DOI 10.1007/s10593-015-1689-2

Chemistry of Heterocyclic Compounds **2015**, *51*(3), 229–233

Synthesis of bis-spiropyrans based on 6,8-diformyl-5,7-dihydroxy-4-methylcoumarin and photochromic properties thereof

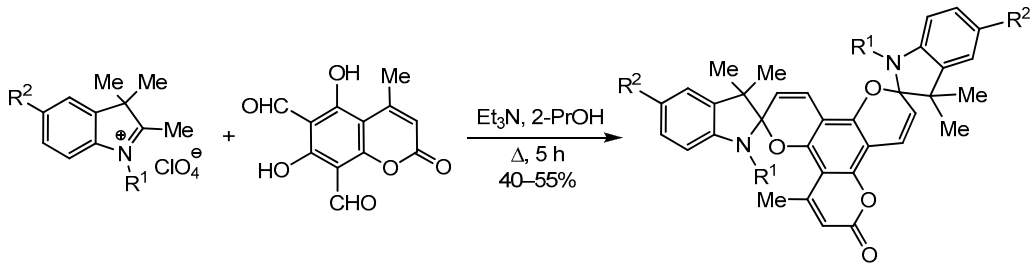
Olga G. Nikolaeva[1]*, Olga Yu. Karlutova[1], Alexander S. Cheprasov[2], Anatoly V. Metelitsa[1], Igor V. Dorogan[1], Alexander D. Dubonosov[2], Vladimir A. Bren'[1]

[1] *Southern Federal University, 194/2 Stachki Ave., Rostov-on-Don 344090, Russia; e-mail: dubon@ipoc.sfedu.ru*

[2] *Southern Scientific Center, Russian Academy of Sciences, 41 Chekhova Ave., Rostov-on-Don 344006, Russia; e-mail: aled@ipoc.sfedu.ru*

Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2015, *51*(3), 229–223

Submitted January 15, 2015
Accepted February 11, 2015



Synthesis of new asymmetric bis-spiropyrans of indoline series based on 6,8-diformyl-5,7-dihydroxy-4-methylcoumarin was realized. Depending on the nature of the substituents in positions 1 and 5 of the indoline moiety the derived compounds may exist in solution in the spiro or merocyanine forms, or as a tautomeric mixture of these forms. UV irradiation of the cyclic forms leads to photocoloring associated with re-opening of one or both of the spiro moieties. The wide variability of spectral kinetic properties of bis-spiropyrans upon fluorescence of photoinduced forms allows one to consider them as molecular switches having absorptive and fluorescent signal functions with the possibility of practical application.

Keywords: 6,8-diformyl-5,7-dihydroxy-4-methylcoumarin, merocyanine, spiropyran, quantum-chemical calculations, photochromism.

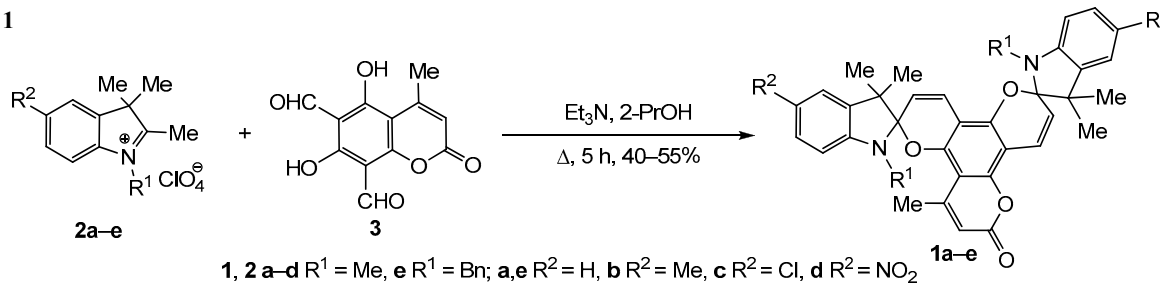
Photochromic spiropyrans are promising materials for optical recording media, molecular switches, and chemosensors.[1–6] Their photoinitiated rearrangement includes reversible dissociation of C_{spiro}–O bond of the cyclic isomer and subsequent *Z*/*E* isomerization to the metastable merocyanine form. The latter can be converted to the original spiro form under irradiation with visible light. Previously, it was shown that spiropyrans containing fused benzopyranone moiety possess not only photochromic but also fluorescent properties.[7–14]

