Spiropyrans and spirooxazines
7.* Novel spirobipyrans and their cationic derivatives

E. V. Solov´eva,[a] S. O. Besuglyi,[b] N. A. Voloshin,[b] A. V. Metelitsa,[a] and V. I. Minkin[a,b]*

[a]*Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 434 667. E-mail: photo@ipoc.rsu.ru*
[b]*Southern Scientific Center, Russian Academy of Sciences, 41 prosp. Chekhova, 344006 Rostov-on-Don, Russian Federation*

Novel photochromic spirobipyrans containing the dimethylamino group in position 7 of the benzopyran moiety and their cationic derivatives with the trimethylammonium substituent exhibiting no photochromic properties were synthesized.

Key words: spirobipyrans, spiropyran salts, merocyanines, photochromism.

Synthesis, structures, and photochemical properties of crystals of spiropyran and spirooxazine salts have recently attracted special attention.[2—5] Cationic spiropyrans Sp^+X^- are promising for the preparation of hybrid polyfunctional materials combining in one crystalline lattice simultaneously photochromic and magnetic properties.[5—9] They can be used for manufacturing miniature electronic devices. The hybrid polyfunctional compounds of the basically new class were prepared.[6,8,10] they combine in one crystalline lattice two sublattices: the photochromic cationic sublattice of spiropyrans and the magnetic anionic sublattice of bimetallic oxalate in which spiropyran acts as a photochemical molecular switch perturbing the magnetic sublattice.

Presently known spiropyran and spirooxazine salts are mainly derivatives of the indoline series. Cationic spiropyran of the isobenzofuran series with photochromic properties has recently been synthesized.[11] Continuing these studies, we synthesized novel 7-dimethylamino-substituted spirobipyrans (SPP) and their cationic derivatives.

Results and Discussion

The reaction of benzo- (**1**) and naphthopyrilium (**2**) salts with 2-hydroxy-4-dimethylaminobenzaldehyde (**3**) in acetic acid followed by the isolation of the formed salts of *o*-hydroxystyryl derivatives **4** and **5** and the treatment of the latter with ammonia gave SPP **6** and **7**. The alkylation of compounds **6** and **7** with methyl iodide resulted in cationic SPP **8** and **9** (Scheme 1).

The electronic absorption spectra (EAS) of SPP **6**—**9** in acetonitrile are characterized by the long-wavelength absorption bands with maxima in the region 295—344 nm (Table 1).

The spectra of benzoannelated SPP **7** and **9** exhibit the long-wavelength shift of the absorption bands compared to the spectra of SPP **6** and **8**. The distinction of cationic SPP **8** and **9** from SPP **6** and **7** is manifested as the most pronounced vibrational structure of the absorption bands (Fig. 1).

The irradiation of solutions of noncationic SPP **6** and **7** results in their coloration with the appearance of absorption bands with maxima at 497 and 525 nm, respectively, in the EAS (Fig. 2, see Table 1).

This absorption is characteristic of merocyanine isomers of spiropyrans **B** formed due to the pyran ring opening.[12] After irradiation is stopped, the solutions are bleached due to the thermal recyclization of the pyran rings. The bleaching kinetics in solutions of SPP **6** and **7** obeys the exponential law and is characterized by time constants of 85 and 2.6 s, respectively (Fig. 3).

It is noteworthy that the lifetime of naphthopyran derivative **7** is substantially shorter than that of benzopyran derivative **6** (see Table 1).

The photobleaching reaction is observed along with the thermal recyclization in solutions of SPP **6** and **7**.

