Protonation and alkylation of cross-conjugated ω,ω´-bis(dimethylamino) ketones (ketocyanines) containing the piperidine ring and the synthesis of the corresponding thiapentacarbocyanine dyes

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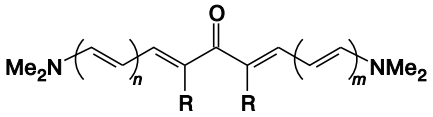
Protonation or alkylation of 3,5-bis(3-dimethylaminoprop-2-enylidene)-1-methylpiperidin-4-one with $Et_2O \cdot HBF_4$, $Et_3O^+BF_4^-$, Me_2SO_4, or Et_2SO_4 (1 equiv.) involves the endocyclic N atom, yielding the corresponding piperidinium salts. With 2 equivalents of the above reagents, the reactions occur at two reactive sites (the N and O atoms) to give doubly charged 4-hydroxy or 4-alkoxy polymethine salts. Protonation and alkylation of ethyl 3,5-bis(3-dimethylaminoprop-2-enylidene)-4-oxopiperidine-1-carboxylate involve only the O atom, affording the corresponding singly charged 4-hydroxy and 4-alkoxy polymethine salts. The latter were used to obtain previously unknown *meso*-alkoxythiapentacarbocyanine dyes containing the 1-ethoxycarbonyl-1,2,3,6-tetrahydropyridine fragment in the polymethine chain.

Key words: ketocyanines, protonation, alkylation, polymethine salts, cyanine dyes, electronic absorption spectra.

Earlier, we have obtained cross-conjugated ω,ω´-bis(dimethylamino polyenyl) ketones (ketocyanines, BDAK) and examined their specific luminescent spectroscopic and chemical properties.[1—4]



BDAK

n = 1, 2; *m* = 1—3

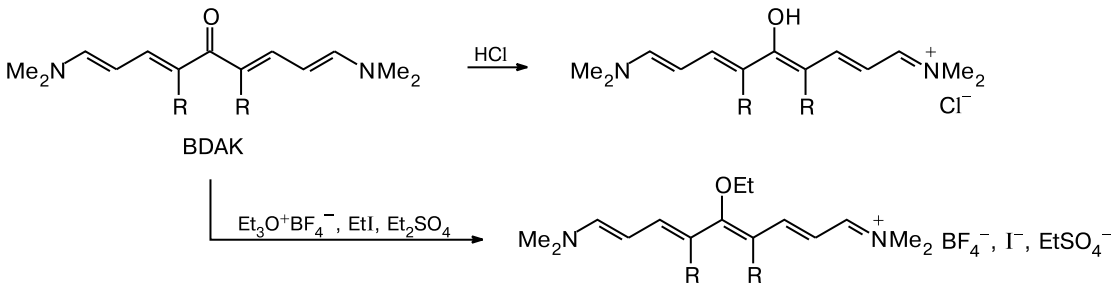
For instance, easy O-protonation of BDAK results in lengthening of the conjugation chain and, accordingly, in considerable deepening of their color (the bathochromic shift of the absorption peak is $\Delta\lambda_{max}$ = 100—105 nm) (Scheme 1).

According to this property, BDAK are very sensitive indicators for acid traces in organic solvents and reagents. The content of an acid in a solvent can be estimated from the color of the solution. More precisely, the concentration of free acid can be determined using spectrophotometry (threshold detectable concentration 10^{-7} mol L^{-1}) suitable for use in aprotic solvents with low dielectric constants (<10), for which direct and highly sensitive methods are absent.[5—7]

Like protonation, alkylation of BDAK occurs at the O atom to give stable crystalline alkoxy polymethine salts in high yields[3,8,9] (see Scheme 1).

Polymethine salts are major intermediate products in the synthesis of cyanine dyes, which are used as sensitizers of silver-halide photographic emulsions, passive Q-switches and active media of lasers in quantum electronics, fluo-

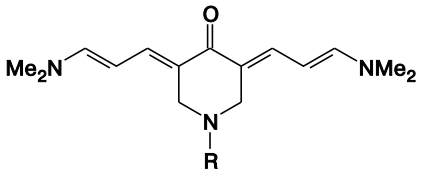
Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 796—803, April, 2010.

rescent probes, photoresistors, and materials for nonlinear optics and recording systems.[10—14]

Recently,[15] we have obtained new ketocyanines **1** and **2**, which are cross-conjugated ω,ω′-bis(dimethylamino) ketones containing the piperidine ring.



