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Reactions of β-dimethylaminoacrolein aminal and 3-dimethylamino-1,1,3-trimethoxypropane with alkylidenemalononitriles

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

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 495 135 5328; e-mail: kra@ioc.ac.ru

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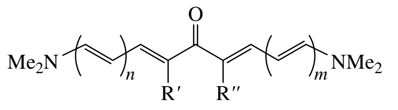
The reaction of alkylidenemalononitriles with β-dimethylaminoacrolein aminal unexpectedly results in (3-dimethylaminopropen-1-ylidene)malononitrile, whereas the reaction of 1-dimethylamino-1,3,3-trimethoxypropane gives unknown ω,ω-bis(3-dimethylaminopropen-2-ylidene)alkylidenemalononitriles.

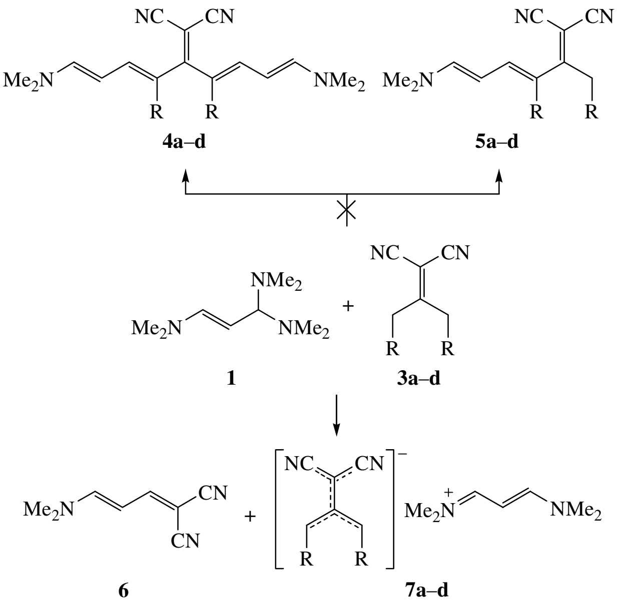
Previously, we developed the synthesis of aminals of conjugated ω-dimethylaminoaldehydes and 1-dialkylamino-1,3,3-trimethoxypropanes that have high reactivity and readily undergo condensation in the absence of a catalyst (and often without a solvent) with aliphatic, cyclic and heterocyclic ketones, diketones and CH acids at the α-methyl and methylene groups to give polyfunctional conjugated polyenes, many of which have unusual spectral properties, and some of which are polymethine dyes or semiproducts for the syntheses of dyes.[1]

A special place belongs to ω,ω-bis(dimethylaminopolyenyl)ketones (BDAK) (ketocyanines), which are bichromophore systems with cross-conjugation containing two polyene chains linked by a carbonyl group.[2,3] They contain electron-donating substituents (dimethylamino groups) at the ends, whereas the central carbonyl group is an electron-withdrawing substituent.



BDAK

These ketones contain chromophores interacting *via* the carbonyl group; they possess an extended π-electronic system absorbing in the visible and near-UV regions with high absorption coefficients. The electronic structure of BDAKs determines their specific properties, such as strong solvatochromism,[4,5] strong thermochromism,[6] intense fluorescence and generation of laser radiation.[7]



a R = H **c** R + R = $(CH_2)_3$
b R + R = $(CH_2)_2$ **d** R + R = $(CH_2)_4$

Scheme 1

Due to their simple structure, they are convenient models for studying photophysical and photochemical processes, including the interactions of chromophores in excited singlet and triplet states.[1]

Of undoubted interest was the synthesis of hitherto unknown cross-conjugated ω,ω-bis(3-dimethylaminopropen-2-ylidene)alkylidenemalononitriles that are BDAK analogues but contain a dicyanomethylene fragment instead of the carbonyl group. Furthermore, polyenes containing nitrile groups were used as materials for nonlinear optics.[8,9] Combining a dimethylaminopolyene chain and nitrile groups in the same molecule could result in polyenes with valuable properties.

