

Synthesis and Reactions of 2-(Dimethylaminomethylidene)-6-methoxynaphtho[1,8-*bc*]pyran-3-one

O. M. Golyanskaya^a, N. A. Voloshin^b, A. V. Chernyshev^a, A. D. Dubonosov^b, A. V. Metelitsa^a, V. V. Mezheritskii^a, and V. A. Bren'^a

^a Institute of Physical and Organic Chemistry, Southern Federal University,
pr. Stachki 194/2, Rostov-on-Don, 344090 Russia
e-mail: mezher@ipoc.rsu.ru

^b Southern Research Center, Russian Academy of Sciences, ul. Chekhova 41, Rostov-on-Don, 344006 Russia

Received July 2, 2007

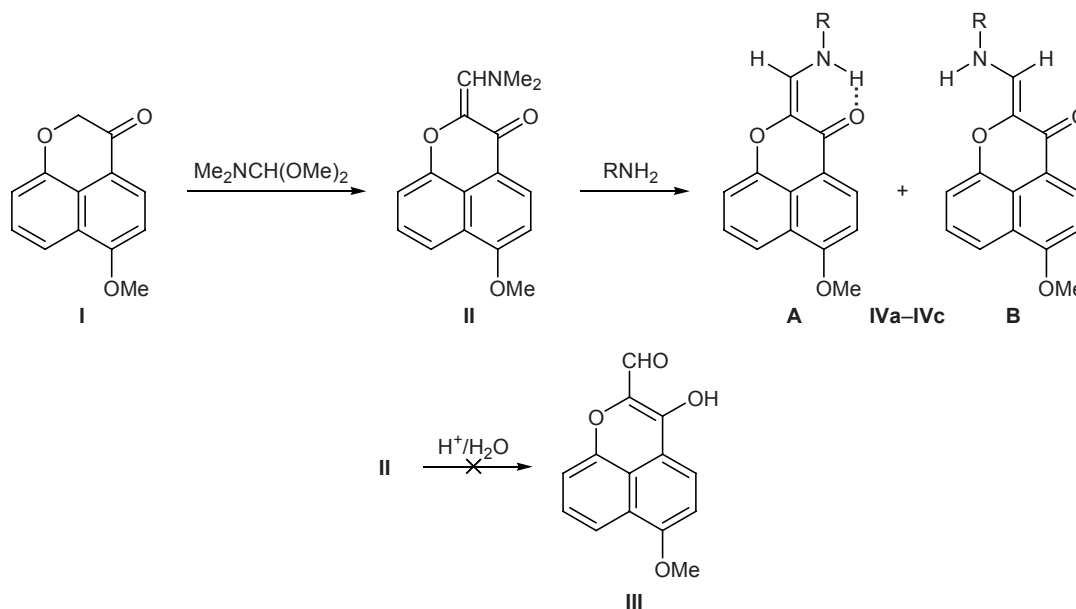
Abstract—The reaction of 6-methoxynaphtho[1,8-*bc*]pyran-3-one with dimethylformamide dimethyl acetal gave the corresponding 2-dimethylaminomethylidene derivative which reacted with amines to form new 2-aminomethylidene-6-methoxynaphtho[1,8-*bc*]pyran-3-ones via replacement of the dimethylamino group. 2-Dimethylaminomethylidene-6-methoxynaphtho[1,8-*bc*]pyran-3-one also reacted with 2,3-dimethylchromenium perchlorate and 1,2,3,3-tetramethyl-3*H*-indolium perchlorate to give the corresponding merocyanine dyes. The latter were examined for chemosensor and photochromic properties.

DOI: 10.1134/S1070428008040222

We previously [1] reported on the synthesis of 2-acyl-substituted 6-methoxynaphtho[1,8-*bc*]pyran-3-ones. These compounds, as well as metal chelates derived therefrom, were found to exhibit strong yellow–orange fluorescence which can be observed visu-