1, 2

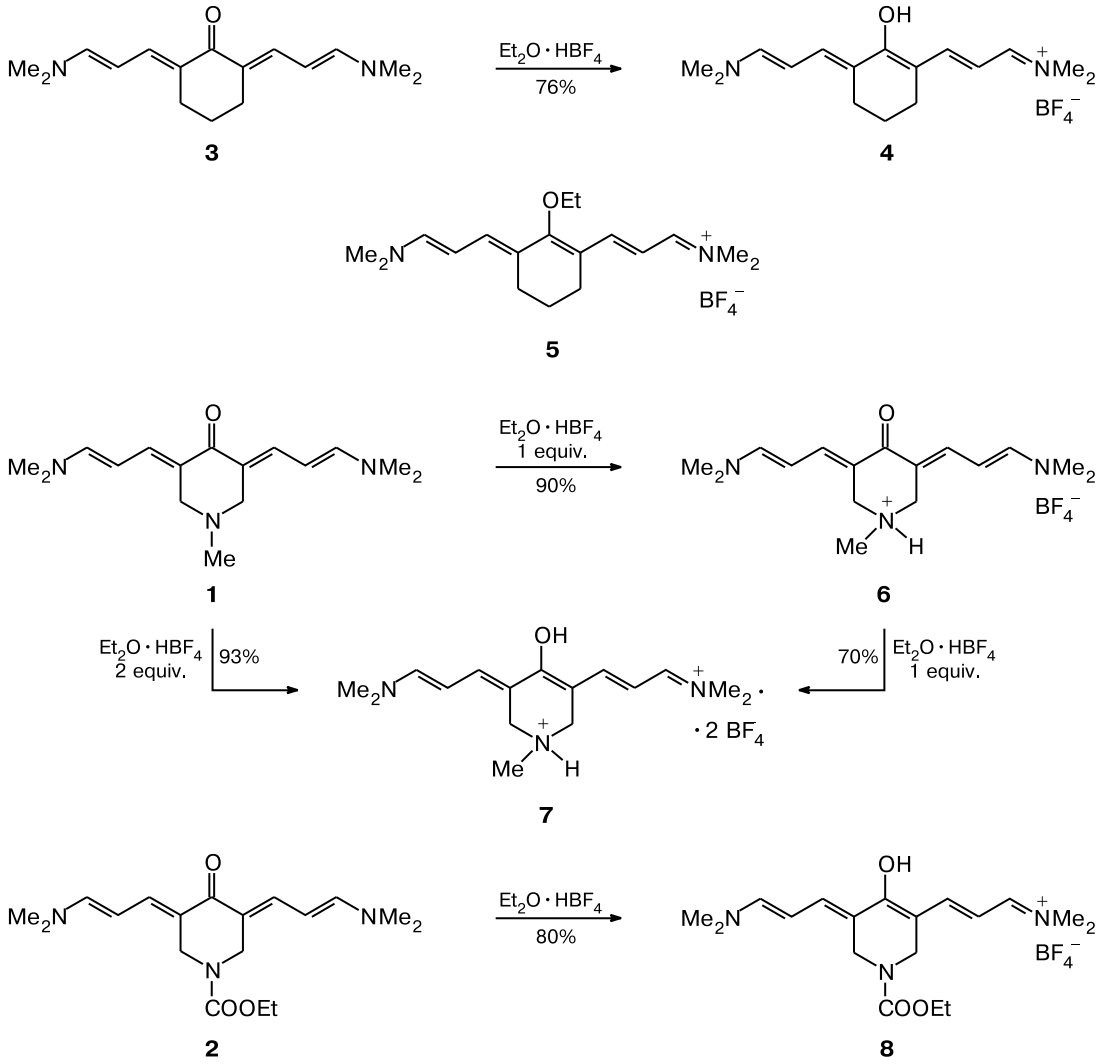
R = Me (**1**), COOEt (**2**)

In the present work, we studied protonation and alkylation of ketocyanines **1** and **2**. Unlike the previously examined ketocyanines, these compounds have two reactive sites suitable for attacks of electrophiles: the carbonyl group and the endocyclic N atom. The complex $Et_2O \cdot HBF_4$ was employed as a proton source (Scheme 2). First of all, we studied for comparison the reaction of this complex with the known[2] ketocyanine **3** and obtained crystalline salt **4** in 76% yield. It turned out that the long-wavelength peak λ_{max} in the electronic absorption spectrum of salt **4** experiences a hypsochromic shift by 30 nm compared to the λ_{max} value for the previously[3] described ethoxy polymethine salt **5**.

Salt **4** is unstable in the crystalline state and especially in $CHCl_3$ and EtOH solutions. In a highly dilute ethanolic solution, salt **4** undergoes rapid (5—10 min) transformation into ketocyanine **3**: the blue solution (λ_{max} = 620 nm) turned yellow (λ_{max} = 490 nm).

The action of an equimolar amount of the complex $Et_2O \cdot HBF_4$ gives tetrafluoroborate **6** in 90% yield as

