Synthesis and properties of cross-conjugated ω,ω´-bis-dimethylamino ketones and dinitriles with *N*-acetyl- and *N*-benzylpiperidine cycles

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Reactions of *N*-acetyl- and *N*-benzyl-4-piperidones with aminal of β-dimethylaminoacrolein yielded ketocyanines bearing piperidine cycle. Reaction of 3-dimethylamino-1,1,3-trimethoxypropane with 1-acetylpiperidin-4-ylidenemalononitrile in the presence of ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), resulted in cross-conjugated ω,ω´-dimethylamino dinitrile. Protonation of ketocyanines bearing *N*-acetyl- and *N*-benzylpiperidine cycles with $Et_2O \cdot HBF_4$ (1 equiv.) furnished piperidinium salts, while protonation of the latter with $Et_2O \cdot HBF_4$ (2 equiv.) afforded doubly charged 4-hydroxypolymethine salts. Unlike protonation, reaction of 3,5-bis(3-dimethylaminoprop-2-enylidene)-1-acetylpiperidin-4-one with Me_2SO_4 involved only the oxygen atom and led to a singly charged 4-methoxypolymethine salt. Methylation of 3,5-bis(3-dimethylaminoprop-2-enylidene)-1-benzylpiperidin-4-one with Me_2SO_4 (1 equiv.) involved cyclic nitrogen atom and resulted in piperidinium salt; heating of the latter with the excess of Me_2SO_4 afforded doubly charged bis-methoxysulfonate. Starting from 4-methoxytetrahydropyridinium salts, *meso*-methoxythiapentacarbocyanine dyes were synthesized.

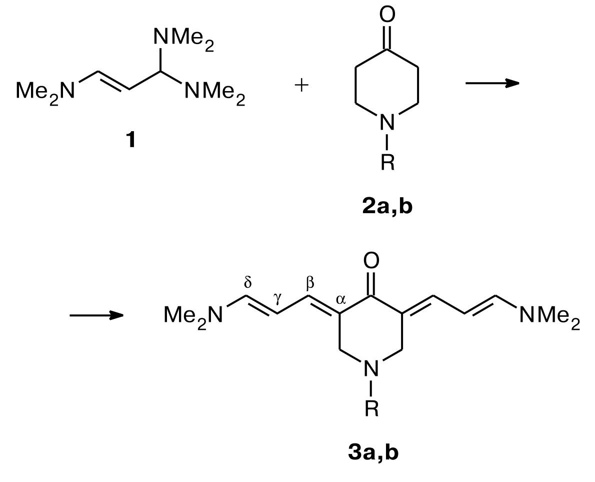
Key words: ketocyanines, malononitrile, protonation, methylation, polymethine salts, cyanines, absorption spectra.

Recently,[1] we synthesized the first representatives of cross-conjugated ω,ω´-bis-dimethylamino ketones bearing piperidine cycle in the polyene chain. In contrast to ketocyanines studied previously,[2] these compounds contain two reactive centers, which can be attacked by electrophiles, *e.g.*, the carbonyl group and the cyclic nitrogen atom. Spectral study and investigation of chemical properties of these compounds revealed several specific features.[3] Earlier,[1] analog of ketocyanine 3,5-bis(3-dimethylaminoprop-2-enylidene)-1-ethoxycarbonylpiperidin-4-one bearing dicyanomethylidene moiety instead of the carbonyl group was also synthesized. This replacement resulted in significant bathochromic shift of the absorption maximum in the electronic absorption spectra.

The present work was devoted to the synthesis and study of the properties of hitherto unknown cross-conjugated ω,ω´-bis-dimethylamino ketones and the corresponding dinitriles with *N*-benzyl and *N*-acetylpiperidine cycles.

Condensation of aminal of β-dimethylaminoacrolein **1** (see Ref. 4) with *N*-substituted 4-piperidones **2a**,**b** (65—70 °C, 40—90 min) afforded ketocyanines **3a**,**b** in 75—85% yields (Scheme 1).

Scheme 1



R = C(O)Me (**a**), CH_2Ph (**b**)

With the aim at synthesizing cross-conjugated dinitriles **4a**,**b** (analogs of ketocyanines **3a**,**b** with dicyanomethylidene fragment instead of the carbonyl group), we studied condensation of aminal **1** and 3-dimethylamino-1,1,3-trimethoxypropane **5** (see Ref. 5) with hitherto unknown (1-acetylpiperidin-4-ylidene)malononitrile **6a** and (1-benzylpiperidin-4-ylidene)malononitrile **6b** (see Ref. 6) (Scheme 2).

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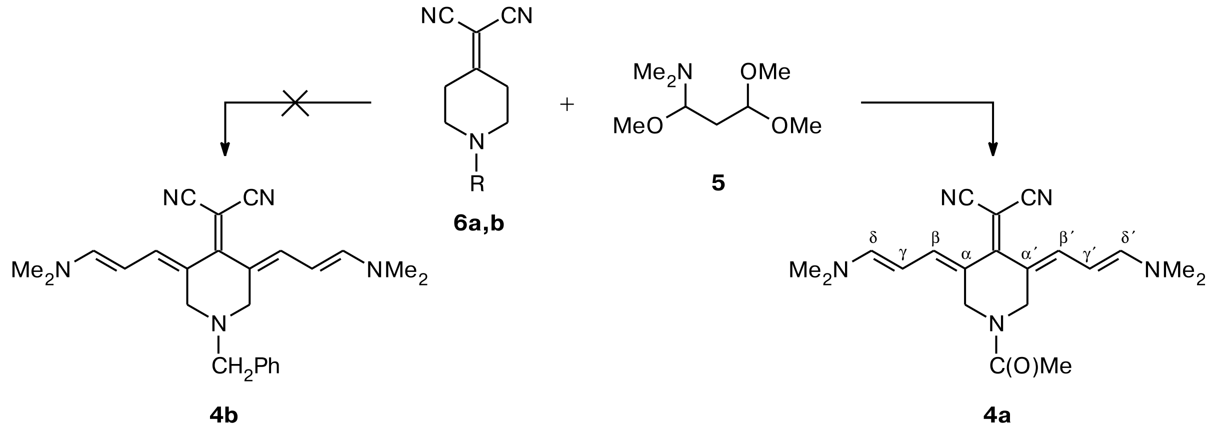
Scheme 2



