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Three-component synthesis of alkylammonium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,5-dihydropyrrol-1-ides

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Abstract This study presents a three-component reaction between malononitrile dimer, α-diketone and aliphatic amine that leads to the formation of previously undescribed alkylammonium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-dimethyl-2,5-dihydropyrrol-1-ides. This reaction is a novel approach for modification of donor–acceptor chromophores containing the buta-1,3-diene-1,1,3-tricarbonitrile moiety.

Keywords Buta-1,3-diene-1,1,3-tricarbonitrile fragment · Pyrroles · Cyano groups · Donor–acceptor chromophores

Introduction

Donor–acceptor chromophores are an important group of the practically useful organic compounds because of their various application areas. [1–4] A polycyano substituted moiety is often used as a strong acceptor in these molecules. For the last 10–15 years, tricyanofuran (**TCF**) derivatives have been one of the most intensively studied groups of the cyano-substituted chromophores containing the buta-1,3-diene-1,1,3-tricarbonitrile (BDTC) acceptor (Scheme 1). These derivatives have been used as essential components of luminescent probes and labels [5–7], non-linear materials [3, 8–11], solar cells [12–14], and solid-state fluorescent dyes [15].

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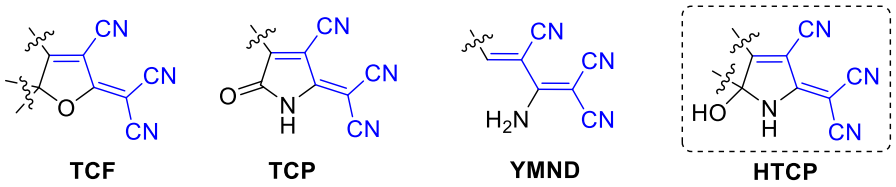


Scheme 1 Chromophores with the BDTC acceptor

Structural analogues of the **TCF** derivatives, such as tricyanopyrroles **TCP** and ylidene malononitrile dimer derivatives **YMND**, containing the similar BDTC moiety, also have been investigated in recent years (Scheme 1). An analysis of the literature shows that the most-studied area is the creation of a highly conjugated π-bonding system via introduction of a substituent in the fourth position of the BDTC fragment. [3, 5–17] In contrast, the possibilities of modification of other reaction centers, such as the fifth position in **TCF**, the first position in **TCP**, and the amino group in **YMND**, have been given much less attention. There are sparse examples in the literature that acceptor properties of **TCF** could be increased by varying the substituent in the fifth position of the furan ring, [18] and that non-linear characteristics of **TCP** derivatives could be improved by N-alkylation. [19, 20] Expanding the group of known structures containing the BDTC fragment, as well as increasing the number of approaches to their modification, is now of increasing interest to researchers.

Hydroxytricyanopyrroles (**HTCP**) are the closest structural analogues of **TCF**, **TCP** and **YMND** (Scheme 1). [21–24] In contrast to well-known analogues, the chemical properties of **HTCP** derivatives are almost unstudied. Only the conversion of the hydroxyl to an alkoxy group is described in the literature. [23] The purpose of this work is to show the possibility of a targeted modification of **HTCP** derivatives which is not described or impossible for the known analogues.

Experimental

Materials and methods

The progress of reactions and the purity of the products were monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor, or by heating). The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO-d_6 on a Bruker DRX-500 spectrometer using tetramethylsilane as an internal reference. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer. Melting points were determined on an OptiMelt MPA100 device.

Crystals of compounds **3f** suitable for X-ray analysis were grown at room temperature from a mixture of ethyl acetate. The data of **3f** were collected by using

an STOE diffractometer Pilatus100 K detector, focusing mirror collimation Cu Kα (1.54086 Å) radiation, rotation method mode. STOE X-AREA software was used for cell refinement and data reduction. Data collection and image processing were performed with X-Area 1.67. Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved and refined with the SHELX program, cell parameters: $a = 11.5827(7)$, $b = 10.5732(5)$, $c = 17.3732(10)$ Å, V = 2085.16 Å^3, $\alpha = 90$, $\beta = 101.467(5)$, $\gamma = 90$, V = 586.0(3), space group P 2_1/n, Z = 4. Absorption correction was not applied. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. The final *R*-factor was 5.71%. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND software.

Synthesis and spectral data

Typical procedure for the preparation of alkylammonium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-dimethyl-2,5-dihydropyrrol-1-ides ***3a–m*** To a solution of 1 mmol of the appropriate 1,2-diketone **1** in 1.5 ml ethanol, 1 mmol of the malononitrile dimer and 3 mmol of the corresponding amine were added. The reaction mixture was stirred for 2–3 h at room temperature until the reaction was complete (TLC). The precipitated product was filtered, washed with cold *i*-PrOH then dried in a vacuum desiccator over $CaCl_2$.

Piperidin-1-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-diphenyl-2,5-dihydropyrrol-1-ide ***3a*** Mp 125–126 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.51–1.56 (2H, m, $C\underline{H}_2(CH_2)_2$), 1.58–1.63 (4H, m, $CH_2(C\underline{H}_2)_2$), 2.94–2.97 (4H, m, $N(CH_2)_2$), 7.14–7.18 (1H, m, C_6H_5), 7.21–7.28 (5H, m, C_6H_5), 7.37–7.39 (2H, m, C_6H_5), 7.78–7.81 (2H, m, C_6H_5). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 21.72, 22.37, 43.86, 102.16, 104.66, 114.79, 121.31, 125.01, 127.97, 128.19, 128.30, 128.40, 129.10, 131.47, 140.86, 161.05, 175.85. MS, (EI, 70 eV): *m/z* (%) 324 [M-BH]$^+$ (11). IR (mineral oil, cm^{-1}): 3342 (OH); 2197, 2153 (C≡N); 1600 (C=C). Anal. Calcd for $C_{25}H_{23}N_5O$: C, 73.33; H, 5.66; N, 17.10. Found: C, 73.12; H, 5.74; N, 16.96.

