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Synthesis of conjugated polynitriles by the reactions of β-dimethylaminoacrolein aminal and 1-dimethylamino-1,3,3-trimethoxypropane with 2-dicyanomethylene-4,5,5-trimethyl-3-cyano-2,5-dihydrofuran

Zhanna A. Krasnaya,* Evgeniya O. Tret'yakova, Vadim V. Kachala and Sergei G. Zlotin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: kra@ioc.ac.ru

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The title reaction gives, depending on conditions, either a substituted tetraenic ω-dimethylaminodinitrile or a substituted 1,1,3,11,13,13-hexacyanotrideca-1,3,5,7,9,11-hexaenide salt; a series of new cation–anionic polymethyne dyes have been obtained from the latter.

Polyenic donor–acceptor chromophores with nitrile groups have been found to possess nonlinear optical properties, which make them promising compounds for optoelectronics, nonlinear optics, information recording and processing, *etc*. These compounds have a 3-cyano-2-dicyanomethylene-4,5,5-trimethyl-2,5-dihydrofuran fragment as an acceptor terminating the conjugated polyene chain.[1–6] Compounds incorporating this acceptor are synthesised from substituted dihydrofuran **1**, which was originally obtained by Melikjan *et al*.[7] and used to synthesise important biologically active compounds.[7,8]

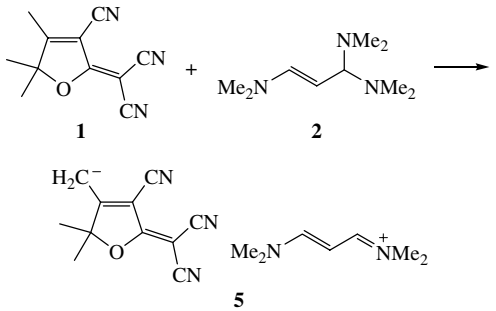
The aim of this work was to synthesise new ω-dimethylaminopolyenes containing nitrile groups at the polyene chain, which can possess very interesting photophysical properties, from substituted dihydrofuran **1**.

We found previously that β-dimethylaminoacrolein aminal **2** and 3-dimethylamino-1,1.3-trimethoxypropane (DTP) **3** are convenient reagents for the incorporation of the ω-dimethylaminopolyene fragment into various aliphatic, alicyclic and heterocyclic ketones, diketones and other CH acids. Many of the aminopolyenes obtained have unusual spectral and luminescent characteristics.[9] The reactivity of compounds **2** and **3** is high so that they can undergo condensation not only at the α-methyl or methylene group adjacent to the carbonyl group but also at the methyl group separated from the carbonyl group by one or two double bonds or a heterocycle.[9,10]

We expected that reagents **2** and **3** would undergo condensation with dihydrofuran **1** at the methyl group to give substituted tetraenic ω-dimethylaminodinitrile **4**. However, the reaction of aminal **2** with dihydrofuran **1** gave dimethylaminopropenylidenedimethylammonium salt **5** (Scheme 1) in a high yield even though the reaction conditions were varied.†

Unlike aminal **2**, 3-dimethylamino-1,1,3-trimethoxypropane **3** undergoes condensation with dihydrofuran **1**. The direction of the reaction depends on reaction conditions. The reaction of compounds **1** and **3** without a solvent (20 °C, 20 min) gave substituted tetraenic ω-dimethylaminodinitrile **4** in 54% yield. However, in contrast to the reaction without a solvent, the reaction of DTP **3** with dihydrofuran **1** in benzene (60 °C, 3 h) unexpectedly gave the dimethylaminopropenylidenedimethylammonium salt of substituted 1,1,3,11,13,13-hexacyanotrideca-1,3,5,7,9,11-hexaenide **6** (Scheme 2)‡ in 55% yield.