In this paper, we describe the synthesis as well as the results of the study on the structure and photochromism of coumarin series indoline bis-spiropyrans, the absorbance of cyclic forms of which can be expected to increase due to the enlargement of the spatial extent of the molecular system.[2,4]

Bis-spiropyrans **1a-e** were synthesized by condensation of 3*H*-indolium perchlorates **2a-e** with 6,8-diformyl-5,7-dihydroxy-4-methylcoumarin (**3**)[15] in the presence of triethylamine as the base in average yields (Scheme 1). In the ground state, the obtained compound may be either in the spirocyclic form **1S** or in different merocyanine forms **1SM**, **1MS**, **1MM** with one or two cycles opened as well as form the corresponding isomers upon irradiation (Scheme 2).

The structure of compounds **1a-e** was established by ^{1}H NMR spectroscopy in deuterated chloroform and confirmed by elemental analysis. The location and nature of the proton signals of the methyl groups at position 3 and *N*-methyl groups of the indoline fragments indicate that compounds **1a**,**b** preferably assume the fully open merocyanine form **1MM**. In the ^{1}H NMR spectra of compounds **1a**,**b**, twelve-proton singlet signals at 1.79 and 1.76 ppm, respectively, and six-proton singlet signals at 3.56 and 3.54 ppm, respectively, are observed. The diene bridge methine proton signals of these compounds appear as two doublets in 7.94-8.00- and 8.82-8.88-ppm ranges.

Scheme 1



Compounds **1c**,**e** exist as a tautomeric mixture of spiro and merocyanine forms. In the upfield region of ^{1}H NMR spectra, along with signals at 1.12-1.20 and 2.70 ppm, corresponding to the two pairs of signals of magnetically nonequivalent protons of the geminal methyl and *N*-methyl groups (for compound **1c**) of the indoline cycle in spirocyclic form, two signals at 1.77-1.81 and 3.52 ppm of the same groups in the merocyanine form are observed. Signals of the spirocyclic form protons H-3',11' appear as two doublets at 5.58-5.74 ppm. Furthermore, proton signals of the diene bridge of the merocyanine form appear as two doublets at 8.91 and 8.77 ppm. As determined by the relative signal intensity, the ratio of the spirocyclic form **1S** to merocyanine form is 1:6 (for compound **1c**) and 1:7 (for compound **1e**). However, NMR spectroscopy data do not allow evaluating the specific contribution of tautomers **1SM**, **1MS**, **1MM** in the steady state equilibrium.

Compound **1d** exists predominantly in its spirocyclic form **1S**; two pairs of signals of magnetically nonequivalent protons of the geminal methyl groups register at 1.16-1.34 ppm, two pairs of signals of diastereotopic protons H-3',11' of the pyran ring double bond appear as two doublets at 5.55 and 5.65 ppm, while signals of protons H-4',12' appear as two doublets at 6.90 and 7.41 ppm.

A sufficiently sensitive method for studying the tautomeric equilibrium is electronic absorption spectroscopy, as spirocyclic forms must possess absorption in the UV region of the spectrum while merocyanine forms in the visible region.[1,2] The presence of characteristic absorption bands in the spectra of bis-spiropyrans **1a**-**e** in toluene (Table 1) indicates that in toluene solutions of these compounds an equilibrium exists between the cyclic **1S** and merocyanine form **1SM**, **1MS**, **1MM** isomers. However, according to the NMR spectral data, the equilibrium position is fundamentally dependent on the nature of the substituents on the indoline moiety of the molecule. Compound **1a**, which does not have a substituent at position 5 of the indoline fragment, and compound **1b** (R^2 = Me) are characterized by intensive peaks at 473-561 nm corresponding to the absorption of merocyanine forms **1SM**, **1MS**, **1MM**. In the case of compound **1d** with electron-withdrawing 5-nitro group, on the contrary, the long-wavelength absorption is almost completely absent indicating the prevalence of spiro form **1S**. The remaining compounds exist as a tautomeric mixture of the spirocyclic and merocyanine forms.