Morpholin-4-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-diphenyl-2,5-dihydropyrrol-1-ide ***3b*** Mp 162–163 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 2.86–2.89 (4H, m, $N(CH_2)_2$), 3.60–3.63 (4H, m, $O(CH_2)_2$), 7.21–7.30 (3H, m, C_6H_5), 7.36–7.47 (5H, m, C_6H_5), 7.81–7.83 (2H, m, C_6H_5). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 44.04, 64.82, 99.55, 103.71, 113.79, 117.53, 125.27, 127.98, 128.20, 128.43, 128.61, 129.30, 131.67, 139.07, 160.95, 173.55. MS, (EI, 70 eV): *m/z* (%) 324 [M-BH]$^+$ (38). IR (mineral oil, cm^{-1}): 3381 (OH); 2195, 2155 (C≡N); 1603 (C=C). Anal. Calcd for $C_{24}H_{21}N_5O_2$: C, 70.06; H, 5.14; N, 17.02. Found: C, 69.93; H, 5.21; N, 16.90.

Propan-1-aminium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-diphenyl-2,5-dihydropyrrol-1-ide ***3c*** Mp 145–146 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-

d_6): δ 0.89 (3H, t, $J = 7.5$ Hz, $CH_2C\underline{H}_3$), 1.47–1.55 (2H, m, $C\underline{H}_2CH_3$), 2.69–2.72 (2H, m, $C\underline{H}_2CH_2$), 7.14–7.18 (1H, m, C_6H_5), 7.20–7.27 (5H, m, C_6H_5), 7.36–7.39 (2H, m, C_6H_5), 7.78–7.81 (2H, m, C_6H_5). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 10.76, 20.64, 40.55, 102.90, 104.82, 114.97, 121.27, 124.95, 127.93, 128.17, 128.36, 129.10, 130.71, 131.46, 141.11, 161.04, 176.16. MS, (EI, 70 eV): *m/z* (%) 324 $[M\text{-}BH]^+$ (54). IR (mineral oil, cm^{-1}): 3401 (OH); 2196, 2162 (C≡N); 1595 (C=C). Anal. Calcd for $C_{23}H_{21}N_5O$: C, 72.04; H, 5.52; N, 18.26. Found: C, 71.90; H, 5.59; N, 18.14.

Piperidin-1-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2-methyl-3-phenyl-2,5-dihydropyrrol-1-ide ***3d*** Mp 126–127 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.30 (3H, s, CH_3), 1.52–1.56 (2H, m, $C\underline{H}_2(CH_2)_2$), 1.57–1.62 (4H, m, $CH_2(C\underline{H}_2)_2$), 2.93–2.96 (4H, m, $N(CH_2)_2$), 7.53–7.55 (3H, m, C_6H_5), 7.98–8.01 (2H, m, C_6H_5). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 21.87, 22.58, 25.40, 43.99, 99.34, 103.21, 114.30, 119.62, 128.09, 128.70, 130.06, 131.26, 159.79, 175.01. MS, (EI, 70 eV): *m/z* (%) 262 $[M\text{-}BH]^+$ (14). IR (mineral oil, cm^{-1}): 3359 (OH); 2198, 2154 (C≡N); 1607 (C=C). Anal. Calcd for $C_{20}H_{21}N_5O$: C, 69.14; H, 6.09; N, 20.16. Found: C, 68.91; H, 6.14; N, 20.01.

Morpholin-4-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2-methyl-3-phenyl-2,5-dihydropyrrol-1-ide ***3e*** Mp 120–121 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.44 (3H, s, CH_3), 2.78–2.81 (4H, m, $N(CH_2)_2$), 3.56–3.59 (4H, m, $O(CH_2)_2$), 7.58–7.63 (3H, m, C_6H_5), 8.01–8.04 (2H, m, C_6H_5). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 24.55, 44.66, 65.60, 96.18, 102.15, 113.04, 116.26, 128.37, 128.96, 132.26, 160.05, 172.70. MS, (EI, 70 eV): *m/z* (%) 262 $[M\text{-}BH]^+$ (38). IR (mineral oil, cm^{-1}): 3372 (OH); 2195, 2152 (C≡N); 1603 (C=C). Anal. Calcd for $C_{19}H_{19}N_5O_2$: C, 65.32; H, 5.48; N, 20.04. Found: C, 65.20; H, 5.55; N, 19.91.

Piperidin-1-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-di(thiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3f*** Mp 138–139 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.53–3.57 (2H, m, CH_2), 1.61–1.65 (4H, m, $2CH_2$), 2.98–3.01 (4H, m, $N(CH_2)_2$), 6.77–6.80 (1H, m, CHTh), 6.84–6.87 (1H, m, CHTh), 7.20–7.23 (1H, m, CHTh), 7.35–7.37 (1H, m, CHTh), 7.83–7.85 (1H, m, CHTh), 7.94–7.97 (1H, m, CHTh). NMR (125.67 MHz, DMSO-d_6): δ 21.56, 22.14, 43.69, 99.15, 100.21, 114.71, 119.75, 123.89, 125.19, 126.57, 128.02, 131.69, 132.89, 133.75, 146.23, 160.61, 167.66. MS, (EI, 70 eV): *m/z* (%) 336 $[M\text{-}BH]^+$ (8). IR (mineral oil, cm^{-1}): 3395 (OH); 2199, 2165 (C≡N); 1584 (C=C). Anal. Calcd for $C_{21}H_{19}N_5OS_2$: C, 59.83; H, 4.54; N, 16.61. Found: C, 59.75; H, 4.62; N, 16.45.