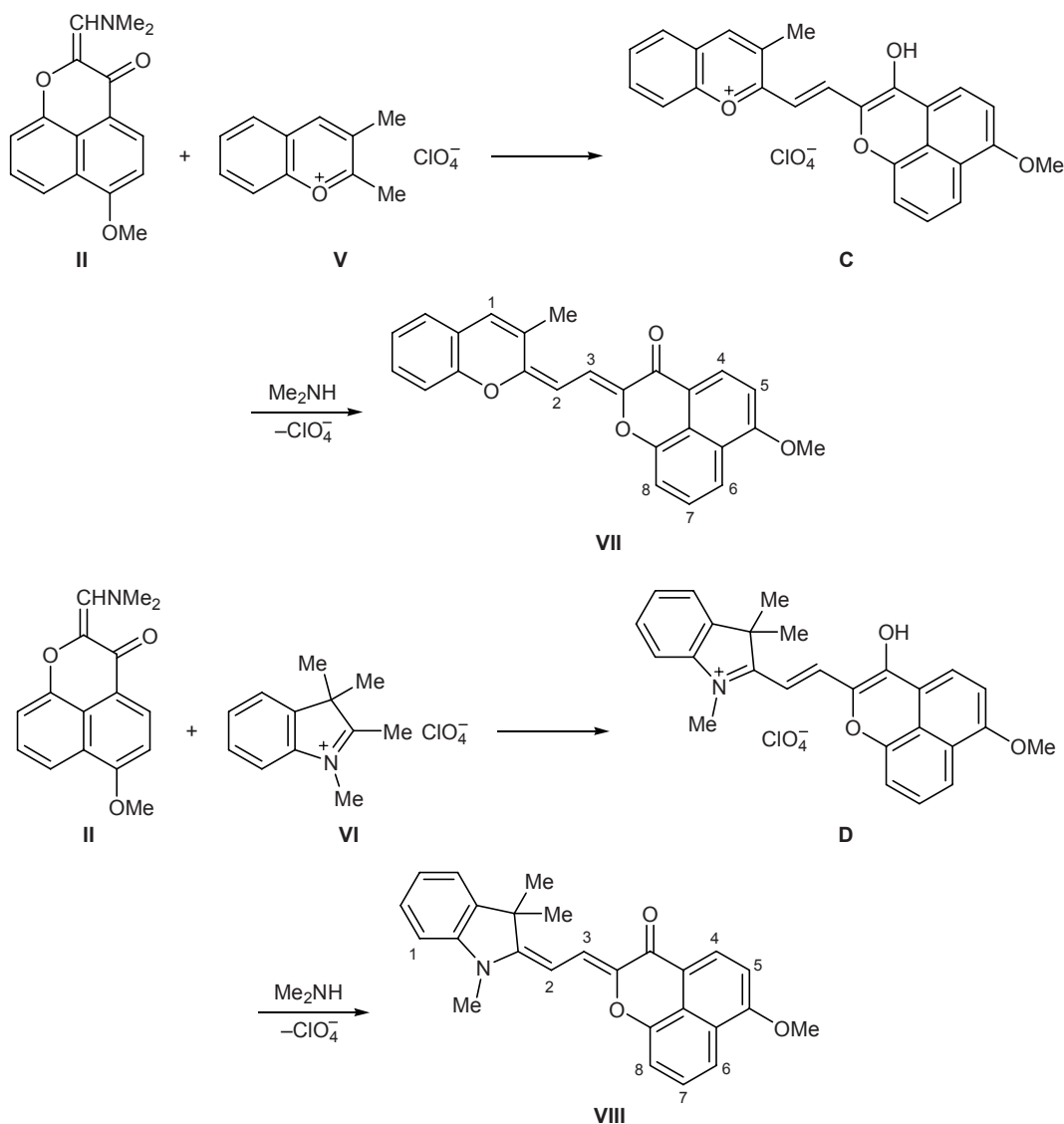
ally. Their fluorescent properties were studied in [2]. We anticipated that 2-formyl derivative of the above *peri*-fused heterocyclic system may be a potential precursor of new chemosensors [3] and photochromic compounds [4]. However, our attempts to effect

Scheme 1.



R = PhCH₂ (a), *p*-MeC₆H₄ (b), *p*-MeOC₆H₄CONH (c).

Scheme 2.



formylation of previously synthesized 6-methoxynaphtho[1,8-*bc*]pyran-3-one (**I**) [5] according to Rieche [6] or Vilsmeier [7] were unsuccessful, whereas heating of compound **I** with dimethylformamide dimethyl acetal gave 2-dimethylaminomethylidene derivative **II** (Scheme 1). Unfortunately, hydrolysis of **II** resulted in the formation of a tarry material instead of expected aldehyde **III**, and we failed to isolate individual compounds.