Scheme 2

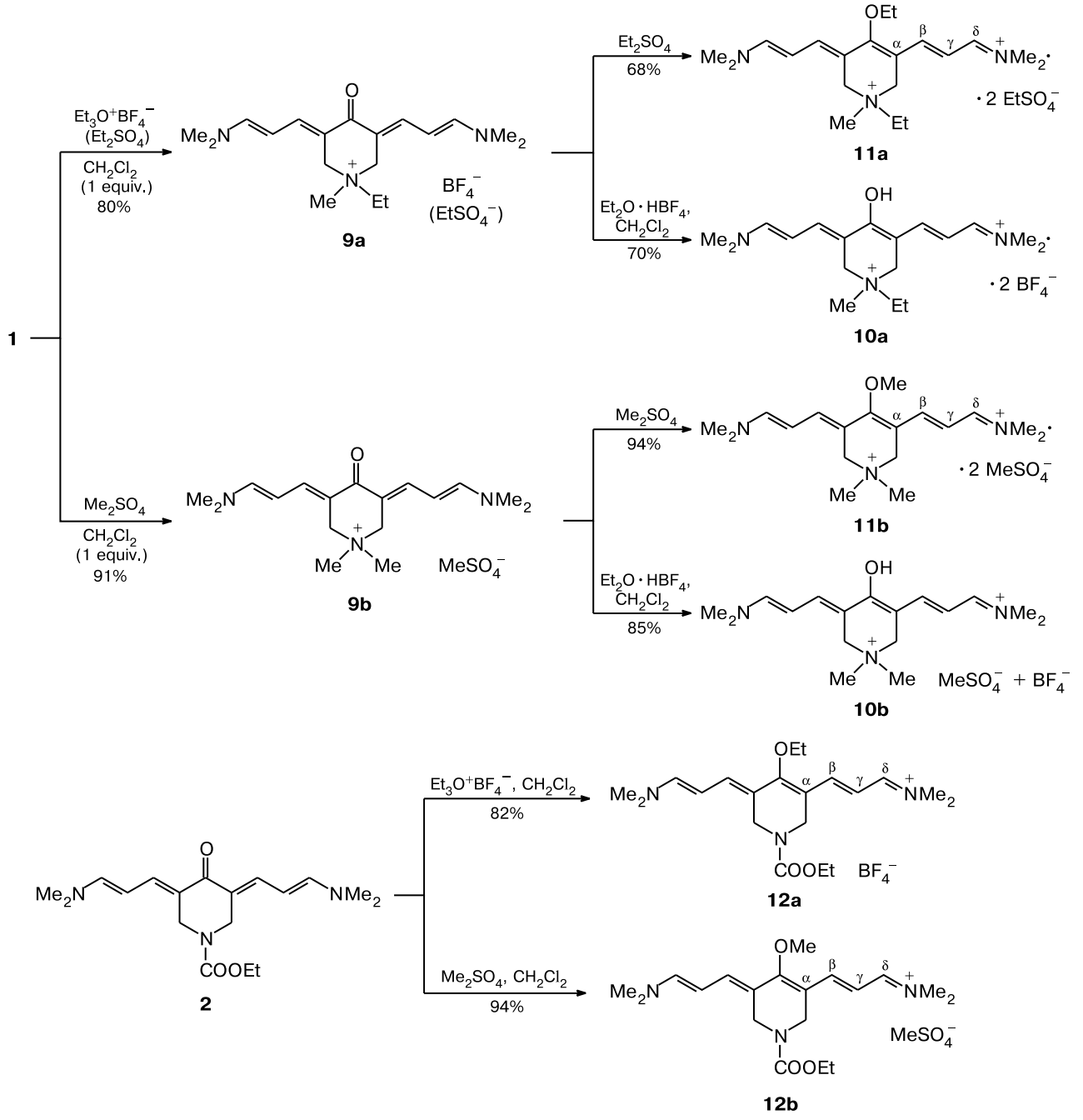


a result of protonation at the endocyclic N atom. The reaction of ketocyanine **1** with two equivalents of $Et_2O \cdot HBF_4$ yields, through protonation at the endocyclic N atom and the O atom, salt **7** in 93% yield. The same salt can also be obtained from tetrafluoroborate **6** under the action of one equivalent of $Et_2O \cdot HBF_4$.

Protonation of ketocyanine **2**, in which the N atom is less basic than that in compound **1**, produces salt **8** in 80% yield. Salts **6**—**8** are even less stable than salt **4**, especially in ethanolic solutions.

Alkylation of ketocyanines **1** and **2** was studied in reactions with such alkylating agents as triethyloxonium tetrafluoroborate $Et_3O^+BF_4^-$ and dialkyl sulfates (Scheme 3). Ketocyanine **1** is readily alkylated at the endocyclic N atom under the action of an alkylating agent (1 equiv.) in dry CH_2Cl_2. The resulting salts **9a** and **9b** can be protonat-

Scheme 3



ed with the complex $Et_2O \cdot HBF_4$ in CH_2Cl_2 to give salts **10a** and **10b** in high yields.

Reactions of salts **9a,b** with dialkyl sulfates in the absence of CH_2Cl_2 produced O-alkylated salts **11a,b**. However, the action of the alkylating reagents ($Et_3O^+BF_4^-$, Me_2SO_4, or Et_2SO_4) on salts **9a,b** in the presence of CH_2Cl_2 resulted in not only O-alkylation but also (in part) O-protonation leading to salts **10a,b** as by-products. Compounds **10a,b** were also obtained when ketocyanine **1** was treated with an excess of the alkylating reagents in CH_2Cl_2. Apparently, the proton source is an acid generated in trace amounts from CH_2Cl_2 under the action of salts **9a,b**. Ketocyanine **2**, which contains no quaternized N atom, reacts with $Et_3O^+BF_4^-$ or Me_2SO_4 in CH_2Cl_2 to give salts **12a,b** as sole products.

The structures of salts **4**, **6**, **7**, **8**, **9a,b**, and **10a,b** were confirmed by ^1H NMR spectroscopy in DMSO-d_6 and electronic absorption spectroscopy.

The electronic absorption spectra of N-protonated salt **6** and tetraalkylammonium salts **9a,b** in $CHCl_3$ (λ_{max} = = 476—482 nm, yellow solution) are much the same as the spectrum of the starting ketocyanine **1** (λ_{max} = 470 nm). The previously described (see Schemes 2, 3) O-protonated salts **4**, **7**, **8**, and **10a,b** absorb at λ_{max} = 600 nm (bright blue solution).

The structures of salts **11a,b** and **12a,b** were determined using electronic absorption spectroscopy (λ_{max} = = 640 nm) and 1D and 2D ^1H and ^{13}C NMR spectroscopy (COSY, NOESY, ^1H—^{13}C HSQC, and ^1H—^{13}C HMBC) for salts **11a,b** (Table 1) and 1D ^1H NMR spectroscopy for salts **12a,b** (Table 2). The signals in the ^1H NMR spectrum of salt **12b** were assigned with the aid of selective NOESY experiment. It follows from the coupling constants of the methine protons ($^3J_{\beta,\gamma}$ = 13.3—13.7 Hz, $^3J_{\gamma,\delta}$ = 11.2—11.3 Hz) that the protons at the double bonds β—γ and γ—δ are *trans* to each other and that the diene fragments in the polymethine chains mainly exist in the *S-trans*-conformation.

Salts **12a,b** were used for the synthesis of earlier unknown *meso*-alkoxythiapentacarbocyanine dyes **13a,b** containing the 1-ethoxycarbonyl-1,2,3,6-tetrahydropyridine fragment in the polymethine chain (Scheme 4).

Dyes **13a,b** were obtained in high yields by condensation of salts **12a,b** with tosylate **14** in acetic anhydride in the presence of triethylamine (see Scheme 4). Dyes **13a** and **13b** are stable black crystalline solids with absorption peaks at λ_{max} = 1006 and 1005 nm (ε = 219 650 and 174 500, respectively) in CH_2Cl_2.