Crystallographic data (excluding structure factors) for the structure in this paper (**3f**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1574658. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: + 44 (0) 1223 336033 or e-mail: http://deposit@ccdc.cam.ac.uk].

Morpholin-4-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-di(thiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3g*** Mp 147–148 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 2.91–2.94 (4H, m, $N(CH_2)_2$), 3.64–3.67 (4H, m, $O(CH_2)_2$),

6.87–6.90 (2H, m, 2CHTh), 7.23–7.26 (1H, m, 1CHTh), 7.41 (1H, dd, $J = 1.4$, $J = 4.9$ Hz, 1CHTh), 7.89 (1H, dd, $J = 1.0$, $J = 3.9$ Hz, 1CHTh), 8.02 (1H, dd, $J = 1.0$, $J = 5.0$ Hz, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 42.64, 63.33, 97.36, 97.81, 113.26, 117.93, 123.32, 124.56, 125.70, 127.17, 130.28, 132.41, 133.52, 144.17, 159.48, 165.68. MS, (EI, 70 eV): *m/z* (%) 336 $[M\text{-}BH]^+$ (82), 111 (100). IR (mineral oil, cm^{-1}): 3391 (OH); 2193, 2168 (C≡N); 1590 (C=C). Anal. Calcd for $C_{20}H_{17}N_5O_2S_2$: C, 56.72; H, 4.05; N, 16.54. Found C, 56.68; H, 4.11; N, 16.44.

Propan-1-aminium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-di(thiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3h*** Mp 136–137 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 0.89 (3H, t, $J = 7.5$ Hz, $CH_2C\underline{H}_3$), 1.49–1.57 (2H, m, $C\underline{H}_2CH_3$), 2.71–2.74 (2H, m, CH_2N), 6.73 (1H, dd, $J = 1.1$, $J = 3.6$ Hz, 1CHTh), 6.83–6.85 (1H, m, 1CHTh), 7.19–7.21 (1H, m, 1CHTh), 7.32 (1H, dd, $J = 1.2$, $J = 5.0$ Hz, 1CHTh), 7.82 (1H, dd, $J = 1.0$, $J = 3.9$ Hz, 1CHTh), 7.92 (1H, dd, $J = 1.0$, $J = 5.0$ Hz, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 9.68, 19.42, 39.39, 98.76, 100.31, 114.02, 119.92, 122.39, 123.76, 125.37, 126.79, 130.94, 131.35, 131.99, 145.96, 159.65, 167.49. MS, (EI, 70 eV): *m/z* (%) 336 $[M\text{-}BH]^+$ (24). IR (mineral oil, cm^{-1}): 3378 (OH); 2191, 2160 (C≡N); 1586 (C=C). Anal. Calcd for $C_{19}H_{17}N_5OS_2$: C, 57.70; H, 4.33; N, 17.71. Found: C, 57.63; H, 4.40; N, 17.59.

Butan-1-aminium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-di(thiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3i*** Mp 133–134 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 0.88 (3H, t, $J = 7.4$ Hz, $CH_2C\underline{H}_3$), 1.28–1.35 (2H, m, $CH_2C\underline{H}_2$-CH_3), 1.45–1.52 (2H, m, $\underline{CH}_2CH_2CH_3$), 2.74–2.78 (2H, m, CH_2N), 6.72–6.74 (1H, m 1CHTh), 6.83–6.85 (1H, m, 1CHTh), 7.18–7.21 (1H, m, 1CHTh), 7.31–7.33 (1H, m, 1CHTh), 7.81–7.83 (1H, m, 1CHTh), 7.91–7.93 (1H, m, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 12.32, 17.92, 27.98, 37.47, 98.69, 100.17, 113.97, 119.91, 122.44, 123.80, 125.38, 126.80, 130.91, 131.41, 132.06, 145.87, 159.65, 167.39. MS, (EI, 70 eV): *m/z* (%) 336 $[M\text{-}BH]^+$ (40). IR (mineral oil, cm^{-1}): 3392 (OH); 2199, 2161 (C≡N); 1593 (C=C). Anal. Calcd for $C_{20}H_{19}N_5OS_2$: C, 58.66; H, 4.68; N, 17.10. Found C, 58.59; H, 4.73; N, 16.99.

Piperidin-1-ium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-bis(5-methylthiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3j*** Mp 109–110 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.52–3.57 (2H, m, CH_2), 1.59–1.64 (4H, m, $2CH_2$), 2.34 (3H, s, CH_3), 2.50 (3H, s, CH_3), 2.96–2.99 (4H, m, $N(CH_2)_2$), 6.51–6.53 (1H, m, CHTh), 6.55–6.56 (1H, m, CHTh), 6.92 (1H, dd, $J = 1.0$, $J = 3.9$ Hz, 1CHTh), 7.67 (1H, d, $J = 3.9$ Hz, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 15.30, 15.64, 22.18, 22.80, 44.29, 98.45, 101.17, 115.57, 121.19, 123.90, 125.02, 127.34, 130.40, 134.07, 138.68, 144.66, 148.49, 161.07, 168.58. MS, (EI, 70 eV): *m/z* (%) 364 $[M\text{-}BH]^+$ (4). IR (mineral oil, cm^{-1}): 3390 (OH); 2191, 2153 (C≡N); 1577 (C=C). Anal. Calcd for $C_{23}H_{23}N_5OS_2$: C, 61.44; H, 5.16; N, 15.58. Found: C, 61.27; H, 5.21; N, 15.47.