We found that enamino ketones **IV** as potential ligands and chemosensors can be obtained by reaction of compound **II** with aliphatic and aromatic amines or carboxylic acid hydrazides (Scheme 1). Unlike structurally related 2-acyl-3-hydroxy-6-methoxynaphtho[1,8-*bc*]pyrans [1], enamino ketones **IV** have exclu-

sively the quinoid rather than benzoid structure, as follows from their IR, ^1H NMR, and UV spectra. In the IR spectra of both compound **II** and amino ketones **IVa–IVc** we observed a strong absorption band at $1660\text{--}1680\text{ cm}^{-1}$, which is typical of a carbonyl rather than $\text{C}=\text{N}$ group [8]. The ^1H NMR spectra of enamino ketones **IVa–IVc** contained a double set of signals from protons in the NH, Me, and OMe groups with an intensity ratio of $(0.3\text{--}0.4):(0.7\text{--}0.6)$. Presumably, these compounds exist as two isomers **A** and **B**. The NH proton in isomer **A** resonates in the ^1H NMR spectrum at δ 10–11 ppm, while the corresponding signal of isomer **B** is located at δ 5.4 ppm in the spectrum of compound **IVa**; the NH signal of **IVb** and **IVc** is overlapped by the aromatic proton signals, and it can be identified only by deuteration.

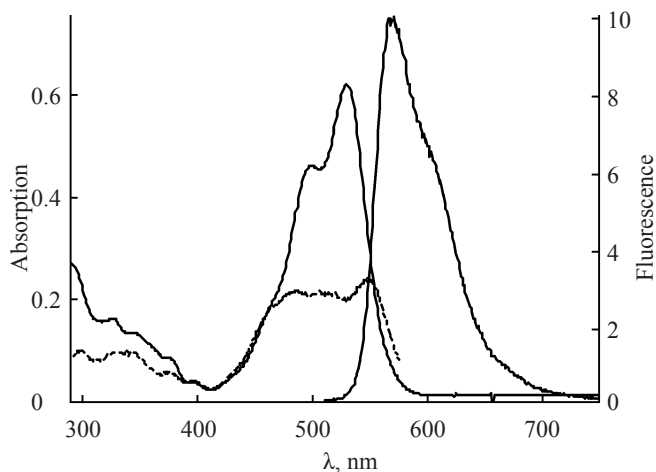


Fig. 1. (1) Electronic absorption, (2) emission, and (3) fluorescence excitation spectra of 6-methoxy-2-[(*Z*)-2-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethylidene]naphtho[1,8-*bc*]pyran-3(2*H*)-one (**VIII**) in toluene ($c = 1.3 \times 10^{-4}$ M).

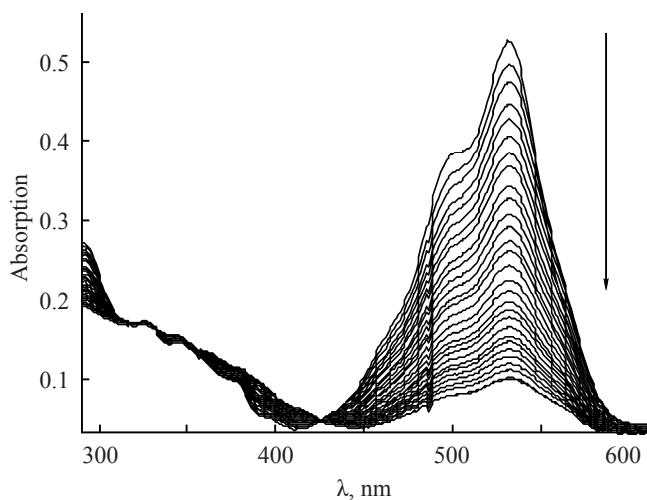


Fig. 2. Variation of the electronic absorption spectrum of 6-methoxy-2-[(*Z*)-2-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethylidene]naphtho[1,8-*bc*]pyran-3(2*H*)-one (**VIII**) in toluene ($c = 1.1 \times 10^{-4}$ M) at 293 K upon irradiation at λ 546 nm; the spectra were recorded at 20-s intervals.

The quinoid structure of compounds **IVa–IVc** is also confirmed by the presence in their electronic absorption spectra of a long-wave absorption band in the region λ 430–470 nm, regardless of the solvent polarity. As noted above, 2-acyl-3-hydroxy-6-methoxynaphtho[1,8-*bc*]pyrans are characterized by strong fluorescence in the region of about λ 570 nm with a considerable Stokes shift due to O \rightarrow N hydrogen transfer in the excited state [9]. Enamino ketones **IV** displayed much weaker fluorescence at λ 480 nm, and the absorption and emission bands are mirror symmetric. The quinoid structure of compounds **IV** under

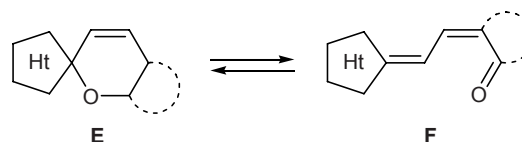
the conditions for determination of their chemosensor properties (room temperature, propan-2-ol or acetonitrile as solvent, $c = 2.5 \times 10^{-5}$ M) hampers chelation with heavy metal cations. Only insignificant changes were observed in the electronic absorption spectra, and the emission maximum did not change its position, regardless of the cation nature (Pb^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+}). Thus compounds **IV** cannot be used as chemosensors.

