.

2-[3-Cyano-5-hydroxy-4-(4-methoxyphenyl)-5-methyl-1*H*-pyrrol-2(5*H*)-ylidene]malononitrile (2c). Yield 0.464 g (53%), mp 156–157°C. IR spectrum, ν, cm^{-1}: 3375 (NH), 2217 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.53 s (3H, CH_3), 3.84 s (3H, OCH_3), 7.19–7.22 m (2H, *m*-H), 7.33 br.s (1H, OH), 8.13–8.16 m (2H, *o*-H), 10.64 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 292 (29) $[M]^+$, 276 (45) $[M - 15]^+$. Found, %: C 65.62; H 4.19; N 19.09. $C_{16}H_{12}N_4O_2$. Calculated, %: C 65.75; H 4.14; N 19.17. *M* 292.30.

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