6a,b

5

4b

4a

R = C(O)Me (**a**), CH$_2$Ph (**b**)

The attempts to prepare polyenic dinitriles **4a**,**b** using aminal **1** failed. Cross-conjugated dinitrile **4a** was accessed in 20% yield by the condensation of compound **5** with dinitrile **6a** only in the presence of ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$). The latter, apparently, contribute in the polarization of the C—H bonds of compound **6a**. All attempts to synthesize benzyl-substituted analog **4b** were unsuccessful.

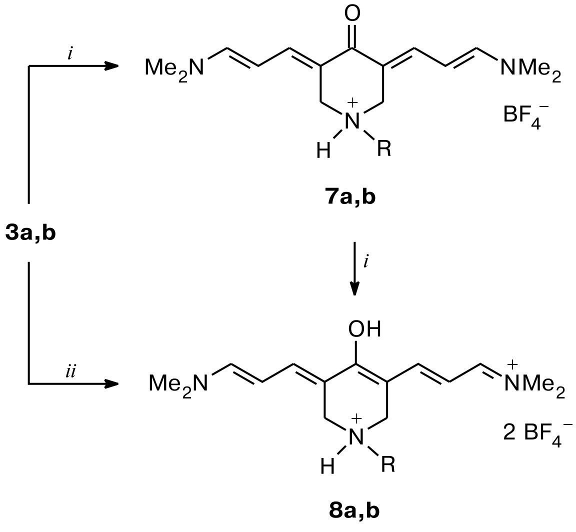
Structures of cross-conjugated polyenes **3a**,**b** and **4a** were established based on ^{1}H and ^{13}C NMR spectroscopy, UV spectroscopy, mass spectrometry and confirmed by microanalysis.

The ^{1}H and ^{13}C NMR spectra were interpreted using 2D NMR experiments (COSY, HSQC, and HMBC). The values of the vicinal coupling constants $^3J_{\beta-\gamma}$ and $^3J_{\gamma-\delta}$ equal 12.0 and 12.4 Hz, respectively, indicate the *trans*-configuration of the protons of the $C_\beta H-C_\gamma H-C_\delta H$ moiety and domination of S-*trans*-conformation for the diene fragments of the polymethine chains.

Comparison of the UV spectra of ketocyanine **3a** and dinitrile **4a** reveals that absorption maximum of dinitrile **4a** shifted to longer wavelengths by 80 nm. It is of note that UV spectra of dinitrile **4a**, unlike that of ketocyanines **3a**,**b**, exhibits not only long wavelength band with high absorption coefficient ε (ε = 70000—90000 L mol^{-1} cm^{-1}) but also short wavelength band with the maximum at 310—320 nm with significantly lower ε value (ε = = 10000—11000 L mol^{-1} cm^{-1}). Ketocyanines **3a**,**b** and dinitrile **4a** show bathochromic solvent effect: on going from non-polar (CHCl$_3$) to polar (EtOH) solvent the absorption band shifted to longer wavelengths by 20 nm.

Ketocyanines **3a**,**b** possess properties of the Lewis bases. Thus, treatment of these compounds with $Et_2O \cdot HBF_4$ (1 equiv.) resulted in the protonation on the cyclic nitrogen atom to give piperidinium salts **7a**,**b** in the yields of 66 and 75%, respectively. Further treatment of the latter with $Et_2O \cdot HBF_4$ (1 eqiuv.) afforded the doubly charged 4-hydroxypolymethine salts **8a**,**b** due to protonation on the oxygen atom. Salts **8a**,**b** can be prepared directly from ketocyanines **3a**,**b** using 2 equiv. of $Et_2O \cdot HBF_4$ (Scheme 3).

Scheme 3



3a,b

7a,b

8a,b

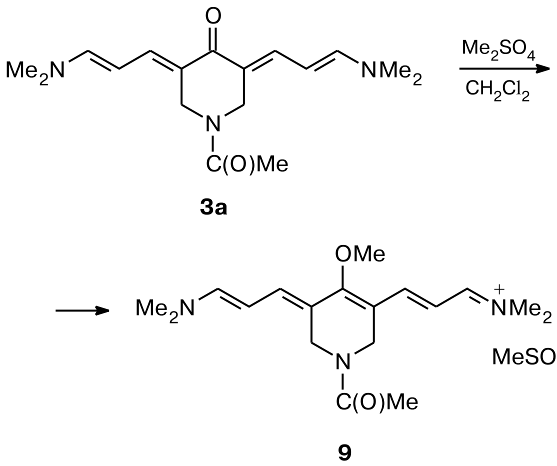
R = C(O)Me (**a**), CH$_2$Ph (**b**)

Reagents and conditions: $Et_2O \cdot HBF_4$, 1 equiv. (*i*), 2 equiv. (*ii*); **7a** (66%), **7b** (75%), **8a** (86% from **7a**, 73% from **3a**), **8b** (45% from **7b**, 77% from **3b**).

In contrast to compounds **3a**,**b**, reaction of dinitrile **4a** with $Et_2O \cdot HBF_4$ failed and dinitrile was recovered.