Merocyanine forms of bis-spiropyrans **1a**-**e** exhibit a fluorescence maximum at 588-595 nm (Fig. 1, Table 1).

In addition to NMR spectroscopy and electronic absorption spectroscopy data, quantum-chemical calculations of relative stability, structural and spectral properties of bis-spiropyrans **1S** and the corresponding merocyanine forms **1SM**, **1MS**, **1MM** were carried out.

Scheme 2

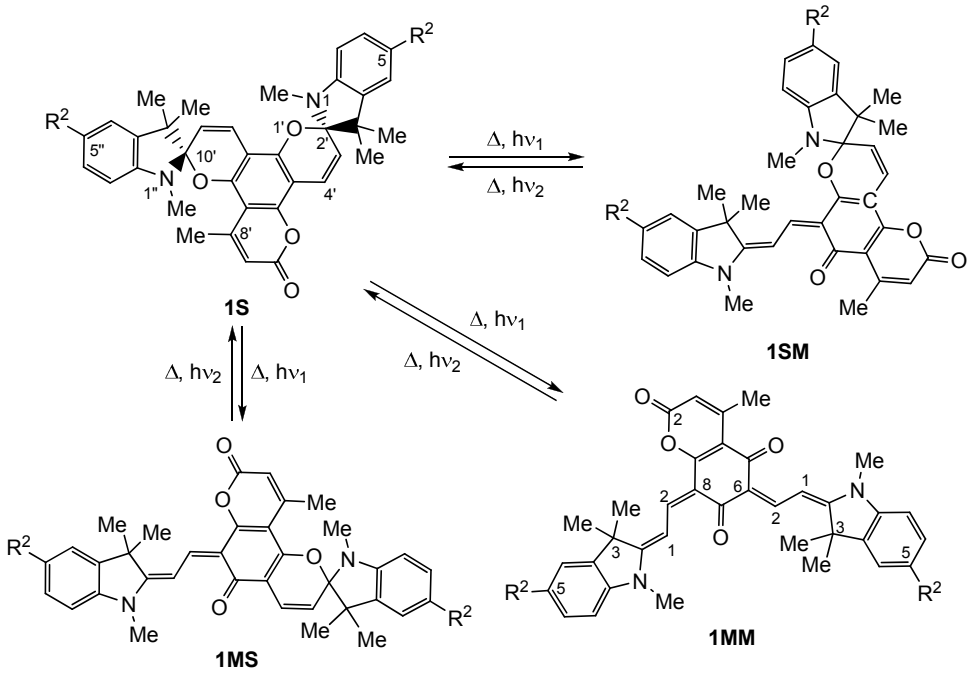


Table 1. Spectral kinetic parameters of compounds **1a-e** in toluene*

Compound	Spiro form 1S		Merocyanine form **1M**			
	λ_{max}^{abs}, nm	$\varepsilon(\lambda_{max}^{abs})$, $l \cdot m^{-1} \cdot cm^{-1}$	λ_{max}^{abs}, nm	λ_{max}^{ex}, nm	λ_{max}^{flu}, nm	τ^B, s
1a	319, 338	11400, 10750	473, 524, 557	475, 543, 571	588, 625 sh	2110
1b	326, 339 sh	11500, 11000	476, 528, 561	460 sh, 492, 543	595, 635 sh	2430
1c	298, 310 sh, 337 sh	9240, 8730, 8130	475, 526, 559	482, 530 sh, 568	584, 630 sh	660
1d	312 sh, 350	23330, 38720	482, 537, 570	482, 543, 573	590, 640	90
1e	299, 315 sh, 339 sh	17300, 15800, 11850	475, 526, 560	475 sh, 540 sh, 571	588, 625 sh, 640 sh	840

* λ_{max}^{abs} – Wavelength of absorption maximum;

$\varepsilon(\lambda_{max}^{abs})$ – extinction coefficient at maximum absorption;

λ_{max}^{ex} – fluorescence excitation wavelength;

λ_{max}^{flu} – wavelength of fluorescence band maximum;

τ^B – time constant of thermal relaxation process.