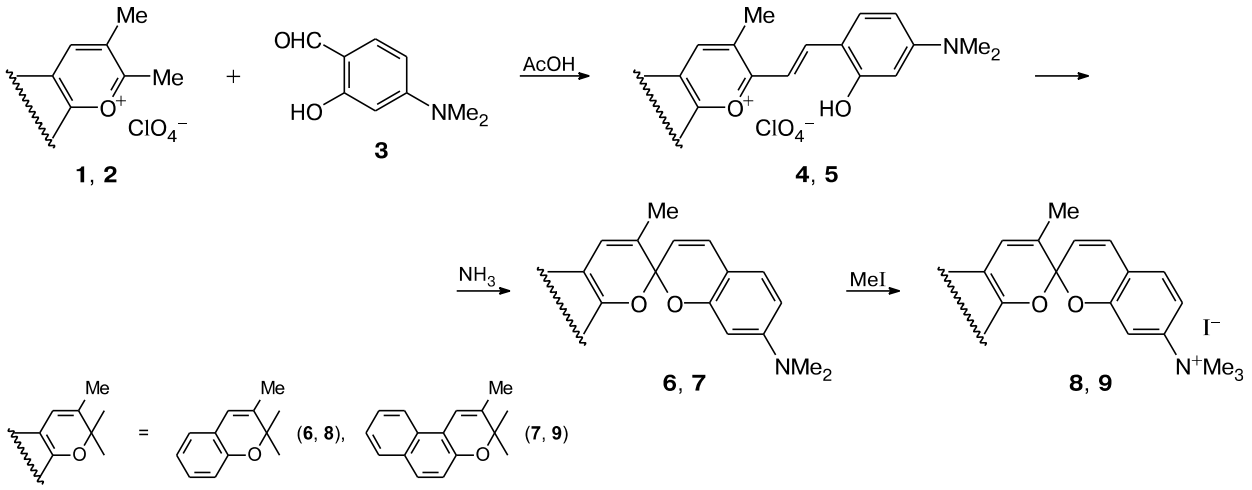
The appearance of the withdrawing trimethylammonium group in SPP **8** and **9** results in the stabilization of photoinduced form $\mathbf{B_2}$. However, it turned out that cationic SPP **8** and **9** exhibit no photochromic properties under analogous experimental conditions including the continuous irradiation of the solutions with the simultaneous detection of the EAS.

The data obtained suggest that the photochromic properties of the synthesized spiropyrans are due to the reversible opening of the pyran ring containing no trimethyl-

* For Part 6, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1884—1887, September, 2011.

Scheme 1



ammonium or dimethylamino group with the formation of merocyanine $\mathbf{B_1}$ (Scheme 2).

This assumption is favored by the data on the kinetics of dark relaxation processes. As it has been shown previously, benzoannulation in the pyran moiety of spiropyrans of the indoline series results in the sharp shortening of the lifetime of the merocyanine isomers, which is related to the higher stabilization energy of the naphthalene ring compared to the benzene ring.[13,14] At the same time, the absence of photochromism in the case of cationic SPP under the stationary conditions can be due to the short lifetime of open isomers $\mathbf{B_1}$, whose thermal destabilization is caused by the presence of the strong electron-withdrawing group in the heterene (not photochromic) moiety of the spirocyclic system, which has earlier been observed for spiropyrans[15,16] and spirooxazines.[16] The experimentally observed effect of decreasing the photocoloration quantum yield caused by transformation $\mathbf{A} \rightarrow \mathbf{B_2}$ upon the in-

Scheme 2

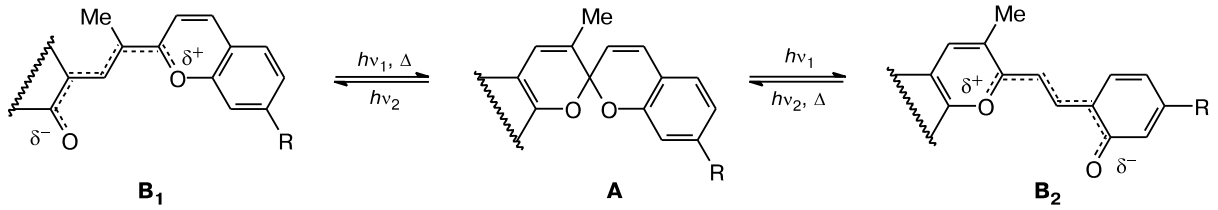


Table 1. Spectral kinetic characteristics of spiropyrans **6**—**9** in acetonitrile at 293 K

Compound	Form **A**		Form **B**	
	λ_{max}^{abs} /nm	ε /L mol^{-1} cm^{-1}	λ_{max}^{abs} /nm	τ_{293}/s
6	250, 317	15380, 21450	497	85.0
7	300 sh, 310, 345 sh	22950, 27240, 8250	525	2.6
8	247, 295, 303 sh	29250, 5380, 4890	—	—
9	241, 297, 308, 329, 344	64700, 9760, 9310, 4610, 5290	—	—

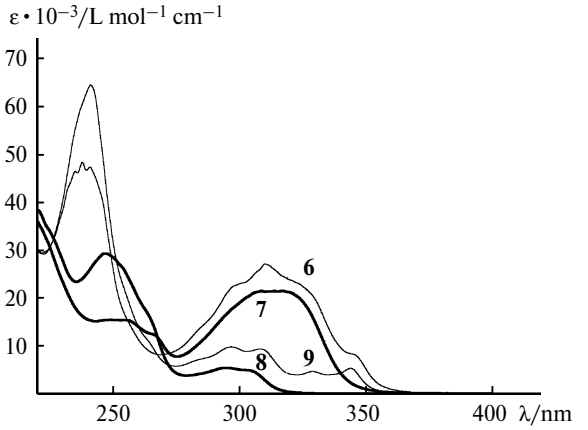


Fig. 1. Electronic absorption spectra of compounds **6**—**9** in acetonitrile at $T = 293$ K.