Structure **13a** was identified using 1D and 2D ^1H and ^{13}C NMR spectroscopy (^{13}C-APT, COSY, NOESY, HSQC, and HMBC), which allowed complete assignment of all signals (Table 3). The coupling constants of the methine protons ($^3J_{\alpha,\beta}$ = 13.5 Hz, $^3J_{\beta,\gamma}$ = 12.2 Hz, and $^3J_{\gamma,\delta}$ = 12.8 Hz) suggested the *trans*-arrangement of the protons at the double bonds in the polymethine chain and the *S-trans*-conformation of the diene fragments.

Comparison of the integral intensities of the signals of the protons in the tosylate anion and in the cationic part

Table 1. ^1H and ^{13}C NMR spectra of salts **11a,b** in DMSO-d_6

Atom	δ (*J*/Hz)			
	11a		**11b**	
	^1H	^{13}C	^1H	^{13}C
α	—	105.1	—	104.77
β	7.55 (d, $^3J_{\gamma,\beta}$ = 13.5)	147.0	7.58 (d, $^3J_{\gamma,\beta}$ = 13.7)	146.87
γ	5.90 (t, $^3J_{\gamma,\beta}$ = 13.5, $^3J_{\gamma,\delta}$ = 11.2)	102.2	5.84 (t, $^3J_{\gamma,\beta}$ = 13.7, $^3J_{\gamma,\delta}$ = 11.2)	102.28
δ	8.05 (d, $^3J_{\gamma,\delta}$ = 11.2)	162.5	8.02 (d, $^3J_{\gamma,\delta}$ = 11.2)	162.43
CH_2 (OEt)	4.0 (q)	73.1	—	—
CH_3 (OEt)	1.45 (t)	15.4	—	—
CH_2 (EtN^+)	3.40 (q)	57.6	—	—
CH_3 (EtN^+)	1.30 (t)	7.8	—	—
CH_2 ($EtSO_4^-$)	3.70 (q)	61.2	—	—
CH_3 ($EtSO_4^-$)	1.10 (t)	15.0	—	—
(MeN^+)*	3.05 (s)	47.6	3.15 (6 H)	51.10
(=NMe_2)*	3.15 (s, 6 H)	39.20	3.20 (s, 6 H)	39.50
	3.35 (s, 6 H)	46.1	3.34 (s, 6 H)	46.05
CH_2	4.30—4.40 (m, 4 H)	57.6	4.38 (s, 4 H)	59.67
<u>C</u>OEt	—	164.5	—	—
OMe	—	—	3.86	64.52
<u>C</u>OMe	—	—	—	165.17
$MeSO_4^-$	—	—	3.4**	52.73

* For compound **11b**, $\delta_{^{15}N}$ ($\delta_{CH_3NO_2}$ = 0.0): −246.6 (=NMe_2); −333.2 (MeN^+).

** Overlap with the signal of HDO in DMSO-d_6.

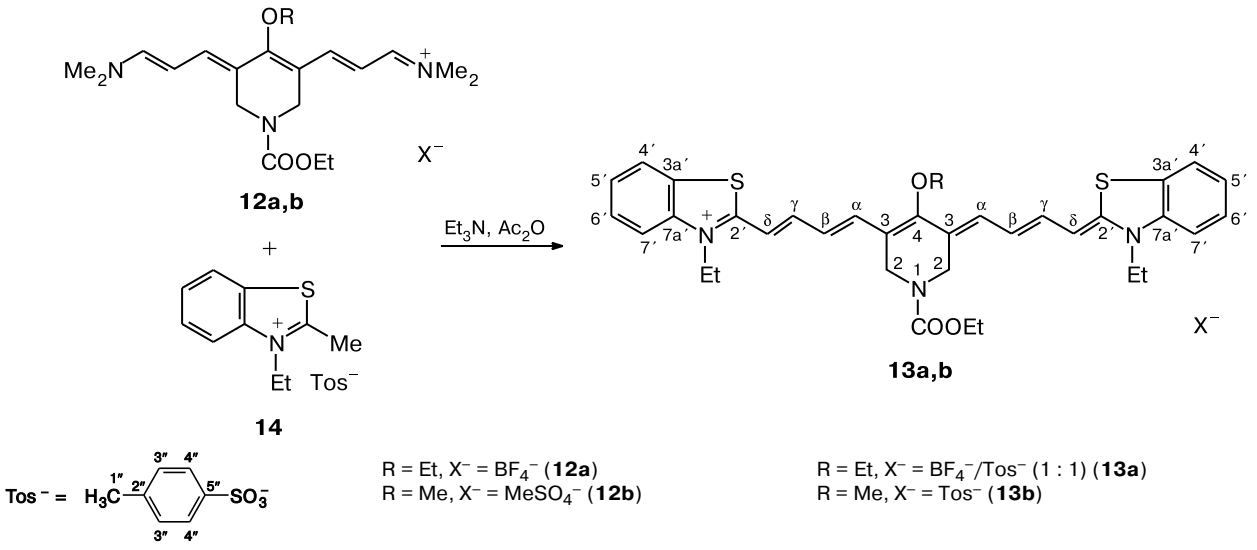
Table 2. ^{1}H NMR spectra of salts **12a,b** in DMSO-d_6