Form **1S** can exist as two diastereoisomers, the most stable of which (ΔE 6.6 kcal/mol) is depicted in Scheme 2. Only isomers thereof were considered in subsequent calculations. Structures of isomeric forms of compounds **1a**,**c**,**d** have been optimized by density functional theory DFT methods using the hybrid functional PBE0 and the 6-31G** basis set. Solvent influence was accounted for within the framework of the polarized continuum model CPCM. The spectral characteristics of the studied isomers were determined on the basis of methods of non-stationary density functional theory (TD PBE0/6-31G**). The energetic characteristics of isomers of compounds **1a**,**c**,**d** are shown in Table 2.

Data of relative stability of various isomers of merocyanine forms indicate that the completely open form **1MM** for structures **1a**,**c** can be formed in toluene solution, whereas form **1MS** is energetically less favorable.

Excitation energy and the oscillator strength of the first four singlet transitions of the cyclic and merocyanine isomers of compounds **1a**,**c**,**d** were calculated by TD PBE0/6-31G** method in toluene. Comparison of the calculated spectral characteristics with the experimental data allows one to attribute the absorption bands at 560–570 and 470-480 nm to S_0–S_1 and S_0–S_3 transitions of **1SM** isomers, respectively, and the absorption band at 525–537 nm to S_0–S_1 transitions of the completely open isomers **1MM**.

Irradiation of solutions of compounds **1a-e** with 365 nm wavelength light at 295 K leads to an increase of the intensity of the absorption bands of the merocyanine forms of the isomers, the shape and structure of which remains unchanged (Fig. 2). This suggests that the product of the thermal ring opening reaction and the photoreaction product are the same. After the cessation of UV irradiation, thermal recyclization reaction in solutions of compounds **1a-e** is observed reverting the system to its original state (photobleaching also occurs when merocyanine forms are irradiated with light of a wavelength matching that of the absorption bands). Thermal relaxation time constant τ^t increases going from an *N*-benzyl substituent to *N*-alkyl substituent (with R^2 = H) (Table 1).

The electron-withdrawing nitro group at position 5 of the indoline moiety (compound **1d**) reduces the duration of thermal relaxation, the methyl group increases the lifetime of the colored form of compound **1b** to 2430 s.

To conclude, photochromic indoline bis-spiropyrans based on 6,8-diformyl-5,7-dihydroxy-4-methylcoumarin have been obtained, which depending on the nature of the substituents at positions 1 and 5 of the indoline moiety may exist in solution in the merocyanine or spiro forms or as a tautomeric mixture of these forms. UV irradiation of the cyclic isomers causes photocoloring associated with reversible opening of one or both of the spiro moieties.

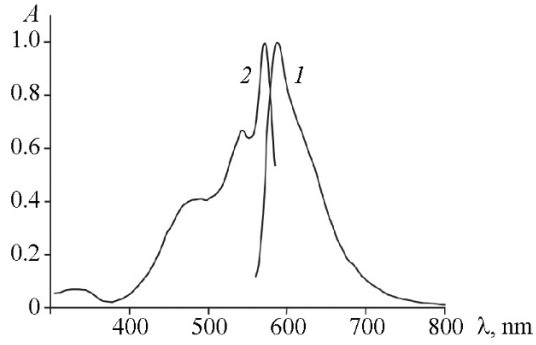


Figure 1. Fluorescence (*1*) and fluorescence excitation (*2*) spectra of merocyanine form of bis-spiropyran **1a** in toluene at 295 K, *c* $3 \cdot 10^{-6}$ M.