Morpholin-4-ium dicyano(4-cyano-2-hydroxy-2,3-bis(5-methylthiophen-2-yl)-2H-pyrrol-5-yl)methanide ***3k*** Mp 155–156 °C (dec.). ^{1}H NMR (500.13 MHz,

DMSO-d_6): δ 2.38 (3H, s, CH_3), 2.54 (3H, s, CH_3), 2.95–2.98 (4H, m, $N(CH_2)_2$), 3.66–3.69 (4H, m, $O(CH_2)_2$), 6.61 (1H, d, $J = 3.4$ Hz, 1CHTh), 6.77 (1H, d, $J = 3.5$ Hz, 1CHTh), 7.02 (1H, d, $J = 3.9$ Hz, 1CHTh), 7.81 (1H, d, $J = 3.9$ Hz, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): 14.84, 15.40, 43.43, 64.02, 95.07, 96.07, 113.71, 116.33, 125.12, 125.22, 127.83, 128.74, 135.72, 139.72, 140.77, 151.59, 160.22, 164.81. MS, (EI, 70 eV): *m/z* (%) 364 $[M\text{-}BH]^+$ (12). IR (mineral oil, cm^{-1}): 3369 (OH), 2192, 2150 (C≡N), 1584 (C=C). Anal. Calcd for $C_{22}H_{21}N_5O_2S_2$: C, 58.52; H, 4.69; N, 15.51. Found: C, 58.46; H, 4.75; N, 15.39.

Propan-1-aminium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-bis(5-methylthiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3l*** Mp 143–144 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 0.89 (3H, t, $J = 7.5$ Hz, $CH_2C\underline{H}_3$), 1.49–1.56 (2H, m, $C\underline{H}_2CH_3$), 2.34 (3H, s, CH_3), 2.49 (3H, s, CH_3), 2.70–2.74 (2H, m, CH_2N), 6.50–6.52 (1H, m, 1CHTh), 6.54–6.55 (1H, m, 1CHTh), 6.92 (1H, dd, $J = 1.0$, $J = 3.9$ Hz, 1CHTh), 7.66 (1H, d, $J = 3.8$ Hz, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): 11.23, 15.30, 15.63, 21.01, 40.97, 98.64, 101.48, 115.66, 121.55, 123.78, 124.98, 127.28, 130.48, 133.95, 138.58, 144.86, 148.27, 161.17, 168.80. MS, (EI, 70 eV): *m/z* (%) 364 $[M\text{-}BH]^+$ (14). IR (mineral oil, cm^{-1}): 3439 (OH); 2192, 2164 (C≡N); 1585 (C=C). Anal. Calcd for $C_{21}H_{21}N_5OS_2$: C, 59.55; H, 5.00; N, 16.53. Found: C, 59.48; H, 5.07; N, 16.39.

Butan-1-aminium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-bis(5-methylthiophen-2-yl)-2,5-dihydropyrrol-1-ide ***3m*** Mp 142–143 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 0.88 (3H, t, $J = 7.4$ Hz, $CH_2C\underline{H}_3$), 1.27–1.35 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.45–1.51 (2H, m, $\underline{CH}_2CH_2CH_3$), 2.33 (3H, s, CH_3), 2.49 (3H, s, CH_3), 2.73–2.77 (2H, m, CH_2N), 6.50–6.52 (1H, m, 1CHTh), 6.53–6.55 (1H, m, 1CHTh), 6.91–6.93 (1H, m, 1CHTh), 7.66 (1H, d, $J = 3.8$ Hz, 1CHTh). ^{13}C NMR (125.67 MHz, DMSO-d_6): 13.38, 14.82, 15.14, 19.01, 29.18, 38.60, 98.26, 101.15, 115.23, 121.24, 123.22, 124.47, 126.76, 130.03, 133.39, 138.03, 144.50, 147.66, 160.65, 168.43. MS, (EI, 70 eV): *m/z* (%) 364 $[M\text{-}BH]^+$ (24). IR (mineral oil, cm^{-1}): 3434 (OH); 2187, 2160 (C≡N); 1584 (C=C). Anal. Calcd for $C_{22}H_{23}N_5OS_2$: C, 60.39; H, 5.30; N, 16.00. Found: C, 60.31; H, 5.36; N, 15.86.

Typical procedure for the preparation of 2-(3-cyano-5-hydroxy-1H-pyrrol-2(5H)-ylidene)malononitriles ***4a–d*** To a suspension of 1 mmol of the corresponding salt **3** in 5 ml of the mixture water/ethanol (9/1), 1 ml of 10% hydrochloric acid was added. The reaction mixture was stirred for 1.5–2 h at room temperature until the reaction was complete (TLC). The precipitated product was filtered, washed with water until a neutral reaction, then dried in a vacuum desiccator over $CaCl_2$.

2-(3-Cyano-5-hydroxy-4,5-di(thiophen-2-yl)-1H-pyrrol-2(5H)-ylidene)malononitrile ***4a*** Mp 230–231 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 7.29–7.36 (3H, m, C_6H_5), 7.44–7.54 (5H, m, C_6H_5), 7.84–7.87 (2H, m, C_6H_5). 8.07 (1H, s, OH), 11.22 (1H, s, NH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 46.52, 96.08, 102.68, 112.68, 113.73, 114.83, 125.71, 128.34, 128.57, 128.84, 129.00, 132.81, 137.06, 160.80, 170.76. MS, (EI, 70 eV): *m/z* (%) 324 $[M]^+$ (52). IR (mineral oil,

cm^{-1}): 3466, 3338 (OH, NH); 2216 (C≡N); 1647, 1586 (C=C). Anal. Calcd for $C_{20}H_{12}N_4O$: C, 74.06; H, 3.73; N, 17.27. Found: C, 74.01; H, 3.80; N, 17.09.