Direction of the alkylation of ketocyanines **3a**,**b** depends on the nature of the substituent at the cyclic nitrogen atom. Unlike protonation, methylation of ketocyanine **3a** by Me_2SO_4 in CH_2Cl_2 involved only the oxygen atom to give a singly charged 4-methoxypolymethine salt **9** (Scheme 4).

Scheme 4



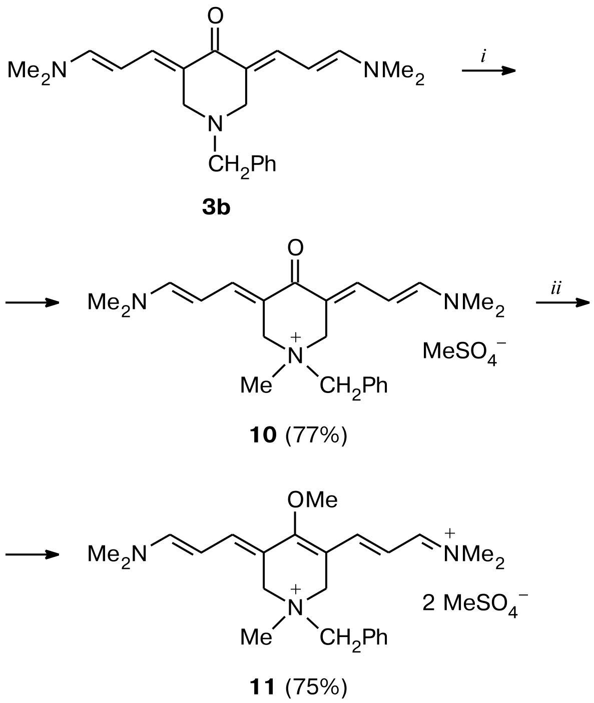
On treatment of ketocyanine **3a** with methyl sulfate (1 equiv.), product **9** begins to form even at 20 °C, its amount increasing during the reaction. When the excess of Me_2SO_4 is used and the reaction carried out at elevated temperature, the reaction rate is higher and the yield of **9** is also higher. In contrast to ketocyanine **3a**, treatment of ketocyanine **3b** with Me_2SO_4 (1 equiv.) resulted in methylation at cyclic nitrogen atom to give piperidinium methoxysulfonate **10**. The latter under the action of large excess of Me_2SO_4 at 50—55 °C was converted into tetrahydropyridinium bis-methoxysulfonate sulfate **11** (Scheme 5).

Structures of salts **7a**,**b**, **8a**,**b**, and **9**—**11** were confirmed by ^1H NMR spectra in DMSO-d_6 and electronic absorption spectra.

The UV spectra of salts **7a**,**b** protonated at the nitrogen atom and quaternary ammonium salt **10** in $CHCl_3$ (λ_{max} = 470—485 nm, yellow colored solution) are almost identical to that of the starting ketocyanines **3a**,**b** (λ_{max} = = 470—475 nm). The absorption band in the spectra of the salts protonated and methylated at the oxygen atom significantly shifted in the longer wavelengths. Thus, salts **8a**,**b** have absorption maxima at 600—620 nm, while salts **9** and **11** exhibit maxima at 640 nm (blue colored solutions).

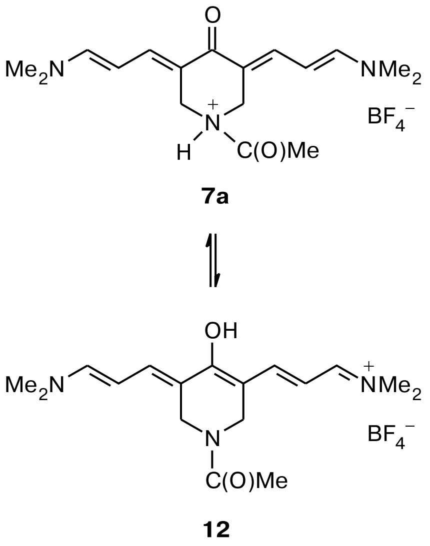
Specific spectral behavior of the salt **7a** is of interest; its absorption spectra are notably solvent dependent. Thus, the spectra of **7a** in DMSO and MeCN exhibit one absorption band with maximum at 475 nm, while in $CHCl_3$ and CH_2Cl_2 they have two bands with maxima at 470 and 615 nm, whose intensity ratio depends on concentration. Removal of $CHCl_3$ and CH_2Cl_2 from the solutions to dryness afforded salt **7a**, whose spectra in DMSO and MeCN have only one maximum at 470 nm. Apparently, in very dilute solutions of salt **7a** in $CHCl_3$ and CH_2Cl_2, proton migration from the nitrogen to oxygen occurs and salts **7a** and **12** equilibrate (Scheme 6).

Scheme 5



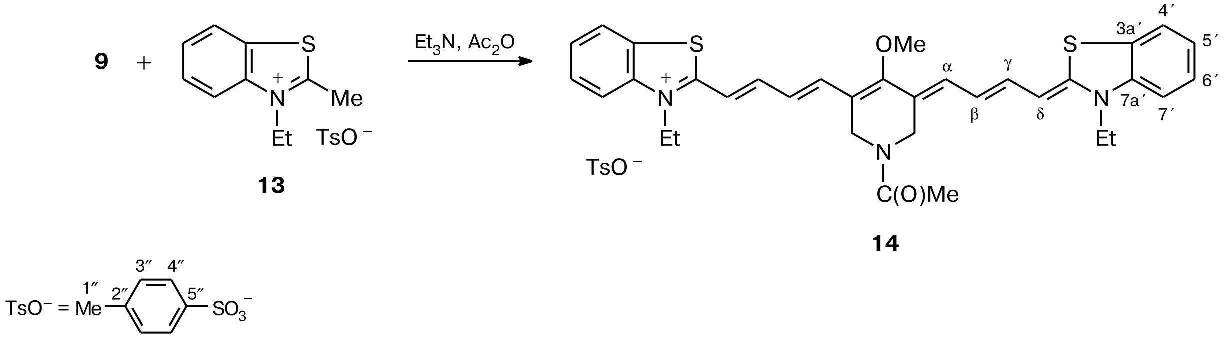
Reagents: Me_2SO_4, CH_2Cl_2, 1 equiv. (*i*); 6 equiv. (*ii*).