Table 2. Total energy (E_{tot}) accounting for zero-point energy vibrations ZPE and relative energy (ΔE) of isomers of compounds **1a**,**c**,**d** according to PBE0/6-31G** calculations data in toluene

Compound	Form	E_{tot} + ZPE, a. u.	ΔE, kcal/mol
1a	**1S**	–1800.095488	0
	1SM	–1800.092324	2.0
	1MS	–1800.08918	4.0
	1MM	–1800.093819	1.0
1c	**1S**	–2718.988419	0
	1SM	–2718.983828	2.9
	1MS	–2718.980698	4.8
	1MM	–2718.984292	2.6
1d	**1S**	–2208.702411	0
	1SM	–2208.693536	5.6
	1MS	–2208.691297	7.0
	1MM	–2208.693096	5.8

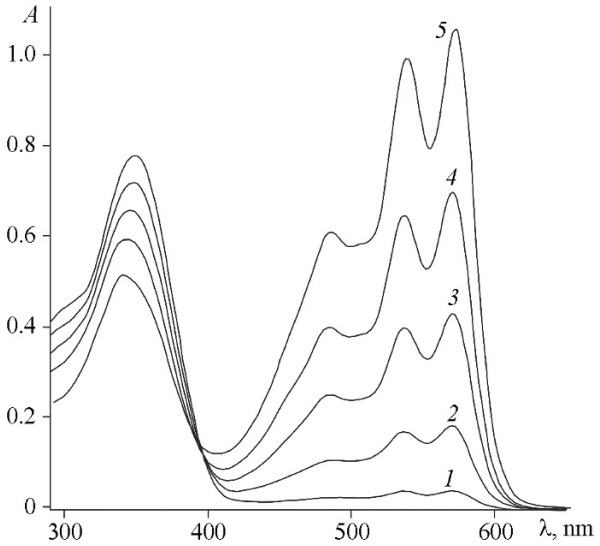


Figure 2. Electron absorption spectra of compound **1d** in toluene before (*1*) and after irradiation with λ_{irr} 365 nm (295 K) light for 10 (*2*), 30 (*3*), 60 (*4*), 120 (*5*) s, *c* $2.1 \cdot 10^{-5}$ M.

Variability of spectral kinetic properties of bis-spiropyrans upon fluorescence of photoinduced forms allows one to consider them as molecular switches having absorptive and fluorescent signal functions with the possibility of practical application.

Experimental

Electronic absorption spectra and kinetics of thermal recyclization reactions of the studied compounds were registered on an Agilent 8453 spectrophotometer at 293 K. Photolysis of solutions was carried out in a Newport system consisting of a 200-W mercury vapor lamp equipped with an interference light filter set. Fluorescence measurements were performed on a Cary Eclipse (Varian) fluorescence spectrophotometer. Spectrophotometric grade toluene (Aldrich) was used to prepare solutions. ^{1}H NMR spectra were acquired on a Varian Unity-300 (300 MHz) spectrometer at 295 K, chemical shifts were assigned relative to the signals of residual solvent $CDCl_3$ protons. IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrophotometer by the attenuated total reflectance technique using a ZnSe crystal. Mass spectra were recorded on a Shimadzu GCMS-QP2010SE GC-MS system with direct sample injection (70 eV ionization energy). Elemental analysis was performed on a KOVO CHN-analyzer. Melting points were determined in glass capillaries on a PTP(M) apparatus. Structures of isomeric forms of compounds **1a**,**c**,**d** were optimized by the DFT method using the PBE0 hybrid functional and the 6-31G** basis set.[16] The agreement of optimized structures with the minima was proven by normal vibrational frequency calculation data (force constant matrix). Solvent influence was calculated with the conductor-like polarized continuum model (CPCM) approach.[17] Dielectric permittivity of media correspond to toluene (ε 2.379). Spectral characteristics of the studied isomers were determined on the basis of non-stationary density functional theory methods (TD PBE0/6-31G**).[18] The systematic heightening of the singlet transition energies of the merocyanine isomers of compounds **1a**,**c**,**d** were corrected according to formula $E_{ex\text{-}corr} = -0.0963 + 0.9321E_{ex}$. All calculations were done using the GAUSSIAN 03 software set.[19]

Synthesis of compounds 1a–e (General method). Triethylamine (2.63 g, 0.26 mmol) was added to a heated solution of 6,8-diformyl-5,7-dihydroxy-4-methylcoumarin (**3**)[15] (0.27 g, 1.1 mmol) and 3*H*-indolium perchlorate **2a–e**[20] (2 mmol) in 2-propanol (20 ml). The reaction mixture was heated under reflux for 5 h, and the solvent evaporated. The residue was purified by column chromatography on Al_2O_3 (eluent chloroform), and the product recrystallized from 2-PrOH.