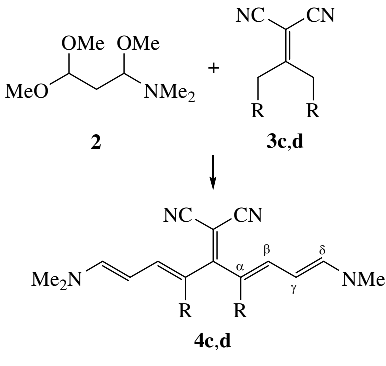
We studied the reaction of β-dimethylaminoacrolein aminal **1** and 1-dimethylamino-1,3,3-trimethoxypropane **2**[1] with alkylidenemalononitriles **3a–d**[11] in an attempt to synthesise ω,ω-bis(3-dimethylaminopropen-2-ylidene)alkylidenemalononitriles **4a–d**.

It was assumed that (by analogy with reactions of aminal **1** and compound **2** with ketones to give, depending on conditions, either BDAK or mono(dimethylaminopropenylidene)ketones, MDAK[2,3]), the reaction of aminal **1** and compound **2** with unsaturated dinitriles **3a–d** would give bis(dimethylaminodinitriles) **4a–d** or mono(dimethylaminodinitriles) **5a–d**.

However, it was found that the reaction of aminal **1** with unsaturated dinitriles **3a–d** occurs by a different pathway and unexpectedly gives (3-dimethylaminopropen-2-ylidene)malononitrile **6**, which is formed in high yields (up to 75%) under mild conditions (20–50 °C) in benzene or without a solvent, regardless of the reagent ratio (Scheme 1). The reaction also gives dimethylaminopropenylidenedimethylammonium salt **7a–d** as a by-product (10–15%).

The structure of compound **6** was confirmed by ^{1}H NMR, ^{13}C NMR, mass and UV spectra, as well as by elemental analyses. We have previously obtained dienedinitrile **6** in the reaction of aminal **1** with malonodinitrile.[12,†]

The reaction discovered in this study shows that unsaturated dinitriles **3a–d** serve as dicyanomethylene group carriers in the reaction with aminal **1**. Note that no reactions where alkylidenemalononitriles are carriers of the dicyanomethylene group have been reported in the literature.



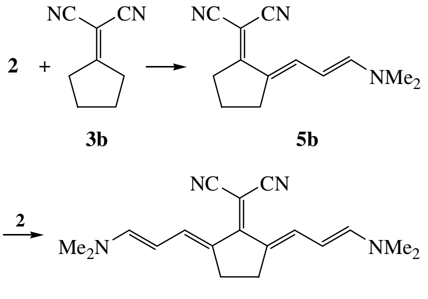
c R + R = $(CH_2)_3$
d R + R = $(CH_2)_4$

Scheme 2

We were able to obtain bis(dimethylaminodinitriles) **4c**,**d** by condensation of dinitriles **3c**,**d** with compound **2** (Scheme 2). In fact, the reaction of compound **2** with dinitriles **3c**,**d** without a catalyst and solvent (80 °C, 3 h) gave bis(dimethylaminodinitriles) **4c**,**d** in 56 and 51% yields, respectively.[‡]

The reaction of dinitrile **3b** with compound **2** gives a mixture of bis and mono(dimethylaminodinitriles) **4b** and **5b**, even if conditions are varied. To obtain pure bis(dimethylaminodinitrile) **4b**, it was more convenient to obtain mono(dimethylaminodinitrile) **5b** and then to use the reaction with compound **2** to convert **5b** to bis(dimethylaminodinitrile) **4b** (Scheme 3).[§]

We failed to obtain dinitriles **4a** and **5a**: the reaction of compound **2** with dinitrile **3a** gave only salt **7a**.



4b

Scheme 3

Bis(dimethylaminodinitriles) **4b–d** and mono(dimethylaminodinitrile) **5b** are dark violet compounds; their structures were confirmed by ^{1}H and ^{13}C NMR, mass and electronic absorption spectra. It was found by ^{1}H NMR that dinitriles **4b–d** and **5b** have the *trans* configuration of methine protons and exist mostly as *S-trans* conformers (J 12.5 Hz).