Scheme 6

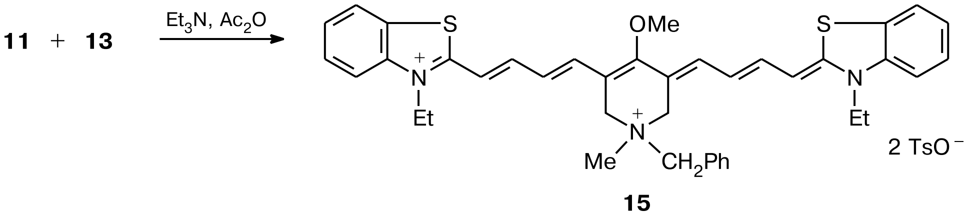


In the presence of triethylamine, salts **9** and **11** react with benzothiazolium salt **13** affording hitherto unknown *meso*-methoxythiapentacarbocyanine dyes **14** and **15**. The

Scheme 7



Scheme 8



structures of dyes **14** and **15** were established by ^{1}H NMR spectroscopy and electronic absorption spectroscopy (Schemes 7 and 8).

Dye **15** is the doubly charged and contains 2 equiv. of TsO$^-$ anions. The absorption spectrum of dye **15** shows longest wavelength absorption with maximum at 964 nm with a very high absorption coefficient $\varepsilon = 237703$ L mol^{-1} cm^{-1}. This band is significantly shifted to shortest wavelengths (by 38—42 nm) as compared with singly charged dyes **14** and *meso*-alkoxythiapentacarcocyanine dyes synthesized earlier.[2,3]

Good solubility in water is the specific feature of dye **15**, which could be used for the study of its complexation with DNA.

In summary, methylation of ketocyanines bearing piperidine cycle afforded 4-methoxytetrahydropyridinium salts, which were used for the synthesis of hitherto unknown alkoxythiapentacarbocyanine dyes. The photochemical and photophysical investigation of the latter will be published elsewhere.

Experimental

^{1}H NMR spectra of compounds **6a**, **7a**,**b**, **8a**,**b**, **9**—**11**, **14**, and **15** were recorded on a Bruker Avance 300 instrument (300.13 MHz) in DMSO-d$_6$. ^{1}H and ^{13}C NMR spectra of compounds **3a**,**b** were measured and 2D NMR experiments (COSY, HSQC, and HMBC) were performed on a Bruker Avance 600 instrument (600.13 MHz (^{1}H) and 150.90 MHz (^{13}C)).

Absorption spectra were recorded on Specord UV-Vis (compounds **6a**, **7a**,**b**, **8a**,**b**, and **9**—**11**) and U 1900 (compounds **14** and **15**) spectrophotometers. For low soluble compounds, the extinction coefficient (ε) was not determined. MS spectra (EI, 70 eV) were recorded on a Kratos MS-30 instrument, high resolution MS were performed on a Bruker micrOTOF II instrument with electrospray ionization (ESI). The reaction course was monitored by UV/VIS spectroscopy. All reactions with $Et_2O \cdot HBF_4$ were performed under argon. Dry, acid-free CH_2Cl_2 was used as a solvent. Due to low stability, microanalysis of the salts protonated by the oxygen atom was not performed.

2-(1-Acetylpiperidin-4-ylidene)malononitrile (6a). A mixture of 1-acetyl-4-piperidone **2a** (4 g, 0.028 mol), malononitrile (2.8 g, 0.045 mol), ammonium acetate (0.84 g, 0.011 mol), glacial acetic acid (2 g, 0.033 mol), and benzene (15 mL) was refluxed for 2 h with azeotropic removal of water. The reaction mixture was concentrated *in vacuo*, diethyl ether (100 mL) was added to the residue, the precipitate that formed was separated and suspended in benzene (100 mL). Benzene solution was filtered, washed with aqueous $NaHCO_3$ and water, the organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. Yield of dinitrile **6a** was 1.55 g (27%), m.p. 101—103 °C. Found (%): C, 63.22; H, 5.61; N, 22.10. $C_{10}H_{11}N_3O$. Calculated (%): C, 63.48; H, 5.86; N, 22.21. UV (EtOH), λ_{max}/nm (ε): 225 (5815), 265 (4500). ^{1}H NMR (CDCl$_3$), δ: 2.17 (s, 3 H, CH$_3$); 2.79 (m, 4 H, CH$_2$); 3.65 (m, 2 H, CH$_2$); 3.79 (m, 2 H, CH$_2$).