4-Methyl-6,8-bis[2-(1,3,3-trimethylindolin-2-ylidene)-ethylidene]-2*H*-chromene-2,5,7(6*H*,8*H*)trione* (1a). Yield 0.30 g (54%), maroon powder, mp 230–232°C. IR spectrum, ν, cm^{-1}: 1737, 1685, 1607, 1573, 1233. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): Form **1MM**: 1.79 (12H, s, $4CH_3$); 2.71 (3H, s, CH_3); 3.56 (6H, s, $2CH_3$); 5.84 (1H, s, CH); 6.99–7.45 (8H, m, H Ar); 8.00 (2H, d, *J* = 13.8) and 8.88 (2H, d, *J* = 14.1, 2CH=CH). Mass spectrum, *m*/*z* (I_{rel}, %): 558 $[M]^+$ (58), 543 (100), 528 (6). Found, %: C 77.64; H 6.65; N 5.82. $C_{36}H_{34}N_2O_4$. Calculated, %: C 77.40; H 6.13; N 5.01.

4-methyl-6,8-bis[2-(1,3,3,5-tetramethylindolin-2-yl-idene)ethylidene]-2*H*-chromene-2,5,7(6*H*,8*H*)trione (1b). Yield 0.31 g (48%), maroon powder, mp >300°C. IR spectrum, ν, cm^{-1}: 1734, 1678, 1608, 1575, 1230. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): Form **1MM**: 1.75 (12H, s, $4CH_3$); 2.37 (6H, s, $2CH_3$); 2.68 (3H, s, CH_3); 3.54 (6H, s, $2CH_3$); 5.80 (1H, s, CH); 6.92 (2H, d, *J* = 7.8, H Ar); 7.10 (2H, d, *J* = 7.8, H Ar); 7.12 (2H, s, H Ar); 7.94 (2H, d, *J* = 14.6) and 8.82 (2H, d, *J* = 14.2, 2CH=CH). Mass spectrum, *m*/*z* (I_{rel}, %): 586 $[M]^+$ (51), 571 (100), 556 (5). Found, %: C 77.66; H 7.05; N 4.52. $C_{38}H_{38}N_2O_4$. Calculated, %: C 77.79; H 6.53; N 4.77.

5,5''-Dichloro-1,1'',3,3,3'',3'',8'-heptamethyl-6'*H*-di-spiro[indoline-2,2'-dipyrano[2,3-*f*:2',3'-*h*]chromene-10',2''-indolin]-6'-one (1c). Yield 0.28 g (40%), maroon powder, mp >300°C. IR spectrum, ν, cm^{-1}: 1744, 1676, 1606, 1574, 1237, 908. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): Form **1S**: 1.12 (6H, s) and 1.17 (6H, s, 3,3,3'',3''-CH_3); 2.70 (6H, s, 1,1''-CH_3); 5.58 (1H, d, *J* = 10.6) and 5.67 (1H, d, *J* = 10.6, 3',11'-CH); 5.80 (1H, s, 7'-CH); 6.41 (1H, d, *J* = 8.1, H Ar); 6.80 (1H, d, *J* = 8.1, H Ar); 6.98–7.20 (5H, m) and 7.67 (1H, d, *J* = 10.6, H Ar, 4',12'-CH). Form **1MM**: 1.77 (12H, s, $4CH_3$); 2.73 (3H, s, CH_3); 3.52 (6H, s, $2CH_3$); 5.86 (1H, s, CH); 6.75 (1H, d, *J* = 8.1, H Ar); 6.84 (1H, d, *J* = 8.1, H Ar); 6.80–7.03 (4H, m, H Ar); 8.48 (2H, d, *J* = 13.5) and 8.78 (2H, d, *J* = 14.0, 2CH=CH). Mass spectrum, *m*/*z* (I_{rel}, %): 627 $[M]^+$ (50), 612 (100), 597 (5). Found, %: C 68.64; H 5.55; N 4.92. $C_{36}H_{32}Cl_2N_2O_4$. Calculated, %: C 68.90; H 5.14; N 4.46.