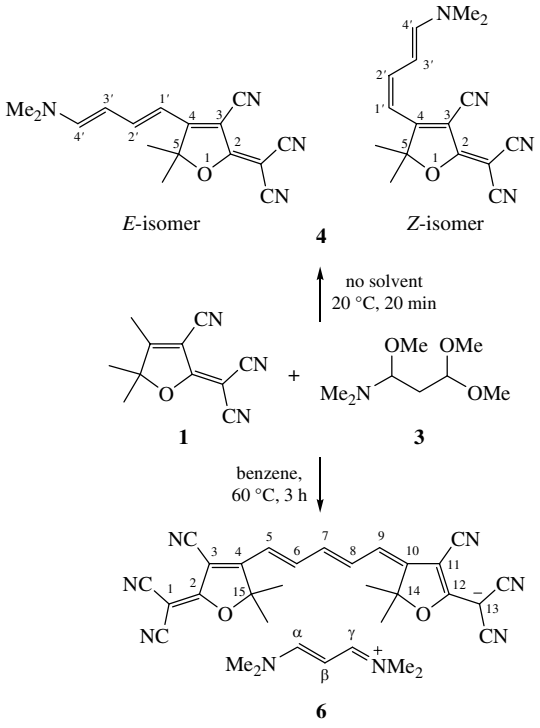
The structure of substituted tetraenic ω-dimethylaminodinitrile **4** was established based on ^{1}H NMR, ^{13}C NMR, UV and mass spectra. According to one- and two-dimensional (COSY, NOESY, HSQC and HMBC) ^{1}H and ^{13}C NMR spectra, dinitrile **4** is a mixture of *E*- and *Z*-isomers with respect to the $C^{1'}$–$C^{2'}$ bond; the isomer ratio is 2:1. The isomers were identified based on the coupling constants in the ^{1}H NMR spectrum (*E*-isomer: $J_{1'-2'}$ 13.5 Hz, $J_{3'-4'}$ 11.5 Hz, $J_{2'-3'}$ 12 Hz; *Z*-isomer:



Scheme 1

† The NMR spectra of compounds **4** and **6** were recorded on a Bruker DRX-500 spectrometer with working frequencies of 500.13 and 125.76 MHz for ^{1}H and ^{13}C nuclei, respectively, in [$^2H_6$]DMSO at 30 °C. The chemical shifts of ^{13}C and ^{1}H were calibrated using the signals of carbon atoms (δ 39.5 ppm) and residual protons (δ 2.5 ppm) of the solvent. Two-dimensional spectra were recorded using standard Bruker techniques. The ^{1}H NMR spectra of compounds **1**, **5** and **7**–**9** were recorded on a Bruker WM-250 instrument (250 MHz). Mass spectra (EI, 70 eV, direct injection) were recorded on an MS-30 instrument. Absorption spectra were measured with a Specord UV-VIS spectrophotometer. Dihydrofuran **1** was obtained according to a procedure.[5] ^{1}H NMR, δ: 1.59 (6H, Me), 2.36 (3H, Me). ^{13}C NMR, δ: 14.1 (Me at C^4), 23.16 (Me at C^5), 54.74 [*C*$(CN)_2$], 101.25 (C^5), 103.57 (C^3), 109.87, 111.40, 112.12 (CN), 177.17 (C^2), 185.66 (C^4). UV [EtOH, λ_{max}/nm (ε)]: 325 (12619).

Synthesis of dimethylaminopropenylidenedimethylammonium 3-cyano-2-dicyanomethylene-4,5,5-trimethyl-2,5-dihydrofurano-4-methylylide **5**. Aminal **2** (0.086 g, 0.5 mmol) was added to dihydrofuran **1** (0.1 g, 0.5 mmol). A colourless precipitate was formed in a short time (UV: λ_{max} = 312 nm); the UV spectrum did not change after heating at 55 °C for 2.5 h. The reaction mixture was concentrated and washed with anhydrous diethyl ether. The precipitate was dissolved in anhydrous acetone and precipitated with Et_2O to give 0.13 g (81%) of salt **5** as a colourless powder, mp 71–75 °C. ^{1}H NMR, δ: 1.3 (s, 6H, Me), 3.05 and 3.25 (2s, 2×6H, NMe_2), 4.15 (br. s, 2H, CH_2), 5.42 (t, 1H, H^β, *J* 12 Hz), 7.2 (d, 2H, H^α and H^γ, *J* 12 Hz). UV [EtOH, λ_{max}/nm (ε)]: 312 (84933).