Compound **II** can be used as a synthetic equivalent of aldehyde **III** in the condensation with heterocyclic cations **V** and **VI** at the activated 2-methyl group with a view to obtain 2-styryl derivatives **C** and **D** and convert the latter into novel potentially photochromic spirochromenes (Scheme 2). By heating 2-dimethylaminomethylidene-6-methoxynaphtho[1,8-*bc*]pyran-3-one (**II**) with 2,3-dimethylchromenium perchlorate (**V**) and 1,2,3,3-tetramethyl-3*H*-indolium perchlorate (**VI**) in acetic acid we obtained deeply colored compounds **VII** and **VIII**, respectively. In this condensation, dimethylamine liberated during the process acted as deprotonating agent. The deep color of compounds **VII** and **VIII** in solution and in the crystalline state indicates that they have open-chain merocyanine structure.

The electronic absorption spectra of **VII** and **VIII** in toluene contained long-wave maxima at λ 517 and 529 nm, respectively (Fig. 1). The position and intensity of these bands are typical of acyclic merocyanine forms **F** of spiropyrans **E** [4] (Scheme 3). 3*H*-Indole derivative **VIII** showed strong fluorescence with a quantum yield of 0.11, the emission maximum being located at λ 571 nm. The fluorescence excitation spectrum of **VIII** coincides with its absorption spectrum (Fig. 1). Compound **VII** possesses no fluorescent properties.

Irradiation of a solution of **VIII** at 293 K at a wavelength corresponding to its long-wave absorption maximum (λ 546 nm) promotes irreversible photoinduced transformation which is accompanied by reduction in the fluorescence intensity at 529 nm (Fig. 2). Compound **VII** is photochemically inactive: no changes in the electronic absorption spectrum was observed upon irradiation of a solution of **VII** in toluene at 293 K with a mercury lamp (λ 546 nm, intensity 1.5×10^{16} quantum/s) over a period of 20 min.

Scheme 3.



Thus we have synthesized new compounds **VII** and **VIII** which have the structure of open-chain merocyanine forms of spiropyrans. These compounds exhibit no photochromic properties (reverse photochromism) at 293 K.

EXPERIMENTAL

The IR spectra were recorded in mineral oil on a Specord IR-71 spectrophotometer. The ^1H NMR spectra were measured on a Varian Unity-300 instrument (USA) from solutions in CDCl_3 using hexamethyldisiloxane as internal reference. The electronic absorption spectra were obtained on a Varian Cary 100 spectrophotometer. The emission and fluorescence excitation spectra were measured on a Varian Cary Eclipse spectrofluorimeter. The fluorescence quantum yields were determined relative to a solution of Eosin in 0.1 M NaOH ($\phi = 0.20$ [10]). Solutions were prepared using toluene of ultrapure grade. A DRSh-250 mercury lamp was used as irradiation source; required spectral bands were isolated with the aid of interference filters.

2-Dimethylaminomethylidene-6-methoxynaphtho[1,8-*bc*]pyran-3-one (II). *N,N*-Dimethylformamide dimethyl acetal, 0.18 ml (1.5 mmol), was added to a hot solution of 0.21 g (1 mmol) of compound **I** in 3 ml of toluene, and the mixture was heated for 3 h under reflux. The orange precipitate was filtered off and recrystallized from alcohol. Yield 0.17 g (71%), mp 202–203°C. IR spectrum, ν , cm^{-1} : 1670 (C=O), 1620, 1580. ^1H NMR spectrum, δ , ppm: 3.30 s (6H, NMe_2), 4.05 s (3H, OCH_3), 6.93 d (1H, 5-H, $J_{5,4} = 8.25$ Hz), 6.98 d (1H, 7-H, $J_{7,8} = 7.85$ Hz), 7.22 s (1H, =CHN), 7.38 t (1H, 8-H, $J_{8,9} = 8.25$, $J_{8,7} = 7.85$ Hz), 7.72 d (1H, 9-H, $J_{9,8} = 8.25$ Hz), 8.11 d (1H, 4-H, $J_{4,5} = 8.25$ Hz). Found, %: C 71.51; H 5.76; N 5.35. $\text{C}_{16}\text{H}_{15}\text{NO}_3$. Calculated, %: C 71.36; H 5.61; N 5.20.