1-Acetyl-3,5-bis(3-dimethylaminopropen-2-enylidene)-4-piperidone (3a). To 1-acetyl-4-piperidone **2a** (0.56 g, 4 mmol), aminal **1** (1.37 g, 8 mmol) was added dropwise. The reaction mixture was heated at 65—70 °C for 40 min. To a crystalline residue, anhydrous diethyl ether (10 mL) was added, the precipitate that formed was filtered, washed with diethyl ether, and dried. The yield of compound **3a** was 1.02 g (85%), bright orange crystals, m.p. 205—208 °C. Found (%): C, 66.96; H, 8.47; N, 14.01. $C_{17}H_{25}N_3O_2$. Calculated (%): C, 67.30; H, 8.31; N, 13.85. UV, λ_{max}/nm (ε): 490 (62300) (EtOH), 470 (54540) ($CHCl_3$). ^1H NMR (DMSO-d_6), δ: 2.05 (s, 3 H, $NCOCH_3$); 2.90 (s, 12 H, NMe_2); 4.28 (s, 2 H, CH_2); 4.31 (s, 2 H, CH_2); 4.97 (t, 1 H, γ-H, *J* = 12.4 MHz); 5.12 (t, 1 H, γ´-H, *J* = 12.4 MHz); 7.03 (d, 1 H, δ-H, *J* = 12.4 MHz); 7.07 (d, 1 H, δ´-H, *J* = 12.4 MHz); 7.17 (d, 2 H, β and β´, *J* = 12.4 MHz). ^1H NMR ($CDCl_3$), δ: 2.16 (s, 3 H, $NCOCH_3$); 2.94 (s, 12 H, NMe_2); 4.33 (s, 2 H, CH_2); 4.52 (s, 2 H, CH_2); 4.96 (t, 1 H, γ-H, *J* = 12.4 MHz); 5.12 (t, 1 H, γ´-H, *J* = 12.4 MHz); 6.76 (d, 2 H, δ-H and δ´-H, *J* = 12.4 MHz); 7.40 (d, 1 H, β-H, *J* = 12.4 MHz); 7.43 (d, 1 H, β´-H, *J* = 12.4 MHz). ^{13}C NMR ($CDCl_3$), δ: 21.53 ($NCO\underline{C}H_3$); 39.5 (NMe_2); 41.97 (CH_2); 46.15 (CH_2); 93.11 (γ-C); 94.5 (γ´-C); 119.10 (α-C); 137.52 (β-C); 138.93 (β´-C); 151.77 (δ-C); 168.91 ($N\underline{C}OCH_3$); 183.61 (CO). MS (ESI), *m/z*: $[M + H]^+$, found 304.2021, calculated 304.2031, $C_{17}H_{25}N_3O_2$.

1-Benzyl-3,5-bis(3-dimethylaminoprop-2-enylidene)-4-piperidone (3b). Aminal **1** (1.37 g, 8 mmol) was added dropwise to 1-benzyl-4-piperidone **2b** (0.76 g, 4 mmol). The reaction mixture was heated with stirring at 65—70 °C for 1.5 h. The crystalline reaction mixture was diluted with anhydrous diethyl ether (10 mL), the bright orange precipitate was filtered, and washed with diethyl ether. The yield of compound **3b** was 1.05 g (75%), m.p. 198—201 °C. Found (%): C, 74.68; H, 8.32; N, 11.97. $C_{22}H_{29}N_3O$. Calculated (%): C, 75.18; H, 8.32; N, 11.96. UV, λ_{max}/nm (ε): 495 (68200) (EtOH), 475 (66200) ($CHCl_3$). ^1H NMR ($CDCl_3$), δ: 2.89 (s, 12 H, NMe_2); 3.51 (s, 4 H, CH_2); 3.71 (s, 2 H, $NC\underline{H}_2Ph$); 4.86 (t, 2 H, γ-H, *J* = 12.4 Hz); 6.69 (d, 2 H, δ-H, *J* = 12.6 Hz); 7.24—7.37 (m, 5 H, Ph); 7.43(d, 2 H, β-H, *J* = 12.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 40.61 (NMe_2); 52.97 (CH_2); 60.99 ($N\underline{C}H_2Ph$); 94.32 (γ-C); 120.88 (α-C); 126.81 (*p*-C, Ph); 128.26 (*m*-C, Ph); 129.21 (*o*-C, Ph); 137.64 (β-C); 138.94 ($NCH_2\underline{C}$); 150.81 (δ-C); 184.41 (CO). MS (EI), *m/z*: 351 $[M]^+$.

[1-Acetyl-3,5-bis(3-dimethylaminoprop-2-enylidene)piperidin-4-ylidene]malononitrile (4a). A mixture of compound **6a** (0.4 g, 2.1 mmol) and ion liquid $[bmim]BF_4$ (1.2 g, 5.3 mmol) was extensively stirred until fine dispersion was formed. Then 3-dimethylamino-1,1,3-trimethoxypropane **5** (0.94 g, 5.3 mmol) was added and the reaction mixture was kept at 20—22 °C for 24 h, and the solvent was removed *in vacuo*. Water (30 mL) was added to the residue, the precipitate that formed was filtered, washed with water, diethyl ether, and dried. The yield of compound **4a** was 0.1 g (20%), brawn crystals, m.p. >260 °C. UV, λ_{max}/nm (ε): 570 (89500) (EtOH), 550 (67100) ($CHCl_3$). ^1H NMR (DMSO-d_6), δ: 2.05 (s, 3 H, $NCOCH_3$); 3.05 (s, 12 H, NMe_2); 4.06 (d, 4 H, CH_2, *J* = 12.4 Hz); 5.38 (t, 1 H, γ-H, *J* = 12 Hz); 5.57 (t, 1 H, γ´-H, *J* = 12 Hz); 7.35 (d, 4 H, β-H and δ-H, *J* = 12.4 Hz). MS (ESI), *m/z*: $[M + H]^+$, found 352.2125, calculated: 352.2143, $C_{20}H_{25}N_5O$.