Atom	δ (*J*/Hz)	
	12a	**12b**
β*	7.40 (d, 2 H, $^3J_{\beta,\gamma}$ = 13.3)	7.44 (d, 2 H, $^3J_{\beta,\gamma}$ = 13.3)
γ	5.72 (t, 2 H, $^3J_{\beta,\gamma}$ = 13.3, $^3J_{\delta,\gamma}$ = 11.5)	5.75 (t, 2 H, $^3J_{\beta,\gamma}$ = 13.3, $^3J_{\delta,\gamma}$ = 11.3)
δ	7.85 (d, 2 H, $^3J_{\delta,\gamma}$ = 11.5)	7.87 (d, 2 H, $^3J_{\delta,\gamma}$ = 11.3)
OMe	—	3.79 (s)
=NMe_2	3.20 (br.s, 12 H)	3.27 (br.s, 12 H)
CH_2	4.28 (s, 4 H)	4.29 (s, 4 H)
CH_2 (COOEt)	4.10 (q, 2 H)	4.10 (q, 2 H)
CH_3 (COOEt)	1.18 (t, 3 H)	1.21 (t, 3 H)
CH_2 (OEt)	3.90 (q, 2 H)	—
CH_3 (OEt)	1.38 (t, 3 H)	—
$MeSO_4^-$	—	3.4**

* The SelNOESY experiment for compound **12b** revealed that only the β-H proton (δ 7.44) remains close to OMe upon its irradiation.

** Overlap with the signal of HDO in DMSO-d_6.

Scheme 4



of the dye shows that the anions in compound **13a** are Tos^- and BF_4^- in a ratio of 1 : 1.

Structure **13b** was confirmed by 1D (^{1}H, selective NOESY for OMe) and 2D ^{1}H NMR spectroscopy (COSY). For assignment of the signals, we used the NMR data obtained for dye **13a**.

Photochemical and photophysical data for dyes **13a,b** will be published elsewhere.

Experimental

The ^{1}H NMR spectra of salts **4**, **6**, **7**, **8**, **9a,b**, **10a,b**, and **12a** were recorded on a Bruker Avance 300 instrument (300.13 MHz) in DMSO-d_6. The ^{1}H and ^{13}C NMR spectra of salts **11a,b** and **12b** and dyes **13a,b** were recorded on a Bruker Avance 600 spectrometer (600.13 and 150.90 MHz, respectively) according to the Bruker standard procedures. The mixing time in NOESY and selective NOESY experiments was 0.7 s.

Electronic absorption spectra were recorded on a Specord UV-Vis spectrophotometer for salts **4**, **6**—**8**, **9a,b**, **10a,b**, **11a,b**, and **12a,b** and on an Agilent 8453 spectrophotometer for dyes **13a,b**. The molar absorption coefficients ε were not determined for sparingly soluble salts. The course of the reactions was monitored by electronic absorption spectroscopy. Since many of the resulting salts are sparingly soluble in CH_2Cl_2 and $CHCl_3$, a sample of a reaction mixture was dissolved in a minimum amount of dry DMSO and then diluted with $CHCl_3$ for recording electronic absorption spectra. All reactions with the complexes $Et_2O \cdot HBF_4$ and $Et_3O^+BF_4^-$ were carried out under argon. Dry CH_2Cl_2 free from acid traces was used.

Elemental analysis of the protonated salts and the dyes containing more than one anion was not carried out.

Table 3. NMR spectra of dyes **13a,b** in DMSO-d_6

Atom	δ (*J*/Hz)		
	13a		**13b**, ^{1}H
	^{1}H	^{13}C	
α	7.20 (d, $^3J_{\alpha,\beta}$ = 13.5)	135.5	7.24 (d, $^3J_{\alpha,\beta}$ = 13.5)
β	6.46 (t, $^3J_{\alpha,\beta}$ = 13.5, $^3J_{\beta,\gamma}$ = 12.2)	120.8	6.50 (t, $^3J_{\alpha,\beta}$ = 13.5, $^3J_{\beta,\gamma}$ = 12.2)
γ	7.41 (t, $^3J_{\gamma,\delta}$ = 12.8, $^3J_{\gamma,\beta}$ = 12.2)	145.2	7.45 (t, $^3J_{\gamma,\delta}$ = 13.0, $^3J_{\gamma,\beta}$ = 12.2)
δ	6.70 (d, $^3J_{\gamma,\delta}$ = 12.8)	103.1	6.73 (d, $^3J_{\gamma,\delta}$ = 13.0)
C(4′)	7.93 (d, $^3J_{4',5'}$ = 7.2)	122.9	7.96 (d, $^3J_{4',5'}$ = 7.8)
C(5′)	7.34 (t, $^3J_{4',5'}$ = 7.2, $^3J_{6',5'}$ = 7.2)	124.6	7.38 (t, $^3J_{4',5'}$ = 7.8, $^3J_{6',5'}$ = 7.2)
C(6′)	7.52 (t, $^3J_{6',5'}$ = 7.2, $^3J_{6',7'}$ = 8.11)	128.0	7.51 (t, $^3J_{6',5'}$ = 7.2, $^3J_{6',7'}$ = 8.1)
C(7′)	7.66 (d, $^3J_{6',7'}$ = 8.11)	112.7	7.65 (t, $^3J_{6',7'}$ = 8.1)
C(3a′)	—	125.6	—
C(7a′)	—	141.2	—
C(2′)	—	159.3	—
CH_2 (ring)	4.35 (s)	42.1	4.37 (s)
C(3) (ring)	—	119.71	—
C(4) (ring)	—	159.7	—
CH_2 (NEt)	4.35 (q)	41.3	4.37 (q)
CH_3 (NEt)	1.32 (t)	12.6	1.32 (t)
CH_2 (OEt)	3.92 (q)	71.3	—
CH_3 (OEt)	1.44 (t)	15.4	—
OMe	—		3.80 (s)
CH_2 (COOEt)	4.14 (q)	61.2	4.11 (q)
CH_3 (COOEt)	1.24 (t)	14.6	1.25 (t)
C=O (COOEt)	—	154.6	—
C(1″)	2.28 (s)	20.7	2.25 (s)
C(2″)	—	137.4	—
C(3″)	7.48 (d, $^3J_{3'',4''}$ = 7.5)	125.4	7.46 (d, $^3J_{3'',4''}$ = 7.5)
C(4″)	7.10 (d, $^3J_{3'',4''}$ = 7.5)	128.0	7.08 (d, $^3J_{3'',4''}$ = 7.5)
C(5″)	—	145.8	—