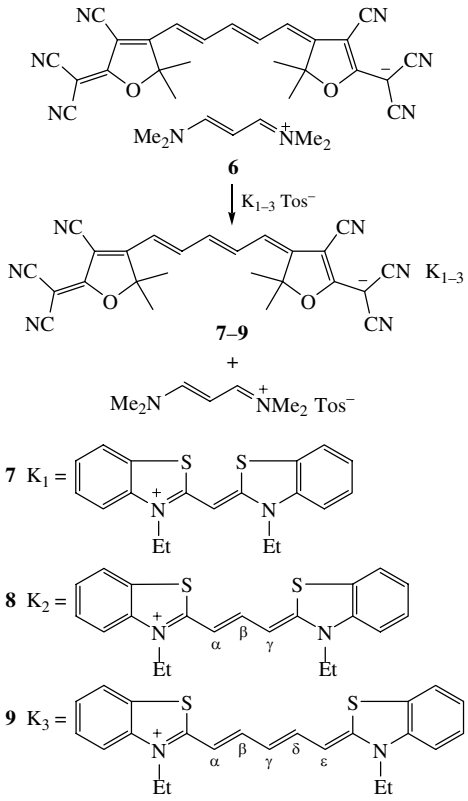
Scheme 2

$J_{1'-2'}$ 10 Hz, $J_{3'-4'}$ 11.5 Hz, $J_{2'-3'}$ 12 Hz). These data, along with the correlations in the NOESY spectrum, showed that both isomers had a *trans* configuration of the protons at the $C^{3'}$–$C^{4'}$ bond and existed predominantly as *S-trans* conformers with respect to the $C^{2'}$–$C^{3'}$ bond. The $H^{3'}$ protons in both isomers have NOE coupling with NMe_2 protons, which indicates their spatial proximity.

The structure of salt **6** was derived from the one- and two-dimensional (COSY, HSQC and HMBC) ^1H and ^{13}C NMR spectra.

The electronic spectrum of salt **6** contains a long-wave maximum with a very high molar absorption coefficient (λ_{max} = = 760 nm, ε = 178889) along with a short-wave maximum (λ_{max} = 312 nm, ε = 31111) belonging to dimethylamino-propenylidenedimethylammonium.

The trimethine cation of salt **6** is readily exchanged for a cyanine dye cation to give new cation-anionic dyes **7**–**9** in 59–90% yields; the electronic absorption spectra of the latter contain absorption maxima of the cationic and anionic components (Scheme 3).§



Scheme 3

‡ *Synthesis of 3-cyano-5,5-dimethyl-4-(4'-dimethylaminobuta-1',3'-dienyl)-2-dicyanomethylene-2,5-dihydrofuran* **4**. DTP **3** (0.36 g, 2 mmol) was added to dihydrofuran **1** (0.4 g, 2 mmol), and the mixture was thoroughly stirred. The reaction cease in 20 min according to UV-spectroscopic data. The reaction mixture was concentrated *in vacuo*; ethanol (5 ml) was added and the mixture was refluxed for 10–15 min. The precipitate was separated and washed with ethanol and diethyl ether. After that, anhydrous methanol (5 ml) was added to the precipitate and the mixture was refluxed for 10–15 min. After cooling, 0.3 g (54%) of substituted tetraenic ω-dimethylaminodinitrile **4** was obtained as purple crystals, mp > 260 °C. ^1H NMR, δ: *E*-isomer: 1.7 (s, 6H, Me), 3.19 and 3.35 (2s, 2×3H, NMe_2), 5.95 (d, 1H, $H^{1'}$, *J* 13.5 Hz), 6.18 (t, 1H, $H^{3'}$, *J* 11.5 Hz), 7.70 (t, 1H, $H^{2'}$, *J* 12 Hz), 8.07 (d, 1H, $H^{4'}$, *J* 11.5 Hz); *Z*-isomer: 1.45 (s, 6H, Me), 3.19 and 3.35 (2s, 2×3H, NMe_2), 5.81 (d, 1H, $H^{1'}$, *J* 10 Hz), 6.10 (t, 1H, $H^{3'}$, *J* 11.5 Hz), 8.07 (d, 1H, $H^{4'}$, *J* 11.5 Hz), 8.17 (t, 1H, $H^{2'}$, *J* 12 Hz). ^{13}C NMR, δ: *E*-isomer: 26.31 (Me), 26.86 (Me), 38.50 (NMe_2), 46.51 (NMe_2), 94.34 (C^6), 113.60, 115.01, 115.73 (CN), 104.11 ($C^{1'}$), 108.36 ($C^{3'}$), 154.43 ($C^{2'}$), 163.81 ($C^{4'}$), 170.04 (C^4), 176.21 (C^2); *Z*-isomer: 26.31 (Me), 26.86 (Me), 38.50 (NMe_2), 46.51 (NMe_2), 94.34 (C^6), 113.60, 115.01, 115.73 (CN), 104.11 ($C^{1'}$), 108.36 ($C^{3'}$), 153.57 ($C^{2'}$), 162.81 ($C^{4'}$). UV [$CHCl_3$, λ_{max}/nm (ε)]: 540 (89600); [EtOH, λ_{max}/nm]: 525. MS, *m*/*z*: 280 $[M]^+$.