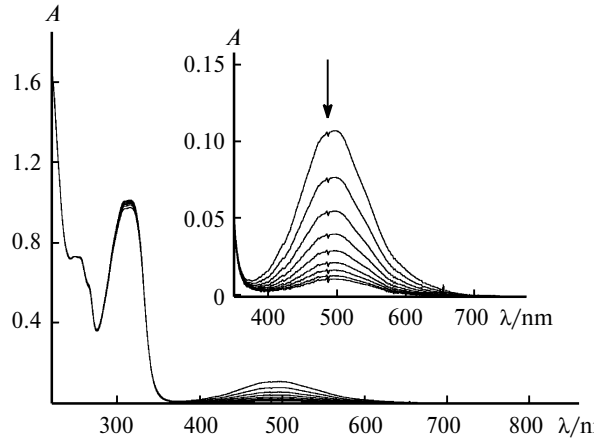


Fig. 2. Electronic absorption spectra of compound **6** during the thermal bleaching reaction ($[C] = 4.75 \cdot 10^{-5}$ mol L^{-1}; dt = 30 s) in acetonitrile at $T = 293$ K.

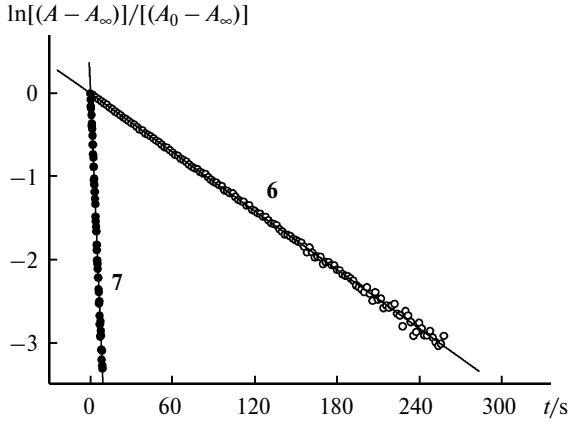


Fig. 3. Kinetics of dark bleaching of compounds **6** and **7** in acetonitrile at $T = 293$ K.

troduction of electron-withdrawing substituents (the exception is the nitro group, whose inclusion noticeably activates the triplet channel of phototransformations), into the benzopyran or benzooxazine moiety of the spirocyclic molecule can serve as an additional fact in favor of the proposed occurrence of photoreaction $\mathbf{A} \rightarrow \mathbf{B_1}$.[17]

Thus, the novel photochromic SPP containing the dimethylamino group in position 7 of the benzopyrane moiety and their cationic derivatives with the trimethylammonium substituent were synthesized. Unlike similar trimethylammonium-substituted spiropyran of the isobenzofuran series, the trimethylammonium derivatives of SPP exhibit no photochromic properties.

Experimental

^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz), signals were assigned relatively to the signal of residual protons of deuterated solvents $CDCl_3$ (δ 7.26) and DMSO-d_6 (δ 2.50), and values of δ were measured with the accuracy to 0.01 (SSCC were measured with the accuracy to 0.1 Hz).

The electronic absorption spectra and the kinetic curves of thermal recyclization reactions of the studied compounds were recorded on an Agilent 8453 spectrophotometer with an attachment for temperature maintenance of samples. Photolysis of solutions (concentration $2 \cdot 10^{-5}$ mol L^{-1}) was carried out with a Newport system based on a mercury lamp (power 200 W) with a set of interferential light filters. Acetonitrile of spectral purity (Aldrich) was used for the preparation of solutions.

Compounds **1**—**3** were synthesized according to known procedures.[18—20]

Dimethylamino-substituted spirobipyrans 6 and 7 (general procedure). Aldehyde **3** (0.18 g, 1.1 mmol) was added to a boiling solution of pyrilium salt **1** or **2** (1 mmol) in glacial acetic acid (10 mL), and the solution was refluxed for 30 min and stored for 12 h at ~20 °C. The precipitate that formed was filtered off, washed with ether, dried, and then used without additional purification. A suspension of the obtained salt **4** or **5** in benzene (15 mL) was purged with a dry ammonia flow until the precipitate was dissolved, the solvent was evaporated, and the residue was purified by column chromatography on Al_2O_3 (benzene as an eluent) and recrystallized.