***N*-(9-Dimethylamino-5-hydroxy-4,6-trimethylenenona-2,4,6,8-tetraenylidene)-*N*,*N*-dimethylammonium tetrafluoroborate (4).** A solution of the complex $Et_2O \cdot HBF_4$ (0.073 g, 0.45 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise at −7 to 0 °C to a stirred solution of ketocyanine **3** (0.0765 g, 0.3 mmol) in dry CH_2Cl_2 (3 mL). The blue reaction mixture was stirred at this temperature for 20 min. Then the mixture characterized by an absorption peak at λ_{max} = 610 nm (salt **4**) instead of the peak at λ_{max} = 460 nm corresponding to ketocyanine **3** was concentrated *in vacuo*. Dry ether was added to the residue and the precipitate was separated and repeatedly washed with ether. The yield of tetrafluoroborate **4** was 0.08 g (76%), black crystals, m.p. 107—108 °C. UV, λ_{max}/nm (ε): (EtOH) 620 (27 235); ($CHCl_3$) 610 (90 729). ^{1}H NMR, δ: 1.70 (br.s, 2 H, CH_2); 2.30 (br.s, 4 H, CH_2); 3.10 (s, 12 H, NMe_2); 5.60 (t, 2 H, γ-H, *J* = 12.5 Hz); 7.50—7.70 (m, 4 H, β-H, δ-H).

3,5-Bis(3-dimethylaminoprop-2-enylidene)-1-methyl-4-oxopiperidinium tetrafluoroborate (6). Dichloromethane (1.4 mL) containing $Et_2O \cdot HBF_4$ (0.07 g, 0.43 mmol) was added dropwise to a solution of ketocyanine **1** (0.1 g, 0.36 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at −8 to 0 °C for 1 h and the precipitate that formed was separated. The mother liquor was concentrated *in vacuo*, the residue was treated with dry ether, and the resulting precipitate was separated. Both precipitates were combined and washed with dry ether. The yield of tetrafluoroborate **6** was 0.12 g (90%), black crystals, m.p. > 250 °C. UV ($CHCl_3$), λ_{max}/nm (ε): 476 (28 750). ^{1}H NMR, δ: 2.90 (s, 3 H, N^+Me); 2.95 (s, 12 H, NMe_2); 4.10 (s, 4 H, CH_2); 5.08 (t, 2 H, γ-H, *J* = 12.5 Hz); 7.18 (d, 2 H, δ-H, *J* = 12.5 Hz); 7.40 (d, 2 H, β-H, *J* = 12.5 Hz).

3-(3-Dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-hydroxy-1-methyl-1,2,3,6-tetrahydropyridinium bis(tetrafluoroborate) (7). *A*. A solution of the complex $Et_2O \cdot HBF_4$ (0.03 g, 0.18 mmol) in CH_2Cl_2 (1 mL) was added dropwise at −7 °C to a solution of tetrafluoroborate **6** (0.4 g, 0.11 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was kept cooled for 1 h and concentrated *in vacuo*. The residue was washed with dry ether and the precipitate was separated. The yield of bis(tetrafluoroborate) **7** was 0.034 g (70%), black crystals, m.p. 152—153 °C. UV ($CHCl_3$), λ_{max}/nm: 600. ^{1}H NMR, δ: 2.95 (s, 3 H, N^+Me); 3.20 (s, 12 H, NMe_2); 4.30 (m, 4 H, CH_2); 5.62 (t, 2 H, γ-H, *J* = 12.5 Hz); 7.65 (d, 2 H, β-H, *J* = 12.5 Hz); 7.70 (d, 2 H, δ-H, *J* = 12.5 Hz); 9.95 (br.s, 1 H, OH).

***B*.** A solution of the complex $Et_2O \cdot HBF_4$ (0.15 g, 1 mmol) in dry CH_2Cl_2 (0.8 mL) was added dropwise at −7 °C to a solution of ketocyanine **1** (0.1 g, 0.36 mmol) in dry CH_2Cl_2 (3 mL). The reaction mixture was kept at −7 °C for 1 h and concentrated. The residue was washed with dry ether. The yield of bis(tetrafluoroborate) **7** was 0.15 g (93%), crystals, m.p. 152—153 °C. The UV and ^{1}H NMR spectra of the product are identical with those of salt **7** obtained according to procedure *A*.

***N*-{3-[3-(3-Dimethylaminoprop-2-enylidene)-1-ethoxycarbonyl-4-hydroxy-1,2,3,6-tetrahydropyridin-5-yl]prop-2-enylidene}-*N*,*N*-dimethylammonium tetrafluoroborate (8).** A solution

of the complex $Et_2O \cdot HBF_4$ (0.05 g, 0.3 mmol) in dry CH_2Cl_2 (1 mL) was added dropwise at −5 °C to a solution of ketocyanine **2** (0.1 g, 0.3 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was kept at −5 °C for 1 h and concentrated *in vacuo*. Dry ether was added and the precipitate that formed was separated and washed with dry ether. The yield of tetrafluoroborate **8** was 0.1 g (80%), m.p. 143—145 °C. UV ($CHCl_3$), λ_{max}/nm: 600. ^{1}H NMR, δ: 1.20 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7 Hz); 3.00 (s, 12 H, NMe_2); 4.05 (q, 2 H, $CH_3C\underline{H}_2O$); 4.20 (br.s, 4 H, CH_2); 5.10 (t, 2 H, γ-H, J = 12.5 Hz); 7.20 (d, 2 H, β-H, J = 12.5 Hz); 7.30 (d, 2 H, δ-H, J = 12.5 Hz).