1,1'',3,3,3'',3'',8'-Heptamethyl-5,5''-dinitro-6'*H*-dispiro-[indoline-2,2'-dipyrano[2,3-*f*:2',3'-*h*]chromene-10',2''-indo-lin]-6'-one (1d). Yield 0.29 g (40%), blue powder, mp >300°C. IR spectrum, ν, cm^{-1}: 1741, 1685, 1606, 1578, 912. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): Form **1S**: 1.16 (3H, s),

* Here and further the name corresponds to the tautomeric form prevalent in $CDCl_3$ solution.

1.22 (3H, s), 1.31 (3H, s) and 1.34 (3H, s, 3,3,3",3"-CH_3); 1.86 (3H, s, 8'-CH_3); 2.78 (3H, s) and 2.88 (3H, s, 1,1"-CH_3); 5.55 (1H, d, J = 10.5) and 5.65 (1H, d, J = 10.5, 3',11'-CH); 5.83 (1H, s, 7'-CH); 6.49 (1H, d, J = 8.7, H Ar); 6.56 (1H, d, J = 8.7, H Ar); 6.90 (1H, d, J = 10.5) and 7.41 (1H, d, J = 10.5, 4',12'-CH); 7.93 (1H, s, H Ar); 7.96 (1H, s, H Ar); 8.15 (1H, d, J = 8.4, H Ar); 8.20 (1H, d, J = 8.4, H Ar). Mass spectrum, *m/z* (I_{rel}, %): 648 $[M]^+$ (66), 633 (100), 603 (5). Found, %: C 66.34; H 5.05; N 8.82. $C_{36}H_{32}N_4O_8$. Calculated, %: C 66.66; H 4.97; N 8.64.

1,1"-Dibenzyl-3,3,3",3",8'-pentamethyl-6'*H*-dispiro[indoline-2,2'-dipyrano[2,3-*f*:2',3'-*h*]chromene-10',2"-indolin]-6'-one (1e). Yield 0.43 g (55%), maroon powder, mp 280–282°C. IR spectrum, ν, cm^{-1}: 1708, 1672, 1609, 1588, 1230, 924. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): Form **1S**: 1.17 (6H, s) and 1.20 (6H, s, 3,3,3",3"-CH_3); 2.63 (3H, s, 8'-CH_3); 4.05 (4H, m, $2CH_2$); 5.64 (1H, d, J = 10.5) and 5.74 (1H, d, J = 10.5, 3',11'-CH); 5.87 (1H, s, 7'-CH); 6.95–7.37 (20H, m, H Ar, 4',12'-CH). Form **1MM**: 1.81 (12H, s, $4CH_3$); 2.69 (3H, s, CH_3); 5.21 (4H, s, $2CH_2$); 5.84 (1H, s, CH); 7.28–7.47 (18H, m, H Ar); 8.42 (2H, d, J = 14.1) and 8.78 (2H, d, J = 14.1, 2CH=CH). Mass spectrum, *m/z* (I_{rel}, %): 710 $[M]^+$ (52), 619 (100), 552 (8). Found, %: C 80.83; H 5.65; N 4.12. $C_{48}H_{42}N_2O_4$. Calculated, %: C 81.10; H 5.96; N 3.94.

This work was performed within the framework of implementing the Project part of State Assignment for scientific activity (project № 4.88.2014/K) of the Ministry of Education and Science of the Russian Federation. A. S. Cheprasov, A. V. Metelitsa, and I. V. Dorogan are grateful to the Russian Foundation for Basic Research for financial support (grant 13-03-00901).