***N*,*N*,3′-Trimethylspirobi[2*H*-1-benzopyran]-7-amine (6).** The yield was 60%, m.p. 148.5—150 °C (from a heptane—toluene (3 : 1) mixture). Found (%): C, 78.83; H, 6.39; N, 4.42. $C_{20}H_{19}NO_2$. Calculated (%): C, 78.66; H, 6.27; N, 4.59. ^{1}H NMR ($CDCl_3$), δ: 1.98 (d, 3 H, 3′-Me, J = 1.5 Hz); 2.89 (s, 6 H, 7-NMe_2); 5.69 (d, 1 H, H(3), J = 9.6 Hz); 6.17 (d, 1 H, H(8), J = 2.5 Hz); 6.34 (dd, 1 H, H(6), J = 8.5 Hz, J = 2.5 Hz); 6.56 (m, 1 H, H(4′)); 6.78 (d, 1 H, H(4), J = 9.6 Hz); 6.83 (m, 1 H, H(8′)); 6.93 (m, 1 H, H(6′)); 7.04 (d, 1 H, H(5), J = 8.5 Hz); 7.10 (d, 1 H, H(5′), J = 7.4 Hz); 7.12 (m, 1 H, H(7′)).

***N*,*N*,2′-Trimethylspiro[2*H*-1-benzopyran-2,3′-[3*H*]naphtho-[2,1-*b*]pyran]-7-amine (7).** The yield was 64%, m.p. 201.5—203 °C (from a heptane—toluene (1 : 1) mixture). Found (%): C, 81.25; H, 5.84; N, 4.03. $C_{24}H_{21}NO_2$. Calculated (%): C, 81.10; H, 5.96; N, 3.94. ^{1}H NMR ($CDCl_3$), δ: 2.13 (d, 3 H, 2′-Me, J = 1.5 Hz); 2.89 (s, 6 H, 7-NMe_2); 5.80 (d, 1 H, H(3), J = 9.6 Hz); 6.15 (d, 1 H, H(8), J = 2.5 Hz); 6.37 (dd, 1 H, H(6), J = 8.5 Hz, J = 2.5 Hz); 6.85 (d, 1 H, H(4), J = 9.6 Hz); 7.09 (d, 1 H, H(5), J = 8.5 Hz); 7.10 (d, 1 H, H(5′), J = 8.8 Hz); 7.33 (m, 1 H, H(1′)); 7.38 (ddd, 1 H, H(8′), J = 8.1 Hz, J = 6.9 Hz, J = 1.1 Hz); 7.52 (ddd, 1 H, H(9′), J = 8.4 Hz, J = 6.9 Hz, J = 1.4 Hz); 7.66 (d, 1 H, H(6′), J = 8.8 Hz); 7.77 (m, 1 H, H(7′)); 8.13 (m, 1 H, H(10′)).

Trimethylammonium-substituted spirobipyrans 8 and 9 (general procedure). A mixture of spiropyran **6** or **7** (1 mmol) iodomethane (0.62 mL, 10 mmol), and THF (10 mL) was refluxed for 10 h and stored for 12 h at ~20 °C. The precipitate that formed was filtered off and washed with THF.

***N*,*N*,*N*,3′-Tetramethylspirobi[2*H*-1-benzopyran]-7-ammonium iodide (8).** The yield was 86%, m.p. 121—122 °C. Found (%): C, 56.54; H, 5.02; N, 3.05. $C_{21}H_{22}INO_2$. Calculated (%): C, 56.39; H, 4.96; N, 3.13. ^{1}H NMR (DMSO-d_6), δ: 1.92 (d, 3 H, 3′-Me, J = 1.5 Hz); 3.51 (s, 9 H, 7-N^+Me_3); 6.33 (d, 1 H, H(3), J = 9.9 Hz); 6.79—6.84 (m, 2 H, H_{Ar}); 7.01 (m, 1 H, H_{Ar}); 7.10—7.21 (m, 2 H, H_{Ar}); 7.26 (m, 1 H, H_{Ar}); 7.55—7.61 (m, 3 H, H_{Ar}).