3,5-Bis(3-dimethylaminoprop-2-enylidene)-1-ethyl-1-methyl-4-oxopiperidinium tetrafluoroborate (9a). A solution of the complex $Et_3O^+BF_4^-$ (0.021 g, 0.11 mmol) in dry CH_2Cl_2 (0.5 mL) was added dropwise at −10 °C to a solution of ketocyanine **1** (0.03 g, 0.109 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was kept at this temperature for 1 h and concentrated *in vacuo*. The resulting precipitate was washed with dry ether. The yield of tetrafluoroborate **9a** was 0.033 g (78%), m.p. 133—135 °C. Found (%): C, 55.45; H, 7.50; N, 11.12. $C_{18}H_{30}N_3O \cdot BF_4$. Calculated (%): C, 55.24; H, 7.67; N, 10.74. UV ($CHCl_3$), λ_{max}/nm: 482. ^{1}H NMR, δ: 1.25 (t, 3 H, $NCH_2C\underline{H}_3$, J = 7 Hz); 2.95 (s, 12 H, NMe_2); 3.05 (s, 3 H, NMe); 3.30 (q, 2 H, $NC\underline{H}_2CH_3$); 4.20—4.40 (m, 4 H, CH_2); 5.12 (t, 2 H, γ-H, J = 12.5 Hz); 7.22 (d, 2 H, δ-H, J = 12.5 Hz); 7.45 (d, 2 H, β-H, J = 12.5 Hz).

3,5-Bis(3-dimethylaminoprop-2-enylidene)-1,1-dimethyl-4-oxopiperidinium methyl sulfate (9b). Dimethyl sulfate (0.14 g, 1.1 mmol) was added to a solution of ketocyanine **1** (0.3 g, 1.1 mmol) in CH_2Cl_2 (1 mL). This immediately resulted in the formation of a precipitate. The reaction mixture was concentrated *in vacuo*. The residue was treated with dry ether and the precipitate that formed was separated and washed with ether. The yield of methyl sulfate **9b** was 0.4 g (91%), brown crystals, m.p. 189—192 °C. Found (%): C, 53.62; H, 7.51; N, 10.32. $C_{17}H_{28}N_3O \cdot MeSO_4$. Calculated (%): C, 53.86; H, 7.73; N, 10.47. UV ($CHCl_3$), λ_{max}/nm (ε): 480 (46 000). ^{1}H NMR, δ: 2.95 (br.s, 12 H, NMe_2); 3.10 (s, 6 H, N^+Me_2); 3.35 (s, 3 H, $MeSO_4$); 4.30 (s, 4 H, CH_2); 5.05 (t, 2 H, γ-H, J = 12.5 Hz); 7.22 (d, 2 H, δ-H, J = 12.5 Hz); 7.45 (d, 2 H, β-H, J = 12.5 Hz).

3-(3-Dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-1-ethyl-4-hydroxy-1-methyl-1,2,3,6-tetrahydropyridinium bis(tetrafluoroborate) (10a). A solution of the complex $Et_2O \cdot HBF_4$ (0.05 g, 0.28 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise at −5 °C to a solution of tetrafluoroborate **9a** (0.1 g, 0.25 mmol) in CH_2Cl_2 (2 mL). After 40 min, the resulting precipitate was separated and washed with dry ether. The yield of bis(tetrafluoroborate) **10a** was 0.08 g (70%), m.p. 132—135 °C. UV ($CHCl_3$ + 5% DMSO), λ_{max}/nm: 600. ^{1}H NMR, δ: 1.10 (t, 3 H, $NCH_2C\underline{H}_3$); 3.10 (s, 3 H, N^+Me); 3.20, 3.35 (both s, 6 H each, NMe_2); 4.20—4.40 (m, 6 H, CH_2, $NC\underline{H}_2CH_3$); 5.75 (t, 2 H, γ-H, J = 12.5 Hz); 7.75 (m, 4 H, β-H, δ-H); 10.00 (br.s, 1 H, OH).

3-(3-Dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-hydroxy-1,1-dimethyl-1,2,3,6-tetrahydropyridinium methyl sulfate and tetrafluoroborate (10b). A solution of the complex $Et_2O \cdot HBF_4$ (0.065 g, 0.4 mmol) in CH_2Cl_2 (0.35 mL) was added dropwise at −7 °C to a solution of methyl sulfate **9b** (0.11 g, 0.27 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred under cooling for 1 h and concentrated *in vacuo*. The precipitate that formed was separated and washed with dry ether. The yield of a mixture of salts **10b** was 0.11 g (85%), very viscous oil. UV ($CHCl_3$), λ_{max}/nm: 580. ^{1}H NMR, δ: 3.15 (s, 6 H, N^+Me_2); 3.20 (br.s, 12 H, NMe_2); 3.40 (s, 2 H, $MeSO_4^-$); 4.25 (s, 4 H, CH_2); 5.60 (t, 2 H, γ-H, J = 12.5 Hz); 7.70 (m, 4 H, β-H, δ-H); 5.00 (br.s, OH (**10b**), HOD (DMSO-d_6)).

3-(3-Dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-ethoxy-1-ethyl-1-methyl-1,2,3,6-tetrahydropyridinium bis(ethyl sulfate) (11a). Diethyl sulfate (0.1 g, 0.7 mmol) was added to a stirred solution of ketocyanine **1** (0.2 g, 0.7 mmol) in CH_2Cl_2 (1 mL). After 10 min, the reaction mixture was concentrated *in vacuo*. Diethyl sulfate (0.53 g, 3.5 mmol) was added to the dry residue of salt **9a** (0.29 g, $\lambda_{max}(CHCl_3)$ = 480 nm). The reaction mixture was stirred at 60—65 °C for 1 h and then treated with dry ether. The resulting precipitate was separated and repeatedly washed with ether. The yield of salt **11a** was 0.28 g (68%), dark gray crystals, m.p. 151—154 °C. Found (%): C, 49.15; H, 7.52; N, 7.05. $C_{20}H_{35}N_3O \cdot 2EtSO_4$. Calculated (%): C, 49.40; H, 7.72; N, 7.20. UV ($CHCl_3$), λ_{max}/nm: 640.