2-(3-Cyano-5-hydroxy-4,5-di(thiophen-2-yl)-1H-pyrrol-2(5H)-ylidene)malononitrile ***4c*** Mp 192–193 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 6.97–7.00 (1H, m, 1CHTh), 7.11 (1H, dd, $J = 1.1$, $J = 3.7$ Hz, 1CHTh), 7.31–7.34 (1H, m, 1CHTh), 7.57 (1H, dd, $J = 1.1$, $J = 5.1$ Hz, 1CHTh), 8.02 (1H, dd, $J = 0.8$, $J = 4.0$ Hz, 1CHTh), 8.20 (1H, dd, $J = 0.8$, $J = 5.0$ Hz, 1CHTh), 8.33 (1H, s, OH), 11.29 (1H, s, NH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 46.35, 94.15, 95.91, 113.02, 113.78, 114.79, 126.24, 127.24, 127.50, 129.11, 130.26, 135.68, 137.67, 141.95, 160.15, 163.30. MS, (EI, 70 eV): *m/z* (%) 336 $[M]^+$ (41). IR (mineral oil, cm^{-1}): 3477, 3386 (OH, NH); 2221 (C≡N); 1656, 1582 (C=C). Anal. Calcd for $C_{16}H_8N_4OS_2$: C, 57.13; H, 2.40; N, 16.66. Found: C, 56.92; H, 2.44; N, 16.57.

2-(3-Cyano-5-hydroxy-4,5-bis(5-methylthiophen-2-yl)-1H-pyrrol-2(5H)-ylidene)-malononitrile ***4d*** Mp 207–208 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 2.40 (3H, s, CH_3), 2.56 (3H, s, CH_3), 6.66–6.68 (1H, m, 1CHTh), 6.88 (1H, d, $J = 3.6$ Hz, 1CHTh), 7.07–7.08 (1H, m, 1CHTh), 7.89 (1H, d, $J = 4.0$ Hz, 1CHTh), 8.22 (1H, s, OH), 11.17 (1H, s, NH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 14.86, 15.51, 45.58, 93.73, 94.90, 113.05, 113.76, 114.76, 125.54, 125.92, 128.19, 128.28, 136.71, 139.18, 140.42, 153.25, 160.04, 163.23. MS, (EI, 70 eV): *m/z* (%) 364 $[M]^+$ (22). IR (mineral oil, cm^{-1}): 3546, 3372 (OH, NH); 2212 (C≡N); 1648, 1585 (C=C). Anal. Calcd for $C_{18}H_{12}N_4OS_2$: C, 59.32; H, 3.32; N, 15.37. Found: C, 59.23; H, 3.42; N, 15.20.

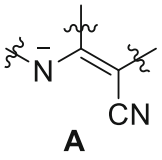
An alternative way to synthesize salts ***3d***, ***e*** To a suspension of 1 mmol of **HTCP 4b** in 1.5 ml of ethanol, 1.1 mmol of the corresponding amine was added. The reaction mixture was stirred for 2–3 h at room temperature until the reaction was complete (TLC). The precipitated product was filtered, washed with cold *i*-PrOH, then dried in a vacuum desiccator over $CaCl_2$.

Results and discussion

We chose the formation of ionic fragment **A** (Scheme 2) as a novel approach for modification of **HTCP** chromophores by the action of the various bases on the NH-group.

It should be noted that there are few examples in the literature of salts with the fragment **A**, and they do not include a BDTC acceptor. Among these salts, several compounds are known as ionic liquids [25], photoelectrochemical photocurrent

Scheme 2 The fragment of the compounds studied in this work



A

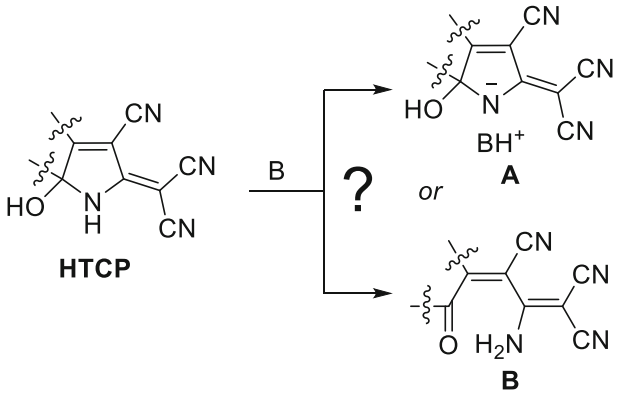
switches [26] or catalysts of thermal decomposition of energetic compounds [27]. The importance of structures **A** containing pyrrole rings is also supported by the practical significance of the cyano-substituted pyrrolides. They have been proven to be ionic liquids for SO_2 capture [28], ionic micropropellants [29] and luminophores. [30–32].

An essential structural feature of the **HTCP** derivatives, in contrast to **TCF**, **TCP** and **YMND**, is a cyclic α-aminoalcohol moiety. According to the literature it is quite unstable in the presence of bases, and undergoes ring-opening to form molecules containing amino and carbonyl groups (structure **B** on Scheme 3) [33, 34]. Therefore, we have another urgent theoretical problem: are the ionic structures **A** stable enough to be isolated as solids, or will the pyrrole cycle undergo ring-opening in the presence of bases (Scheme 3)?