Synthesis of substituted dimethylaminopropenylidenedimethylammonium 1,1,3,11,13,13-hexacyanotrideca-1,3,5,7,9,11-hexaenyde **6**. DTP **3** (0.35 g, 2 mmol) was added dropwise to dihydrofuran **1** (0.4 g, 2 mmol) in 8 ml of anhydrous benzene. The mixture was stirred for 3 h at 60 °C and concentrated *in vacuo*, and $CHCl_3$ was added to the crystalline residue. The precipitate was separated and washed with $CHCl_3$ and diethyl ether to give 0.31 g (55%) of salt **6** as a dark-brown powder, mp 204–208 °C. ^1H NMR, δ: 1.66 (s, 12H, Me), 3.07 and 3.25 (2s, 2×6H, NMe_2), 5.42 (t, 1H, H^{β}, *J* 12 Hz), 6.03 (d, 2H, H^9 and H^5, *J* 14 Hz), 6.42 (t, 1H, H^7, *J* 12.5 Hz), 7.05–7.73 (m, 4H, H^{α}, H^{γ}, H^6, H^8). ^{13}C NMR, δ: 26.97 (Me), 38.32 and 46.10 (NMe_2), 82.78 (C^3 and C^{11}), 90.43 (C^{β}), 94.3 (C^1 and C^{13}), 95.70 (C^4 and C^{10}), 109.36 (C^5 and C^9), 114.03, 114.94, 115.74 (CN), 126.45 (C^7), 150.09 (C^6 and C^8), 163.27 (C^{α} and C^{γ}), 169.02 (C^{14} and C^{15}), 176.65 (C^2 and C^{12}). UV [$CHCl_3$, λ_{max}/nm (ε)]: 312 (40444), 545 (24889), 760 (155556); [EtOH, λ_{max}/nm (ε)]: 312 (31111), 530 (25926), 760 (178889).

§ *General procedure for the synthesis of cation–anionic dyes* **7**–**9**. A filtered solution of K_1 tosylate (0.1 mmol) in a mixture of CH_2Cl_2 (4 ml) and EtOH (3 ml) was added to a filtered solution of salt **6** (0.13 mmol) in a mixture of anhydrous CH_2Cl_2 (5 ml) and anhydrous DMSO (0.2 ml). After 2 h, the solution was concentrated *in vacuo* and 5–7 ml of H_2O was added to the residue. The resulting precipitate was isolated and washed with H_2O, EtOH and diethyl ether to give 0.046 g (58%) of dye **7**, mp 225–230 °C. ^1H NMR, δ: 1.35 (t, 6H, $NCH_2\mathit{Me}$), 1.65 (s, 12H, Me), 4.65 (q, 4H, NCH_2Me), 6.0 (d, 2H, H^5 and H^9, *J* 14 Hz), 6.4 (t, 1H, H^7, *J* 12.5 Hz), 6.75 (s, 1H, CH), 7.5 (t, 2H, H^6 and H^8, *J* 12.5 Hz), 7.65–7.9 (m, 6H, Ph), 8.2 (d, 2H, Ph). UV [$CHCl_3$, λ_{max}/nm (ε)]: 430 (30880), 540 (16578), 770 (68622); [EtOH, λ_{max}/nm]: 430, 530, 770.

Dye **8** was obtained similarly from K_2Tos (0.1 mmol) and salt **6** (0.2 mmol), yield 90%, mp 168–172 °C. ^1H NMR, δ: 1.35 (t, 6H, $NCH_2\mathit{Me}$), 1.65 (s, 12H, Me), 4.4 (q, 4H, NCH_2Me), 6.02 (d, 2H, H^5 and H^9, *J* 14 Hz), 6.4 (t, 1H, H^7, *J* 12.5 Hz), 6.6 (d, 2H, H^{α} and H^{γ}, *J* 12.5 Hz), 7.4–7.8 (m, 9H, Ph, H^{β}, H^6 and H^8), 8.0 (d, 2H, Ph). UV [$CHCl_3$, λ_{max}/nm (ε)]: 540 (sh), 560 (82460), 770 (114380); [EtOH, λ_{max}/nm]: 530, 550, 750.

Dye **9** was obtained similarly from K_3Tos (0.1 mmol) and salt **6** (0.15 mmol), yield 65%, mp 242–245 °C. ^1H NMR, δ: 1.3 (t, 6H, $NCH_2\mathit{Me}$), 1.7 (s, 12H, Me), 4.4 (q, 4H, NCH_2Me), 6.0 (d, 2H, H^5 and H^9), 6.5 (m, 4H, H^{α}, H^{γ}, H^{ε}, H^7), 7.4–7.7 (m, 10H, Ph, H^{β}, H^{δ}, H^6, H^8), 8.0 (d, 2H, Ph). UV [$CHCl_3$, λ_{max}/nm (ε)]: 540 (15695), 665 (131840), 775 (97310); [EtOH, λ_{max}/nm]: 540, 650, 750.

The spectral and luminescent properties of conjugated polynitriles **4**, **6**, **7**–**9** along with the photophysical and photochemical processes involving these compounds will be published elsewhere.

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