1-Acetyl-3,5-bis(3-dimethylaminoprop-2-enylidene)-4-oxopiperidinium tetrafluoroborate (7a). To a mixture of ketocyanine **3a** (0.1 g, 0.33 mmol) in CH_2Cl_2 (3 mL) cooled to –5 °C, a solution of $Et_2O \cdot HBF_4$ (0.06 g, 0.34 mmol) in CH_2Cl_2 (1 mL) was added dropwise. The reaction mixture was stirred at –5 °C for 1 h and the solvent was removed *in vacuo*. Anhydrous diethyl ether was added to the crystalline residue, the precipitate was filtered and thoroughly washed with anhydrous diethyl ether. The yield of tetrafluoroborate **7a** was 0.085 g (66%), black crystals, m.p. >235 °C. Found (%): C, 52.40; H, 6.52; N, 10.66. $C_{17}H_{26}BF_4N_3O_2$. Calculated (%): C, 52.19; H, 6.70; N, 10.74. UV, λ_{max}/nm: 475 (DMSO), 475 (CH_3CN), 470 and 615 ($CHCl_3$), 470 and 615 (CH_2Cl_2). ^1H NMR (DMSO-d_6), δ: 2.03 (s, 3 H, $NCOCH_3$); 3.00 (s, 12 H, NMe_2); 4.28 (s, 2 H, CH_2); 4.31 (s, 2 H, CH_2); 5.25 (t, 1 H, γ-H, *J* = 12.5 Hz); 5.38 (t, 1 H, γ´-H, *J* = 12.5 Hz); 7.23 (d, 2 H, δ-H and δ´-H, *J* = 12.5 Hz); 7.32 (d, 2 H, β-H and β´-H, *J* = 12.5 Hz).

1-Benzyl-3,5-bis(3-dimethylaminoprop-2-enylidene)-4-oxopiperidinium tetrafluoroborate (7b). To a stirred mixture of ketocyanine **3b** (0.06 g, 0.17 mmol) in CH_2Cl_2 (1.5 mL) cooled to –5—0 °C, a solution of $Et_2O \cdot HBF_4$ (0.03 g, 0.17 mmol) in CH_2Cl_2 (1 mL) was added dropwise. After 30 min, the solvent was removed *in vacuo*, the residue was triturated with diethyl ether, the precipitate that formed was filtered, and washed with anhydrous diethyl ether. The yield of tetrafluoroborate **7b** was 0.055 g (75%), black crystals, m.p. >240 °C. Found (%): C, 59.80; H. 6.62; N, 9.35. $C_{22}H_{30}BF_4N_3O$. Calculated (%): C, 60.15; H, 6.88; N, 9.57. UV ($CHCl_3$), λ_{max}/nm (ε): 480 (54468). ^1H NMR (DMSO-d_6), δ: 2.90 (br.s, 12 H, NMe_2); 3.90 (br.s, 4 H, CH_2); 4.20 (s, 2 H, CH_2Ph); 4.85 (t, 2 H, γ-H and γ´-H, *J* = 12.5 Hz); 7.15 (d, 2 H, δ-H and δ´-H, *J* = 12.5 Hz); 7.38 (d, 2 H, β-H and β´-H, *J* = 12.5 Hz); 7.45 (br.s, 5 H, Ph).

1-Acetyl-3-(3-dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-hydroxy-1,2,3,6-tetrahydropyridimium bis-tetrafluoroborate (8a). ***A.*** To a mixture of compound **7a** (0.071 g, 0.18 mmol) in anhydrous CH_2Cl_2 (1.5 mL) cooled to –5 °C, a solution of $Et_2O \cdot HBF_4$ (0.03 g, 0.17 mmol) in CH_2Cl_2 (1 mL) was added dropwise. The reaction mixture was kept for 30 min and the solvent was removed *in vacuo*, the residue was washed several times with anhydrous diethyl ether. The yield of compound **8a** was 0.075 g (86%), black crystals, m.p. 168—170 °C. UV, λ_{max}/nm (ε): 620 (89619) (CH_2Cl_2); 620 ($CHCl_3$). ^1H NMR (DMSO-d_6), δ: 2.10 (s, 3 H, NCOMe); 3.15 (br.s, 12 H, NMe_2); 4.25 (br.s, 4 H, CH_2); 5.61 (t, 1 H, γ-H, *J* = 12.5 Hz); 5.75 (t, 1 H, γ´-H, *J* = 12.5 Hz); 7.50—7.65 (m, 4 H, β-H, β´-H, δ-H, and δ´-H).

B. To a mixture of ketocyanine **3a** (0.10 g, 0.33 mmol) in CH_2Cl_2 (3 mL) cooled to –5—0 °C, a solution of $Et_2O \cdot HBF_4$ (0.12 g, 0.68 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The reaction mixture was stirred at –5—0 °C for 1 h and the solvent was removed *in vacuo*. Anhydrous diethyl ether was added to the residue, the precipitate that formed was filtered and washed with anhydrous diethyl ether. The yield of compound **8a** was 0.11 g (73%), the product was identical to the one described above.

1-Benzyl-3-(3-dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-hydroxy-1,2,3,6-tetrahydropyridinium bis-tetrafluoroborate (8b). ***A.*** To a mixture of tetrafluoroborate **7b** (0.028 g, 0.06 mmol) in CH_2Cl_2 (1 mL) cooled to –5—0 °C, a solution of $Et_2O \cdot HBF_4$ (0.012 g, 0.07 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise with stirring. In the reaction mixture, the precipitate immediately formed. The UV spectrum of the precipitate in $CHCl_3$ showed absorption maximum at 600 nm, no absorption for the starting tetrafluoroborate **7b** (λ_{max} = 470 nm) was detected. After 15 min, the solution was decanted, the precipitate was successfully washed with anhydrous diethyl ether. The yield of bis-tetrafluoroborate **8b** was 0.015 g (45%), black crystals, m.p. 120—124 °C (decomp.) UV ($CHCl_3$), λ_{max}/nm (ε): 600 (28745). ^1H NMR (DMSO-d_6), δ: 3.10 (br.s, 6 H, NMe_2); 3.20 (br.s, 6 H, Me_2N^+); 3.90 (br.s, 2 H, CH_2); 4.15 (br.s, 2 H, CH_2); 4.35 (s, 2 H, $C\underline{H}_2Ph$); 5.45 (t, 2 H, γ-H and γ´-H, *J* = 12.5 Hz); 7.47 (br.s, 5 H, Ph), 7.60—7.80 (m, 4 H, β-H, β´-H, δ-H, δ´-H); 10.35 (br.s, 1 H, OH).