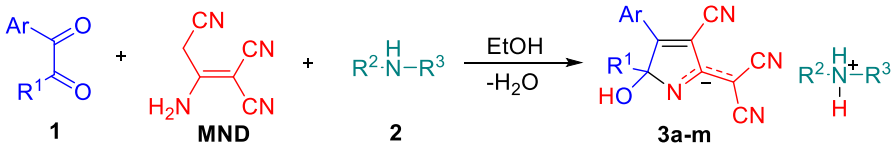
An approach we have used in this work is the reaction of malononitrile dimer (**MND**) with 1,2-diketones. This process was previously described for symmetrical [24] as well as for unsymmetrical α-diketones [22] to form **HTCP** derivatives. Synthesis of **HTCP** was carried out in ethanol in the presence of a catalytic amount of piperidine. For the synthesis of ionic structures **A**, we modified this approach. It was found that previously undescribed alkylammonium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-dimethyl-2,5-dihydropyrrol-1-ides **3a–m** could be isolated in 15–89% yields using a three-component interaction between **MND**, corresponding 1,2-diketone and excess of aliphatic amine (Scheme 4; Table 1).

Synthesis of compounds **3** is characterized by using a threefold excess of amine and a minimal amount of ethanol as a solvent. The structures of compounds **3** were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry (see ESI). The ^{1}H NMR spectra exhibited signals of alkyl, aryl substituents and amine fragments with typical values of chemical shifts. The characteristic of ^{1}H NMR spectra is an absence of clear signals of OH and NH_2^+ protons. These signals are broadened or missing, probably due to an exchange process with protons of water which is present in DMSO-d6 as an impurity.

The ^{13}C NMR spectra of salts **3** exhibited signals of downfielded signals of C-atoms of fifth and third positions of the pyrrole cycle at 167.5–170.8 and



Scheme 3 The plausible transformations of **HTCP** derivatives under the action of bases



Scheme 4 Synthesis of alkylammonium 4-cyano-5-(dicyanomethylene)-2-hydroxy-2,3-dimethyl-2,5-dihydropyrrol-1-ides **3a–m**

Table 1 Synthesis of compounds **3a–m**

Entry	Ar	R^1	R^2	R^3	Product	Yield (%)[a]
1	C_6H_5	C_6H_5	$(CH_2)_5$		**3a**	78
2	C_6H_5	C_6H_5	$(CH_2)_2O(CH_2)_2$		**3b**	85
3	C_6H_5	C_6H_5	*n*-C_3H_7	H	**3c**	83
4	C_6H_5	CH_3	$(CH_2)_5$		**3d**	15
5	C_6H_5	CH_3	$(CH_2)_2O(CH_2)_2$		**3e**	18
6	2-Th	2-Th	$(CH_2)_5$		**3f**	82
7	2-Th	2-Th	$(CH_2)_2O(CH_2)_2$		**3g**	89
8	2-Th	2-Th	*n*-C_3H_7	H	**3h**	80
9	2-Th	2-Th	*n*-C_4H_9	H	**3i**	81
10	5-Me-2-Th	5-Me-2-Th	$(CH_2)_5$		**3j**	67
11	5-Me-2-Th	5-Me-2-Th	$(CH_2)_2O(CH_2)_2$		**3k**	63
12	5-Me-2-Th	5-Me-2-Th	*n*-C_3H_7	H	**3l**	64
13	5-Me-2-Th	5-Me-2-Th	*n*-C_4H_9	H	**3m**	73

Reagents and conditions: compound **1** (1 mmol), **MND** (1 mmol), amine **2** (3 mmol), EtOH (1.5 mL), r.t., 2–3 h

[a]Isolated yields

160.1–161.1 ppm, respectively, and signals of C-atoms of the second and the fourth position of pyrrole ring at 95.5–100.82 and 101.35–104.10 ppm. The characteristic of ^{13}C NMR spectra is an appearance of signals of three cyano groups as two peaks: one of them at 112.23–115.56 ppm is fairly clear, while the second at 117.32–121.85 ppm, probably corresponding to anionic cyano groups, is broadened. Also ^{13}C NMR spectra are missing signals of $\underline{C}(CN)_2$ atom of BDTC-moiety, probably due to its anionic character. The mass spectra are characterized by the presence of peaks of $[M–NHR^2R^3]^+$ fragments with 4–82% intensity.

To unambiguously prove the structure of salts **3**, a single crystal X-ray diffraction analysis was carried out for compound **3f** (Fig. 1).

The result of the implemented reaction (Scheme 4) is the developed novel approach to the modification of chromophores with BDTC-moiety. The formation of salts **3** is probably facilitated by the delocalization of the negative charge between the nitrogen atom of the pyrrole ring and ylidene malononitrile moiety. As a result, an alternative process of the pyrrole ring-opening was not realized (Scheme 3).

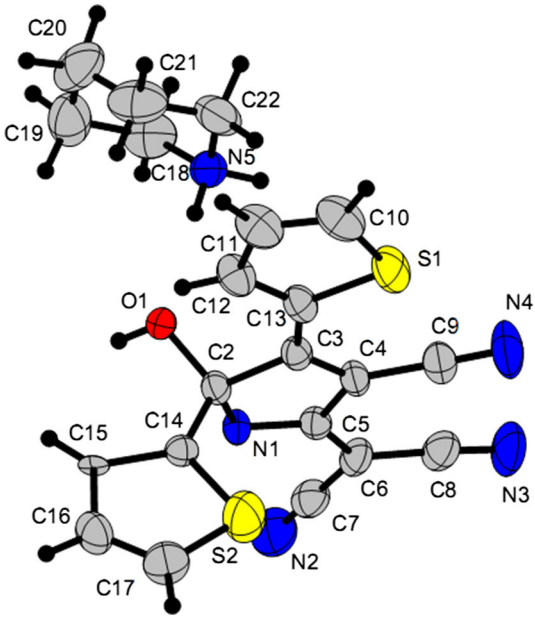
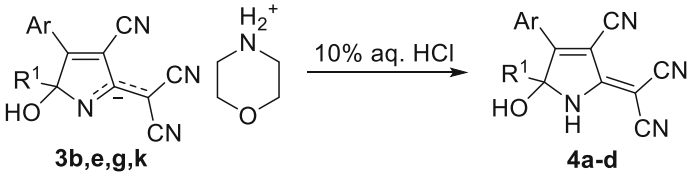