References

1. Minkin, V. I. *Russ. Chem. Rev.* **2013**, *82*, 1. [*Usp. Khim.* **2013**, *82*, 1.]
2. Bertelson, R. C. In *Organic Photochromic and Thermochromic Compounds*, Crano, J. C.; Guglielmetti, R. J., Eds.; Plenum Press: New York, 1999, vol. 1, p. 11.
3. Minkin, V. I. *Chem. Rev.* **2004**, *104*, 2751.
4. Guglielmetti, R. In *Photochromism: Molecules and Systems*, Dürr, H.; Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 2003, p. 314.
5. Bercovic, J.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741.
6. Minkin, V. I. In *Molecular Switches*, Feringa, B. L.; Browne, W. R., Eds.; Wiley: Weinheim, 2011, p. 37.
7. Traven, V. F.; Manaev, A. V.; Bochkov, A. Yu.; Chibisova, T. A.; Ivanov, I. V. *Russ. Chem. Bull., Int. Ed.* **2012**, *61*, 1342. [*Izv. Akad. Nauk SSSR, Ser. Khim.* **2012**, 1327.]
8. Traven, V. F.; Miroshnikov, T. A.; Chibisova, T. A.; Barachevsky, V. A.; Venidiktova, O. V.; Strokach, Yu. P. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 2417. [*Izv. Akad. Nauk SSSR, Ser. Khim.* **2005**, 2342.]
9. Barachevsky, V. A.; Karpov, R. E.; Venidiktova, O. V.; Valova, T. M.; Strokach, Yu. P.; Miroshnikov, T. A.; Chibisova, T. A.; Traven, V. F. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 2425. [*Izv. Akad. Nauk, Ser. Khim.* **2005**, 2350.]
10. Dolotov, S. M.; Miroshnikov, T. A.; Chibisova, T. A.; Sin, S.-L.; Venidiktova, O. V.; Valova, T. M.; Dunaev, A. A.; Strokach, Yu. P.; Barachevsky, V. A.; Traven, V. F. *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 904. [*Izv. Akad. Nauk, Ser. Khim.* **2007**, 870.]
11. Nikolaeva, O. G.; Tsukanov, A. V.; Shepelenko, E. N.; Lukyanov, B. S.; Metelitsa, A. V.; Kostyrina, O. Yu.; Dubonosov, A. D.; Bren, V. A.; Minkin, V. I. *Int. J. Photoenergy* **2009**, ID 238615, doi: 10.1155/2009/238615.
12. Nikolaeva, O. G.; Gaeva, E. B.; Shepelenko, E. N.; Tsukanov, A. V.; Metelitsa, A. V.; Lukyanov, B. S.; Dubonosov, A. D.; Bren, V. A.; Minkin, V. I. *Russ. J. Org. Chem.* **2009**, *45*, 1091. [*Zh. Org. Khim.* **2009**, *45*, 1102.]
13. Nikolaeva, O. G.; Shepelenko, E. N.; Tsukanov, A. V.; Kozyrev, V. S.; Metelitsa, A. V.; Dubonosov, A. D.; Bren', V. A.; Minkin, V. I. *Bull. SSC RAN* **2010**, *6*(3), 12.
14. Nikolaeva, O. G.; Kostyrina, O. Yu.; Shepelenko, E. N.; Tsukanov, A. V.; Metelitsa, A. V.; Borodkin, G. S.; Dubonosov, A. D.; Bren, V. A.; Minkin, V. I. *Russ. J. Org. Chem.* **2011**, *47*, 1370. [*Zh. Org. Khim.* **2011**, *47*, 1348.]
15. Minkin, V. I.; Dubonosov, A. D.; Bren, V. A.; Nikolaeva, O. G.; Tsukanov, A. V.; Burov, O. N.; Fedyanina, A. Yu. *Russ. J. Org. Chem.* **2013**, *49*, 374. [*Zh. Org. Khim.* **2013**, *49*, 387.]
16. Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
17. Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.
18. Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997.
19. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. *Gaussian 03, Revision E.01*, 2004.
20. Pottier, E.; Sergent, M.; Phan Tan Luu, R.; Guglielmetti, R. *Bull. Soc. Chim. Fr.* **1992**, *101*, 719.