3-(3-Dimethylaminoprop-2-enylidene)-5-(3-dimethyliminioprop-1-enyl)-4-methoxy-1,1-dimethyl-1,2,3,6-tetrahydropyridinium bis(methyl sulfate) (11b). Dimethyl sulfate (0.8 g, 6 mmol) was added with stirring to methyl sulfate **9b** (0.26 g, 0.66 mmol). The reaction mixture was heated at 55—60 °C for 30 min, cooled, and treated with dry ether. The resulting precipitate was separated and washed with CH_2Cl_2 and ether. The yield of bis(methyl sulfate) **11b** was 0.32 g (94%), dark violet crystals, m.p. > 260 °C. Found (%): C, 45.15; H, 6.85; N, 7.62. $C_{18}H_{31}N_3O \cdot 2MeSO_4$. Calculated (%): C, 45.24; H, 7.02; N, 7.97. UV ($CHCl_3$), λ_{max}/nm: 640.

***N*-{3-[3-(3-Dimethylaminoprop-2-enylidene)-4-ethoxy-1-ethoxycarbonyl-1,2,3,6-tetrahydropyridin-5-yl]prop-2-enylidene}-*N*,*N*-dimethylammonium tetrafluoroborate (12a).** A solution of $Et_3O^+BF_4^-$ (0.07 g, 0.37 mmol) in CH_2Cl_2 (1 mL) was added dropwise at −7 °C to a solution of ketocyanine **2** (0.1 g, 0.3 mmol) in CH_2Cl_2 (3 mL). After 1 h, the reaction mixture was concentrated *in vacuo* and the residue was treated with dry ether. The resulting precipitate was separated and washed with dry ether. The yield of tetrafluoroborate **12a** was 0.11 g (82%), m.p. 168—170 °C. Found (%): C, 53.15; H, 6.85, N, 9.12. $C_{20}H_{32}N_3O_3 \cdot BF_4$. Calculated (%): C, 53.45; H, 7.13; N, 9.35. UV, λ_{max}/nm (ε): ($CHCl_3$) 640 (143 360); (EtOH) 640 (204 800).

***N*-{3-[3-(3-Dimethylaminoprop-2-enylidene)-1-ethoxycarbonyl-4-methoxy-1,2,3,6-tetrahydropyridin-5-yl]prop-2-enylidene}-*N*,*N*-dimethylammonium methyl sulfate (12b).** A solution of Me_2SO_4 (0.24 g, 1.9 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of ketocyanine **2** (0.2 g, 0.6 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was refluxed with stirring for 7 h until ketocyanine **2** was completely consumed (disappearance of the absorption band with λ_{max} = 485 nm from the UV spectrum ($CHCl_3$)) and then concentrated *in vacuo*. The residual viscous oil was triturated six times with dry ether in portions of 5—6 mL. The precipitate that formed as a dark brown powder was separated and washed with dry ether. The yield of methyl sulfate **12b** was 0.26 g (94%), black crystals, m.p. 132—134 °C. Found (%): C, 51.95; H, 7.32; N, 8.86. $C_{19}H_{30}N_3O_3 \cdot MeSO_4$. Calculated (%): C, 52.28; H, 7.19; N, 9.15. UV ($CHCl_3$), λ_{max}/nm (ε): 640 (72 000).

2-(4-{4-Ethoxy-1-ethoxycarbonyl-3-[4-(3-ethylbenzothiazolin-2-ylidene)but-2-en-1-ylidene]-1,2,3,6-tetrahydropyridin-5-yl}buta-1,3-dien-1-yl)-3-ethylbenzothiazolium tosylate and tetrafluoroborate (1 : 1 mixture) (13a). A 1 *M* solution of Et_3N (1 mL) in Ac_2O was added dropwise at 20 °C to a mixture of

3-ethyl-2-methylbenzothiazolium tosylate **14** (0.25 g, 0.7 mmol) and tetrafluoroborate **12a** (0.08 g, 0.18 mmol) in Ac_2O (4 mL). The reaction mixture was kept for 1.5 h and diluted with ether. After 30 min, the resulting precipitate was separated and washed with ether, a small amount of water, and again ether. The yield of dye **13a** was 0.105 g (83%), black crystals, m.p. 187—189 °C. UV, λ_{max}/nm (ε): (CH_2Cl_2) 1006 (219 650); (EtOH) 989.

2-(4-{1-Ethoxycarbonyl-3-[4-(3-ethylbenzothiazolin-2-ylidene)but-2-en-1-ylidene]-4-methoxy-1,2,3,6-tetrahydropyridin-5-yl}buta-1,3-dien-1-yl)-3-ethylbenzothiazolium tosylate (13b). A 1 *M* solution of Et_3N (1.1 mL) in Ac_2O was added dropwise at 20 °C to a mixture of 3-ethyl-2-methylbenzothiazolium tosylate **14** (0.3 g, 0.8 mmol) and methyl sulfate **12b** (0.1 g, 0.2 mmol) in Ac_2O (4 mL). The reaction mixture was kept for 1.5 h. After the workup described above, the yield of dye **13b** was 0.09 g (63%), black crystals, m.p. 170—171 °C. UV (CH_2Cl_2), λ_{max}/nm (ε): 1005 (174 500).

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Received May 26, 2009;
in revised form October 2, 2009