Fig. 1 Molecular structure of **3f** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii

Further, we were able to successfully neutralize the series of morpholinium salts **3b, e, g, k** to isolate corresponding **HTCP 4a–d** (Scheme 5; Table 2). The reaction was carried out using diluted hydrochloric acid and led to the isolation of 2-(3-cyano-5-hydroxy-1*H*-pyrrol-2(5*H*)-ylidene)malononitriles **4a–d** in excellent 89–95% yields.

Thienyl substituted pyrroles **4c, d** which were prepared according to this procedure are previously undescribed. Moreover, we have found that the known synthetic procedures [21–24] are not so efficient in this case, as they allowed us to isolate compounds **4c, d** in lower yields. This fact increases the value of the developed approach to the synthesis of salts **3** and the subsequent synthesis of pyrroles **4** on their basis.

The structures of compounds **4** were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry (see ESI). Mass spectra showed molecular ion peaks with 22–52% intensity. ^{1}H NMR spectra are characterized with the downfielded NH-singlets at 11.17–11.29 ppm and the signals of hydroxyl protons at 8.06–8.33 ppm. The ^{13}C NMR spectra of heterocycles **4** exhibited the downfielded signals of C3- and C5-atoms of the pyrrole cycle at 163.24–170.67



Scheme 5 Synthesis of 2-(3-cyano-5-hydroxy-1*H*-pyrrol-2(5*H*)-ylidene)malononitriles **4a–d**

Table 2 Synthesis of compounds **4a–d**[a]

Entry	Ar	R^1	Product	Yield[a] (%)[b]
1	C_6H_5	C_6H_5	**4a**	93
2	C_6H_5	CH_3	**4b**	92
3	2-Th	2-Th	**4c**	95
4	5-Me-2-Th	5-Me-2-Th	**4d**	89

[a]Reagents and conditions: compound **3** (1 mmol), H_2O/EtOH (9/1, 5 mL), 10% HCl (1 mL), r.t., 1.5-2 h

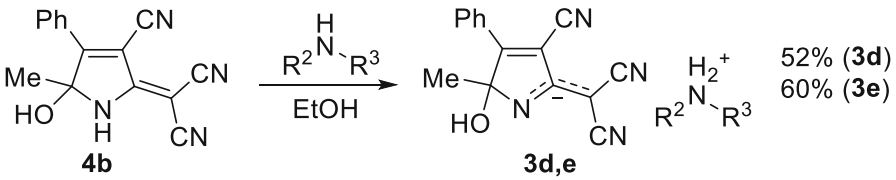
[b]Isolated yields

and 160.05–160.70 ppm, respectively, three signals of cyanogroups at 112.56–114.80 ppm and the upfielded signals of C-atoms of $\underline{C}(CN)_2$ moiety at 45.58–46.43 ppm.

Further, we found that salts **3** could be easily prepared from the corresponding pyrroles **4** in moderate yields (Scheme 6).

However, for the salts **3a–c**, **f–m** this approach is not efficient. These compounds could be synthesized in better yields using the three-component system (Scheme 3; Table 1). For the compounds **3d, e** a stepwise manner makes sense because of the poor yields of the three-component approach (Scheme 3; Table 1). Corresponding pyrrole **4b** could be obtained by the described method [22] in 61% yield for the subsequent synthesis of salts **3d**, **e** in 52–60% yields. Therefore, a total yield for two stages is 32-37%.

Solid-state fluorescence properties are one of the most important directions in studying compounds with the BDTC fragment, as it is related to the possibility of practical use of chromophores with this property, for example, **TCF** derivatives [5–7, 15]. It should be noted that information about the fluorescent properties of **HTCP** derivatives, in contrast to **TCF**, **TCP** and **YMND**, is completely absent. Our investigations showed that **HTCP 4** in powder form possesses fluorescence at room temperature. Emission maxima are in the range of 480–553 nm (Fig. 2) and depend on the R^1 and Ar substituents. For the salts **3** the emission intensity decreases dramatically. For instance, the fluorescence intensity of pyrrole **4d** is about for 5–6 times higher than for corresponding salts **3j–m** (Fig. 3). Emission maxima of the salts **3** are bathochromically shifted in comparison to the appropriate pyrrole **4**. This is clearly shown for the diphenyl derivative **4a**—its emission maximum is 513 nm, while the salts **3a–c** have emission maxima in the range 542–554 nm. (Table 3).