2-Benzylaminomethylidene-6-methoxynaphtho[1,8-*bc*]pyran-3-one (IVa). A mixture of 0.1 g (0.4 mmol) of compound **II** and 0.06 g (0.6 mmol) of benzylamine in 2 ml of toluene was heated for 3.5 h under reflux. After cooling, the precipitate was filtered off. Yield 0.09 g (70%), yellow crystals, mp 180–181°C (from toluene). IR spectrum, ν , cm^{-1} : 3260, 1665, 1580. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.06 s (0.3 CH_3 , OCH_3), 4.08 s (0.7 CH_3 , OCH_3), 4.49 d (0.3 CH_2 , $^3J = 4.94$ Hz), 4.54 d (0.7 CH_2 , $^3J = 5.97$ Hz), 5.38 m (0.7H, NH), 6.90–8.60 m (11H, H_{arom} , =CHN), 9.80 m (0.3H, NH). Found, %: C 76.39; H 5.31; N 4.08. $\text{C}_{21}\text{H}_{17}\text{NO}_3$. Calculated, %: C 76.13; H 5.14; N 4.23.

6-Methoxy-2-(4-methylphenylaminomethylidene)naphtho[1,8-*bc*]pyran-3-one (IVb) was synthesized in a similar way. Yield 62%, red crystals, mp 128–129°C (from ethanol). IR spectrum, ν , cm^{-1} : 3200, 1670, 1590. ^1H NMR spectrum, δ , ppm: 2.34 s (3H, CH_3), 4.18 s (0.3 CH_3 , OCH_3), 4.20 s (0.7 CH_3 , OCH_3), 6.90–7.50 m (7H, H_{arom} , =CHN), 7.66 d (0.7H, NH, $^3J = 12$ Hz), 7.70–8.26 m (3H, H_{arom}), 11.38 d (0.3H, NH, $^3J = 12$ Hz). Found, %: C 76.43; H 4.95; N 4.39. $\text{C}_{21}\text{H}_{17}\text{NO}_3$. Calculated, %: C 76.13; H 5.14; N 4.23.

6-Methoxy-2-[2-(4-methoxybenzoyl)hydrazinomethylidene]naphtho[1,8-*bc*]pyran-3-one (IVc). A mixture of 0.1 g (0.4 mmol) of compound **II** and 0.07 g (0.45 mmol) of *p*-methoxybenzohydrazide in 1 ml of toluene was heated for 2 h under reflux. After cooling, the precipitate was filtered off. Yield 0.08 g (58%), yellow crystals, mp 227–228°C (from acetonitrile). IR spectrum, ν , cm^{-1} : 3486, 3406, 3260, 1670, 1660, 1600. ^1H NMR spectrum ($\text{DMSO-}d_6$), δ , ppm: 3.80 s (0.4 CH_3 , $\text{C}_6\text{H}_4\text{OCH}_3$), 3.83 s (0.6 CH_3 , $\text{C}_6\text{H}_4\text{OCH}_3$), 4.05 s (0.6 CH_3 , 6- OCH_3), 4.10 s (0.4 CH_3 , 6- OCH_3), 6.95–8.20 m (10H, H_{arom} , =CHN), 8.4 s (0.4H, NHCO), 9.25 d [0.6H, NHNHCO , $J(\text{NH}, \text{CH}) = 10.36$ Hz], 10.80 s (0.6H, NHCO), 11.80 d [0.4H, NHNHCO , $J(\text{NH}, \text{CH}) = 10.36$ Hz]. Found, %: C 67.91; H 4.55; N 7.38. $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_5$. Calculated, %: C 67.69; H 4.62; N 7.18.