B. To a mixture of ketocyanine **3b** (0.12 g, 0.34 mmol) in CH_2Cl_2 (3 mL) cooled to –5—0 °C, a solution of $Et_2O \cdot HBF_4$ (0.12 g, 0.75 mmol) in CH_2Cl_2 (1 mL) was added dropwise with stirring. The color of the reaction mixture immediately turned blue. In the UV spectra of the reaction mixture, new absorption band with maximum at 600 nm appeared, while absorption band with maximum at 470 nm disappeared. After 30 min, the solution was decanted, the precipitate that formed was successfully washed with anhydrous diethyl ether. The yield of bis-tetrafluoroborate **8b** was 0.14 g (77%), m.p. 124—127 °C (decomp.). The UV and ^{1}H NMR spectra of the sample are identical to the described above.

N*-{1-Acetyl-3-[3-(3-dimethylaminoprop-2-enylidene)-4-methoxy-1,2,3,6-tetrahydropyridin-5-yl]prop-2-enylidene}-*N,N*-dimethylammonium methoxysulfonate (9).** ***A. To a solution of ketocyanine **3a** (0.3 g, 1 mmol) in CH_2Cl_2 (4.5 mL), a solution of Me_2SO_4 (0.36 g, 2.86 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise. The reaction mixture was refluxed with stirring for 8 h, then the solvent was removed *in vacuo*. The residue was triturated with anhydrous diethyl ether, the precipitate that formed was filtered, and washed with diethyl ether. The yield of compound **9** was 26 g (62%), black powder, m.p. 168—170 °C. Found (%): C, 53.34; H, 7.15; N, 9.52. $C_{19}H_{31}N_3O_6S$. Calculated (%): C, 53.13; H, 7.27; N, 9.78. UV, λ_{max}/nm (ε): 640 (103350) (EtOH); 640 (70928) ($CHCl_3$). ^{1}H NMR (DMSO-d_6), δ: 2.05 (s, 3 H, NCOMe); 3.20 (br.s, 12 H, NMe_2, Me_2N^+); 3.78 (s, 3 H, OMe); 4.30 (br.s, 4 H, CH_2); 5.75 (t, 1 H, γ-H, *J* = 12.5 Hz); 5.88 (t, 1 H, γ´-H, *J* = 12.5 Hz); 7.40 (m, 2 H, β-H and β´-H); 7.85 (m, 2 H, δ-H and δ´-H); 3.40 (the signal of the methyl group of anion $MeSO_4^-$ overlaps with the signal of the protons of H_2O in DMSO-d_6).

B. To a solution of ketocyanine **3a** (0.1 g, 0.33 mmol) in CH_2Cl_2 (1.5 mL), a solution of Me_2SO_4 (0.04 g, 0.33 mmol) in CH_2Cl_2 (1 mL) was added dropwise with stirring. The reaction mixture was stirred at 20—25 °C monitoring the reaction course with UV spectroscopy. After 3.5 h, the main absorption band was the band with maximum at 470 nm, but the bans of low intensity at 640 nm was also observed. The aliquot of the reaction mixture was taken, the solvent was removed *in vacuo*, the precipitate that formed was washed with anhydrous diethyl ether, and dried. The ^{1}H NMR spectrum of this precipitate was similar to that of the starting ketocyanine **3a** and contained signals of low intensity attributed to methyl sulfate **9**. The reaction mixture was then stirred for 3 days until the band with the maximum at 470 nm disappeared in the UV spectra; the intensity of the band with maximum at 640 nm increased. Methyl sulfate **9** was separated as described above.

1-Benzyl-3,5-bis(3-dimethylaminoprop-2-enylidene)-1-methyl-4-oxopiperidinium methoxysulfonate (10). To a mixture of ketocyanine **3b** (0.15 g, 0.44 mmol) in CH_2Cl_2 (1 mL), a solution of Me_2SO_4 (0.056 g, 0.44 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise at 20 °C. The reaction mixture turned dark, the absorption band shifted to longer wavelengths by 10 nm as compared with that of starting ketocyanine **3b**. (The UV spectra became symmetrical in contrast to the spectra of starting ketocyanine **3b** with the shoulder). After 20 min, the solvent was removed *in vacuo*, the residue was triturated with anhydrous diethyl ether. The yield of compound **10** was 0.16 g (77%), dark violet crystals, m.p. 120—122 °C. Found (%): C, 60.05; H, 7.21; N, 8.52. $C_{24}H_{35}N_3O_5S$. Calculated (%): C, 60.35; H, 7.39; N, 8.80. UV ($CHCl_3$), λ_{max}/nm (ε): 485 (75202). ^{1}H NMR (DMSO-d_6), δ: 2.95 (br.s, 12 H, NMe_2); 3.35 (s, 3 H, MeN^+); 3.40 (s, 3 H, $MeSO_4$); 4.30 (s, 4 H, CH_2); 4.45 (s, 2 H, $C\underline{H}_2Ph$); 5.05 (t, 2 H, γ-H and γ´-H, *J* = 12.5 Hz); 7.25—7.40 (m, 4 H, β-H, β´-H, δ-H, δ´-H); 7.45—7.60 (m, 5 H, Ph).