Scheme 6 An alternative synthesis of salts **3d, e**

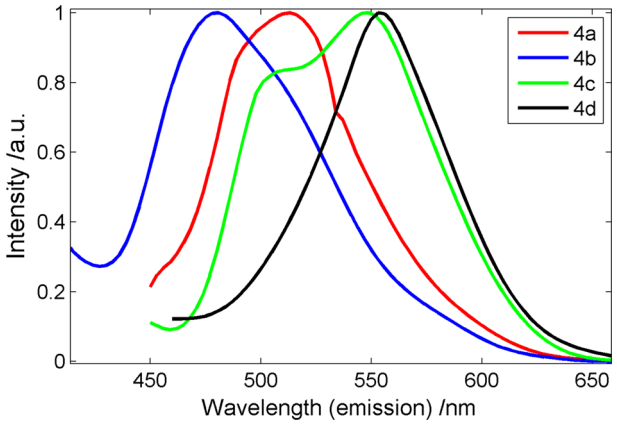


Fig. 2 Normalized emission spectra of compounds **4a–c** in the solid state

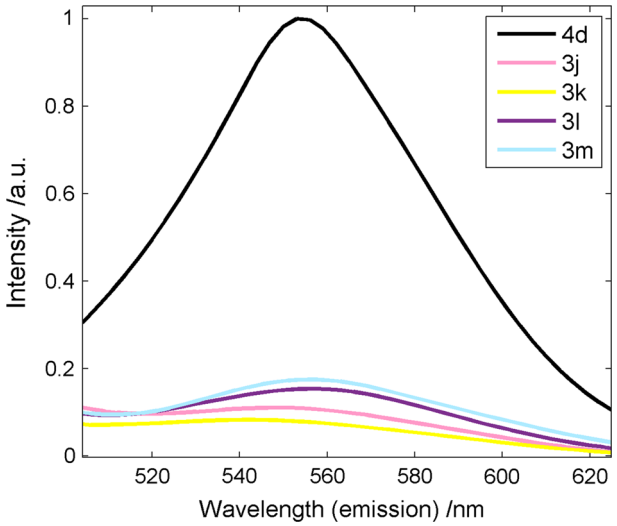


Fig. 3 Comparison of emission spectra of compound **4d** and the corresponding salts **3j–k**

Fluorescence quenching of the of salts **3** in comparison with pyrroles **4** is apparently caused by crystal packing. The analysis of the XRD data of compound **3f** showed that the molecules form dimeric pairs by the hydrogen bonding between 2-hydroxypyrrole moieties (N1A… O1B = N1B… O1A = 2.648 Å, Fig. 4). This apparently leads to an aggregation-caused quenching (ACQ) of the solid-state fluorescence.

Table 3 Fluorescence properties of compounds **3** and **4** in solid state (powder)

Compound	λ_{ex} max, nm	λ_{em} max, nm	[a]Rel. Em. Int. I_3/I_4
4a	432	513	1.0
3a	450	542	0.10
3b	459	550	0.10
3c	453	554	0.18
4b	429	480	1.0
3d	438	523	0.23
3e	435	487	1.36
4c	447	504, 549	1.0
3f	450	550	0.13
3g	489	546	0.06
3h	489	546	0.07
3i	488	549	0.06
4d	486	551	1.0
3j	489	549	0.16
3k	490	543	0.15
3l	480	558	0.18
3m	486	555	0.19

[a]Relative emission intensity is given as the ratio between the intensity of emission of salts **3** (I_3, a.u.) and the appropriate pyrrole **4** (I_4, a.u.). Emission intensity of pyrroles **4** was normalized and taken as 1.0)

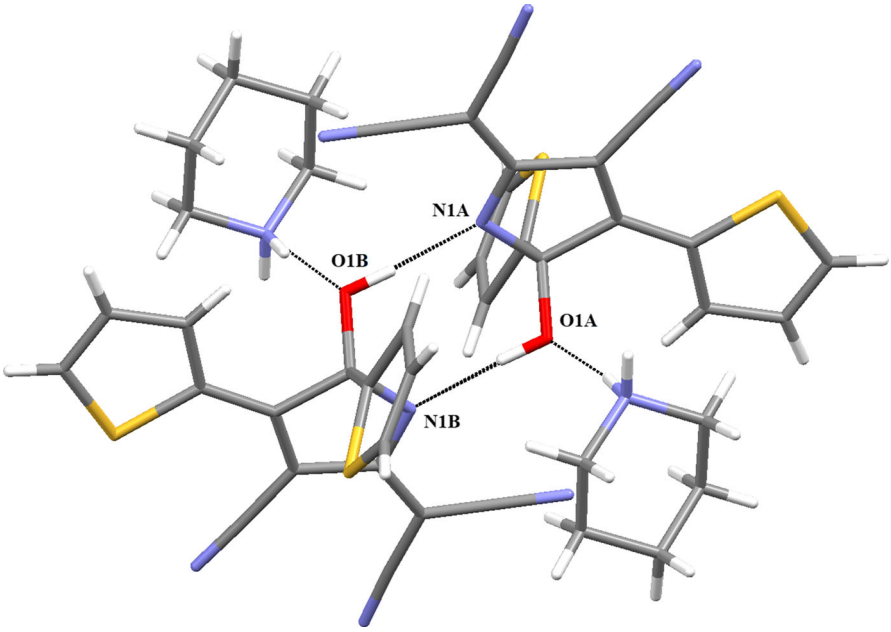


Fig. 4 Dimeric associations in crystal of compound **3f**

Conclusion

A new direction of the interaction of malononitrile dimer with 1,2-diketones was investigated, and was realized in the presence of amines to form ionic derivatives of pyrrole **3** as a result of the three-component reaction. This interaction is a completely new approach for modification of chromophores containing buta-1,3-diene-1,1,3-tricarbonitrile moiety. Also, for the first time, the solid-state fluorescence of **HTCP** derivatives was shown and characterized, while it was also found that for **HTCP** salts **3** this property is less pronounced because of the features of crystal packing.

Acknowledgements This work was supported by Russian Foundation for Basic Research, Grant No. 16-33-60156 mol_a_dc. The XRD study was carried out using the equipment purchased from the funds of the Program of development of Moscow University and within the framework of the Agreement on collaboration between the Chemical Department of the Lomonsov Moscow State University and the Chemical-Pharmaceutical Department of the I.N. Ulyanov Chuvash State University.

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