***N*,*N*,*N*,2′-Tetramethylspiro[2*H*-1-benzopyran-2,3′-[3*H*]-naphtho-[2,1-*b*]pyran]-7-ammonium iodide (9).** The yield was

83%, m.p. 166—167 °C. Found (%): C, 60.24; H, 4.80; N, 2.89. $C_{25}H_{24}INO_2$. Calculated (%): C, 60.37; H, 4.68; N, 2.82. ^{1}H NMR (DMSO-d_6), δ: 2.07 (d, 3 H, 2´-Me, J = 1.3 Hz); 3.50 (s, 9 H, 7-N^+Me_3); 6.43 (d, 1 H, H(3), J = 9.8 Hz); 7.11 (d, 1 H, H(5´), J = 8.9 Hz); 7.19 (d, 1 H, H(4), J = 9.8 Hz); 7.45 (m, 1 H, H_{Ar}); 7.52 (d, 1 H, H(8), J = 2.5 Hz); 7.57—7.66 (m, 4 H, H_{Ar}); 7.80 (d, 1 H, H(6´), J = 8.9 Hz); 7.89 (m, 1 H, H_{Ar}); 8.31 (m, 1 H, H_{Ar}).

This work was financially supported by the Federal Target Program "Scientific and Scientific—Pedagogical Personnel of the Innovative Russia in 2009—2013" (State Contract No. P2435) and the Russian Foundation for Basic Research (Project No. 09-03-00813).

References

1. A. V. Chernyshev, I. V. Dorogan, N. A. Voloshin, A. V. Metelitsa, V. I. Minkin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2011, 447 [*Russ. Chem. Bull., Int. Ed.*, 2011, **60**, 456].
2. S. Bénard, P. Yu, *Adv. Mater.*, 2000, **12**, 48.
3. S. M. Aldoshin, L. A. Nikonova, V. A. Smirnov, G. V. Shilov, N. K. Nagaeva, *J. Mol. Struct.*, 2005, **750**, 158.
4. S. M. Aldoshin, L. A. Nikonova, V. A. Smirnov, G. V. Shilov, N. K. Nagaeva, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 2050 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2113].
5. I. Kashima, M. Okubo, Y. Ono, M. Itoi, N. Kida, M. Hikita, M. Enomoto, N. Kojima, *Synth. Met.*, 2005, **153**, 473.
6. S. Benard, E. Riviere, P. Yu, K. Nakatani, J. F. Delonis, *Chem. Mater.*, 2001, **13**, 159.
7. S. Benard, P. Yu, *Chem. Commun.*, 2000, 65.
8. S. M. Aldoshin, N. A. Sanina, V. I. Minkin, N. A. Voloshin, V. N. Ikorskii, V. I. Ovcharenko, V. A. Smirnov, N. K. Nagaeva, *J. Mol. Struct.*, 2007, **826**, 69.
9. K. Nakatani, P. Yu, *Adv. Mater.*, 2001, **13**, 1411.
10. I. Kashima, M. Okubo, Y. Ono, M. Itoi, N. Kida, M. Hikita, M. Enomoto, N. Kojima, *Synth. Met.*, 2005, **155**, 703.
11. E. V. Solov´eva, N. A. Voloshin, S. O. Bezuglyi, A. V. Metelitsa, *Khim. Geterotsikl. Soedin.*, 2010, 630 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2010, **46**, 500].
12. R. C. Bertelson, *Organic Photochromic and Thermochromic Compounds. Topics in Applied Chemistry*, Eds J. C. Crano, R. J. Guglielmetti, Plenum Press, New York, 1999, Vol. **1**, p. 11.
13. N. A. Voloshin, E. B. Gaeva, A. V. Chernyshev, A. V. Metelitsa, V. I. Minkin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 156 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 156].
14. O. G. Nikolaeva, E. B. Gaeva, E. N. Shepelenko, A. V. Tsukanov, A. V. Metelitsa, B. S. Luk´yanov, A. D. Dubonosov, V. A. Bren´, V. I. Minkin, *Zh. Org. Khim.*, 2009, **45**, 1102 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2009, **45**, 1091].
15. O. G. Nikolaeva, A. V. Tsukanov, E. N. Shepelenko, B. S. Lukyanov, A. V. Metelitsa, O. Yu. Kostyrina, A. D. Dubonosov, V. A. Bren, V. I. Minkin, *J. Photoenergy*, 2009, 1.
16. A. V. Metelitsa, V. Lokshin, J. C. Micheau, A. Samat, R. Guglielmetti, V. Minkin, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4340.
17. V. Lokshin, A. Sama, A. V. Metelitsa, *Usp. Khim.*, 2002, **71**, 1015 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2002, **71**, 893].
18. C. Schiele, A. Wilhelm, D. Hendriks, M. Stepec, G. Paal, *Tetrahedron*, 1968, **24**, 5029.
19. A. Löwenbein, W. Katz, *Chem. Ber.*, 1926, **59**, 1377.
20. D. P. Specht, P. A. Martic, S. Farid, *Tetrahedron*, 1982, **38**, 1203.

Received October 29, 2010