6-Methoxy-2-[(2*Z*)-2-(methyl-2*H*-chromen-2-ylidene)ethylidene]naphtho[1,8-*bc*]pyran-3(2*H*)-one (VII). A mixture of 0.1 g (0.4 mmol) of compound **II** and 0.12 g (0.45 mmol) of 2,3-dimethylchromenium perchlorate in 3 ml of acetonitrile was heated for 0.5 h under reflux. After cooling, the precipitate was filtered off. Yield 0.08 g (54%), green crystals with metallic luster, mp 249–251°C (from acetonitrile). IR spectrum, ν , cm^{-1} : 1646, 1566, 1540. ^1H NMR spectrum, δ , ppm: 2.20 s (3H, CH_3), 4.10 s (3H, OCH_3), 6.06 d (1H, 2-H, $J_{2,3} = 12.15$ Hz), 6.60 s (1H, 1-H), 6.98–7.36 m (6H, H_{arom}), 7.48 t (1H, 7-H, $J_{7,8} = 8.21$, $J_{7,6} = 7.91$ Hz), 7.65 d (1H, 3-H, $J_{3,2} = 12.15$ Hz), 7.86 d (1H, 7-H, $J_{8,7} = 8.21$ Hz), 8.32 d (1H, 4-H, $J_{4,5} = 8.20$ Hz). Found, %: C 78.91; H 4.55. $\text{C}_{25}\text{H}_{18}\text{O}_4$. Calculated, %: C 78.53; H 4.71.

6-Methoxy-2-[(2*Z*)-2-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethylidene]naphtho[1,8-*bc*]pyran-3(2*H*)-one (VIII). A solution of 0.1 g (0.4 mmol) of compound **II** and 0.14 g (0.5 mmol) of 1,2,3,3-tetramethyl-3*H*-indolium perchlorate in 2 ml of acetic acid was heated for 0.5 h under reflux. The mixture was diluted with water, and the precipitate was

filtered off and purified by column chromatography on aluminum oxide using chloroform as eluent. Yield 0.09 g (62%), dark red crystals, mp 217–219°C. IR spectrum, ν , cm^{-1} : 1646, 1593, 1540. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.65 s (6H, CMe_2), 3.27 s (3H, NCH_3), 4.10 s (3H, OCH_3), 5.94 d (1H, 2-H, $J_{2,3} = 13.11$ Hz), 6.74 d (1H, 1-H, $J = 7.77$ Hz), 6.90–7.30 m (5H, H_{arom}), 7.46 t (1H, 7-H, $J_{7,8} = 8.17$, $J_{7,6} = 7.98$ Hz), 7.64 d (1H, 3-H, $J_{3,2} = 13.11$ Hz), 7.86 d (1H, 8-H, $J_{8,7} = 8.17$ Hz), 8.24 d (1H, 4-H, $J_{4,5} = 8.13$ Hz). Found, %: C 78.81; H 5.65; N 3.70. $\text{C}_{26}\text{H}_{23}\text{NO}_3$. Calculated, %: C 78.59; H 5.79; N 3.53.

This study was performed under financial support by the Ministry of Education and Science of the Russian Federation (project nos. RNP.2.2.2.2.5592, RNP.2.1.1.1938).

REFERENCES

1. Mezheritskii, V.V., Minyaeva, L.G., and Golyanskaya, O.M., *Zh. Org. Khim.*, 1992, vol. 28, p. 1187.
2. Tsukanov, A.V., Dubonosov, A.D., Golyanskaya, O.M., Mezheritskii, V.V., Revinskii, Yu.V., Bren', V.A., and Minkin, V.I., *Russ. J. Gen. Chem.*, 2006, vol. 76, p. 841.
3. Bren', V.A., *Usp. Khim.*, 2001, vol. 70, p. 1017.
4. Guglielmetti, R., *Photochromism*, Durr, H. and Bouas-Laurent, H., Eds., Amsterdam: Elsevier, 1990, p. 314.
5. Minyaeva, L.G., Golyanskaya, O.M., and Mezheritskii, V.V., *Zh. Org. Khim.*, 1994, vol. 30, p. 258.
6. Rieche, A., Gross, H., and Hoft, E., *Chem. Ber.*, 1960, vol. 93, p. 88.
7. Vilsmeier, A. and Haack, A., *Chem. Ber.*, 1927, vol. 60, p. 121.
8. Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London: Methuen, 1958.
9. Knyazhanskii, M.I. and Metelitsa, A.V., *Fotoinitsirovannye protsessy v molekulakh azometinov i ikh strukturnykh analogov* (Photoinitiated Processes in Molecules of Schiff Bases and Their Structural Analogs), Rostov-on-Don: Rostov. Gos. Univ., 1992.
10. Fleming, G.R., Knight, A.W.E., Morris, J.M., Morrison, R.J.S., and Robinson, G.W., *J. Am. Chem. Soc.*, 1977, vol. 99, p. 4306.