The spectral and luminescent properties of bis(dimethylaminodinitriles) **4b–d** will be published elsewhere.

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[†] ^{1}H NMR spectra were recorded with a Bruker WM-250 instrument (250 MHz). ^{13}C NMR spectra were obtained with a Bruker AC-200 instrument (50.32 MHz). Mass spectra (EI, 70 eV, direct injection) were obtained using an MS-30 instrument. Absorption spectra were recorded with a Specord UV-VIS spectrophotometer. The reaction was monitored by UV spectroscopy.

General procedure for reactions of aminal **1** *with alkylidenemalononitriles* **3a–d**. Aminal **1** (1.2 g, 7 mmol) was added dropwise to a solution of compound **3c** (1 g, 7 mmol) in dry benzene (6 ml). The reaction mixture was stirred for 7 h at 50 °C and concentrated *in vacuo* (< 50 °C); the residue (a semicrystalline mass) was treated by preparative TLC on SiO_2 (hexane–Me_2CO–EtOH, 5:2:1). The yellowish zone was eluted with $CHCl_3$ and the start zone was eluted with EtOH. A yellowish brown precipitate was obtained from the $CHCl_3$ eluate and washed with dry diethyl ether on filter to give 0.8 g (78%) of (3-dimethylaminopropen-2-ylidene)malononitrile **6**, mp 121–123 °C. ^{1}H NMR ($CDCl_3$) δ: 3.0 (s, 3H, NMe_2), 3.2 (s, 3H, NMe_2), 5.5 (t, 1H, H_γ, J 12 Hz), 7.12 (d, 1H, H_δ, J 12 Hz), 7.20 (d, 1H, H_β, J 12 Hz). ^{13}C NMR ($CDCl_3$) δ: 37.7 (Me), 45.7 (Me), 61.4 (C_α), 97.1 (C_γ), 115.6 (CN), 117.6 (CN), 157.5 (C_β), 160.0 (C_δ). UV [EtOH, λ_{max}/nm (ε)]: 376 (67301). MS, m/z: 147 [M]$^+$. Found (%): C, 65.34; H, 6.48. Calc. for $C_8H_9N_3$ (%): C, 65.30; H, 6.12.

Salt **7c** (0.2 g) was obtained as a viscous red oil from the EtOH eluate. ^{1}H NMR ($CDCl_3$) δ: 1.6, 2.25, 2.75 (m, 9H, cyclohexane protons), 3.05 (s, 6H, Me), 3.30 (s, 6H, Me), 5.05 (t, 1H, H_β, J 12 Hz), 7.9 (d, 2H, H_α and H_β, J 12 Hz). UV [EtOH, λ_{max}/nm (ε)]: 312 (32000).

[‡] *General procedure for the synthesis of ω,ω-bis(3-dimethylaminopropen-2-ylidene)alkylidenemalononitriles* **4c**,**d**. A mixture of nitrile **3c** (0.18 g, 1.2 mmol) and compound **2** (0.45 g, 2.5 mmol) was stirred for 3 h at 80–85 °C, cooled and concentrated *in vacuo*. The residue was washed with diethyl ether and then with water under stirring, and after that dried in a vacuum desiccator.

2,6-Bis(3-dimethylaminopropen-2-ylidene)cyclohexylidenemalononitrile **4c**: yield 56%, mp > 260 °C. ^{1}H NMR ($CDCl_3$) δ: 1.65 (t, 2H, CH_2), 2.25 (t, 4H, CH_2), 2.95 (s, 12H, Me), 5.2 (t, 2H, H_γ, J 12.5 Hz), 6.8 (d, 2H, H_δ, J 12.5 Hz), 7.3 (d, 2H, H_β, J 12.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.0 and 25.8 (CH_2), 41.0 (Me), 96.6 (C_γ), 122.2 (C_α), 122.9 (CN), 142.8 (C_β), 152.4 (C_δ), 171.3 (*C*CN), C-1 was not accumulated. MS, m/z: 308 [M]$^+$. UV [EtOH, λ_{max}/nm (ε)]: 560 (24640), 310 (8800); [$CHCl_3$, λ_{max}/nm (ε)]: 540 (52799), 310 (16133). IR (in KBr pellets, ν/cm^{-1}): 2104 (CN), 2148 (CN).