1-Benzyl-3-(3-dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-methoxy-1-methyl-1,2,3,6-tetrahydropyridinium bis-methoxysulfonate (11). To compound **10** (0.15 g, 0.31 mmol), Me_2SO_4 (0.24 g, 1.9 mmol) was added and the reaction mixture was heated at 50—55 °C; the course of the reaction was monitored with UV spectroscopy. After 1.5 h, no absorption with maximum at 485 nm attributed to methyl sulfate **10** was detected, the observed band with maximum at 640 nm was ascribed to compound **11**. The reaction mixture was cooled to ambient temperature and triturated with anhydrous diethyl ether, the precipitate that formed was filtered, and washed with anhydrous diethyl ether. The yield of compound **11** was 0.14 g (75%), black crystals, m.p. >240 °C. Found (%): C, 51.32; H, 6.58; N, 6.65. $C_{26}H_{41}N_3O_9S_2$. Calculated (%): C, 51.72; H, 6.84; N, 6.96. UV ($CHCl_3$), λ_{max}/nm (ε): 640 (110550). ^{1}H NMR (DMSO-d_6), δ: 3.12 (s, 6 H, NMe_2); 3.35 (s, 6 H, Me_2N^+); 3.4 (s, the signal of the methyl group of anion $MeSO_4^-$ overlaps with the signal of the protons of H_2O in DMSO-d_6); 3.90 (s, 3 H, OMe); 4.32 (s, 4 H, CH_2); 4.50 (s, 2 H, $C\underline{H}_2Ph$); 5.85 (t, 2 H, γ-H and γ´-H, *J* = 12.5 Hz); 7.40—7.50 (m, 5 H, Ph); 7.62 (d, 2 H, β-H and β´-H, *J* = 12.5 Hz); 8.08 (d, 2 H, δ-H and δ´-H, *J* = 12.5 Hz).

2-(4-{3-[1-Acetyl-4-methoxy-4-(3-ethylbezothiazolin-2-ylidene)but-2-en-1-ylidene]-1,2,3,6-tetrahydropyridin-5-yl}-buta-1,3-dien-1-yl)-3-ethylbenzothiazolium tosylate (14). Compounds **9** (0.10 g, 0.23 mmol) and **13** (0.32 g, 0.93 mmol) were carefully grinded and mixed with Ac_2O (4 mL). To the obtained mixture, a solution of 1 *M* Et_3N (1.6 mL) in Ac_2O was added dropwise at room temperature with stirring. Soon the bright blue color of the reaction mixture turned green brownish. After 2 h, diethyl ether (20 mL) was added, the reaction mixture was triturated, and after another 30 min the precipitate that formed was filtered, washed with diethyl ether, small portion of cold water and again with diethyl ether. The yield of dye **14** was 0.08 g (49%), black crystals, m.p. 143—145 °C. UV (CH_2Cl_2), λ_{max}/nm (ε): 1002 (217500), 894 (81743). ^{1}H NMR (DMSO-d_6), δ: 1.32 (t, 6 H, $C\underline{H}_3CH_2N$); 2.14 (s, 3 H, NCOMe; 2.26 (s, 3 H, Me, TsO^-); 3.78 (s, 3 H, OCH_3); 4.25—4.45 (m, 8 H, $CH_3C\underline{H}_2N$ and NCH_2, cycl.); 6.56 (t, 2 H, β-H, *J* = 13 Hz); 6.82 (d, 2 H, δ-H, *J* = 13 Hz); 7.10 (d, 2 H, H(4″), *J* = 7.5 Hz); 7.16—7.70 (m, 10 H, γ-H, α-H, H(5´), H(6´), H(3″)); 7.89 (d, 2 H, H(7´), *J* = 7.7 Hz); 7.98 (d, 2 H, H(4´), *J* = 7.8 Hz).

2-(4-{1-Benzyl-4-methoxy-1-methyl-3-[4-(3-ethylbenzothiazolin-2-ylidene)but-2-en-1-ylidene]-1,2,3,6-tetrahydropyridin-1-ium-5-yl}buta-1,3-dien-1-yl)-3-ethylbenzothiazolium bistosylate (15). Compounds **11** (0.10 g, 0.17 mmol) and **13** (0.24 g, 0.68 mmol) were carefully grinded and mixed with Ac_2O (4 mL). To the obtained mixture, a solution of 1 *M* Et_3N (1.2 mL) in Ac_2O was added dropwise with stirring. The color of the reaction mixture immediately changed, in the UV spectra, the absorption band with maximum at 640 nm disappeared. After 1 h, diethyl ether (15 mL) was added, the reaction mixture was triturated, the precipitate that formed was filtered, and successfully washed with diethyl ether. The yield of dye **15** was 0.06 g (41%), black crystals, m.p. 224—226 °C. Found (%): C, 65.21; H, 5.56;

N, 3.95. $C_{54}H_{57}N_3O_7S_4$. Calculated (%): C, 65.63; H, 5.81; N, 4.25. UV (CH_2Cl_2), λ_{max}/nm (ε): 964 (237703), 856 (124869). ^1H NMR (DMSO-d_6), δ: 1.32 (t, 6 H, $C\underline{H}_3CH_2N$); 2.25 (s, 6 H, CH_3, TsO^-); 3.10 (s, 3 H, MeN^+); 3.90 (s, 3 H, OCH_3); 4.40 (m, 8 H, $CH_3C\underline{H}_2N$ and NCH_2, cycl.); 4.65 (s, 2 H, $C\underline{H}_2Ph$); 6.40 (t, 2 H, β-H, J = 13.5 Hz); 6.65 (d, 2 H, δ-H, J = 13.5 Hz); 7.10 (d, 4 H, H(4″), J = 7.5 Hz); 7.40—7.60 (m, 17 H, Ph, γ-H, α-H, H(5´), H(6´), H(3″)); 7.75 (d, 2 H, H(7´), J = 8.1 Hz); 8.00 (d, 2 H, H(4´), J = 7.8 Hz).

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