2,7-Bis(3-dimethylaminopropen-2-ylidene)cycloheptylidenemalononitrile **4d**: yield 51%, mp 210–214 °C. ^{1}H NMR ($CDCl_3$) δ: 1.65 (br. s, 4H, CH_2), 2.5 (br. s, 4H, CH_2), 2.8 (s, 12H, Me), 5.4 (t, 2H, H_γ, J 12.5 Hz), 6.45 (d, 2H, H_δ, J 12.5 Hz), 6.75 (d, 2H, H_β, J 12.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 28.5 and 30.3 (2CH_2), 40.8 (Me), 95.2 (C_γ), 119.4 (C_α), 125.7 (CN), 142.4 (C_β), 151.1 (C_δ), 164.6 and 180.9 [*C*=C(CN)$_2$ and *C*(CN)$_2$, arbitrary assignment]. MS, m/z: 322 [M]$^+$. UV [EtOH, λ_{max}/nm (ε)]: 515 (13417), 310 (9392); [$CHCl_3$, λ_{max}/nm (ε)]: 500 (52325), 305 (26162), 320 (27671), 333 (sh., 18615).

[§] *Synthesis of 2-(3'-dimethylaminopropen-2'-ylidene)cyclopentylidenedinitrile* **5b**. A mixture of dinitrile **3b** (1.8 g, 13 mmol) and compound **2** (2.3 g, 13.6 mmol) in dry benzene (4 ml) was heated for 1.5 h at 60 °C. The solvent was evaporated *in vacuo*. Preparative TLC of the residue on Al_2O_3 (Me_2CO–hexane, 1:2; elution with $CHCl_3$) gave 0.58 g (20%) of mono(dimethylaminodinitrile) **5b** as a dark violet precipitate, mp 122–127 °C. ^{1}H NMR ($CDCl_3$) δ: 1.7 (m, 2H, CH_2), 2.5 (m, 2H, CH_2), 2.8 (m, 2H, CH_2), 3.0 (s, 6H, NMe_2), 5.1 (m, 1H, H_γ, J 12.5 Hz), 7.0 (d, 1H, H_δ, J 12.5 Hz), 8.0 (d, 1H, H_β, J 12.5 Hz). MS, m/z: 213 [M]$^+$. UV [EtOH, λ_{max}/nm (ε)]: 520 (33281).

Synthesis of 2,5-bis(3'-dimethylaminopropen-2'-ylidene)cyclopentylidenedinitrile **4b**. Compound **2** (0.52 g, 0.33 mmol) was added dropwise with stirring to mono(dimethylaminodinitrile) **5b** (0.63 g, 3 mmol) in dry benzene (8 ml). The reaction mixture was heated for 2 h at 80 °C, cooled and concentrated. The residue was repeatedly washed with dry diethyl ether to give 0.16 g (18%) of dinitrile **4b** as dark violet viscous oil containing minor impurities according to NMR spectroscopic data. The product was purified by preparative TLC on Al_2O_3 (C_6H_{14}–Me_2CO, 2:1; elution with $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 2.5 (s, 4H, CH_2), 2.96 (s, 12H, Me), 5.05 (t, 2H, H_γ), 6.82 (d, 2H, H_δ), 7.9 (d, 2H, H_β). MS, m/z: 294 [M]$^+$. UV [EtOH, λ_{max}/nm (ε)]: 580 (14257), 280 (3866.3), 310 (2658); [$CHCl_3$, λ_{max}/nm (ε)]: 560 (15876), 280 (4939), 310 (2940).