Full Articles

Synthesis and spectral studies of photochromism of 1,3-benzoxazinone spiropyrans

*L. D. Popov,[a] I. N. Shcherbakov,[a] A. O. Bulanov,[a] O. I. Kobeleva,[b] T. M. Valova,[b] and V. A. Barachevsky[b]**

[a]*Southern Federal University,*
105 ul. B. Sadovaya, 344104 Rostov-on-Don, Russian Federation.
E-mail: shcherbakov@rsu.ru
[b]*Photochemistry Center, Russian Academy of Sciences,*
7a ul. Novatorov, 119421 Moscow, Russian Federation.
E-mail: barva@photonics.ru

Photochromism of the spiropyran derivatives of the 1,3-benzoxazinone series was studied. A relationship between the structure of substituents and photochromic properties of the compounds was revealed.

Key words: photochromism, 1,3-benzoxazinone spiropyrans, absorption spectra, photoinduced absorbance.

Interest in extension of the area of using photochromic spiro compounds, in particular, for the development of reversive photocontrolled chemosensors, has recently increased.[1—3] In this work we present the results of the spectral kinetic study of photochromism of the recently synthesized new 1,3-benzoxazinone spiropyrans.

Results and Discussion

The objects of the study were solutions of 1,3-benzoxazinone spiropyrans **1**—**9**.

It is known[4] that spiro compounds of general formula **A** (Q = CH, N) experience reversible phototransformations between two forms, in particular, between the initial closed colorless spiropyran form **A** and the photoinduced colored merocyanine form **B** (Scheme 1).

Under the action of the UV light absorbed by the closed form **A**, a spiro compound molecule is transformed into the merocyanine (open) form **B** due to the photodissociation of the C_{spiro}—O bond followed by thermal *cis—trans*-isomerization. The form **B** can spontaneously undergo recyclization to the form **A**. This process can be accelerated by the light absorbed by the form **B** or by heating of the solution. The processes of reversible photo- and thermal transformations can multiply be repeated. Fatigue resistance of photochromic transformations is

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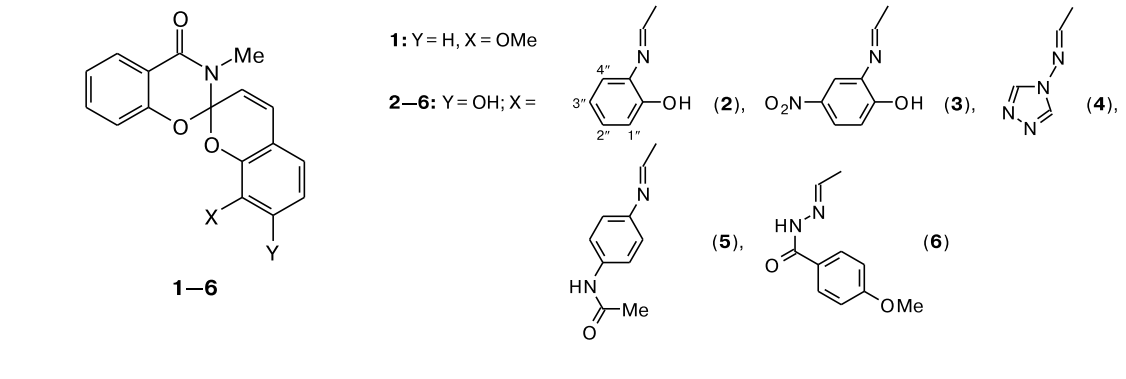
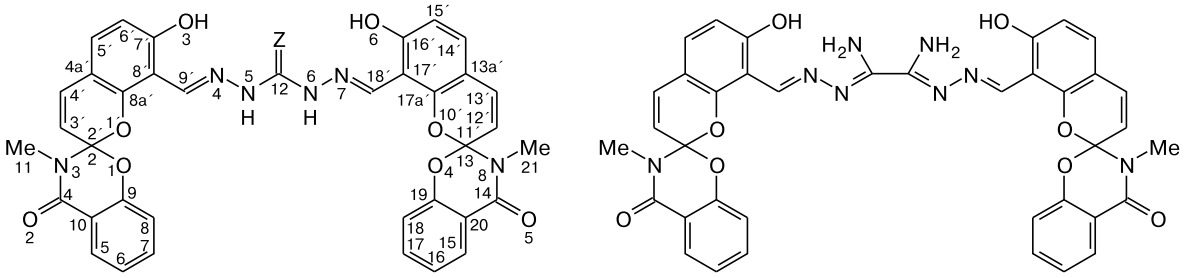
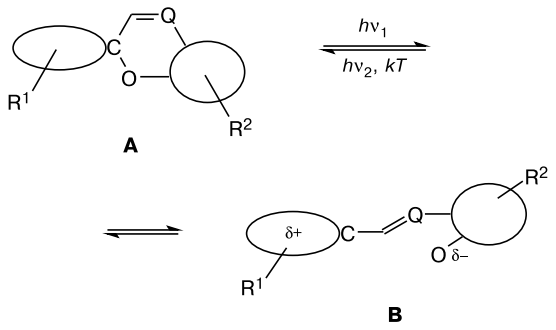




Z = O (**7**), S (**8**)

Scheme 1



limited by irreversible photo- and thermodegradation processes of the forms **A** and **B**, which usually accompany these transformations.

The results of studies of photochromism of benzoxazinone spiropyrans are presented in Table 1 and in Figs 1—4.

Compound **2** in DMSO in the initial spiropyran form is characterized by absorption bands at 283, 362, and 453 nm (see Fig. 1, curve *1*). After the solution was UV-irradiated, the intensity of the absorption band at 283 nm decreases and the absorption at 400—500 nm increases (see Fig. 1, curve *2*). After switching off the UV-radiation source, the initial absorption spectrum is recovered (see Fig. 1, curves *3*—*7*) due to the spontaneous transformation of the form **B** into the form **A**, which is characterized by the rate constant $k = 0.06\ s^{-1}$.

Due to the slow process of thermal relaxation, the photoinduced change in the absorbance (ΔD^{ph}) at the wavelength of the absorption band maximum of the photoinduced merocyanine form reaches the value $\Delta D^{ph} = 0.64$

Table 1. Results of the spectral kinetic study of phototransformations of solutions of compounds **1—9** in DMSO and MeCN

Compound	Solvent	λ_A^{max}	λ_B^{max}	ΔD^{ph}
		nm		
1	DMSO	260, 294	400	<0.02
	MeCN	258, 295	400	0.03
2	DMSO	282, 362	453	0.64
	MeCN	281, 351	445	0.76
3	DMSO	270, 317, 375	505	0.47
4	DMSO	286, 347	450, 587	0.09
5	DMSO	280, 350	455	0.15
6	DMSO	315	490	0.07
	MeCN	305	478	0.02
7	DMSO	282, 325	490	0.18
	MeCN	285, 315	475	0.08
8	DMSO	282, 338	480	0.05
9	DMSO	285, 354	483	0.02

Note. λ_A^{max} and λ_B^{max} are the wavelengths of absorption band maxima of the spiropyran and photoinduced merocyanine forms, respectively; ΔD^{ph} is the maximum photoinduced change in the absorbance of the solution at the absorption band maximum of the photoinduced merocyanine form.

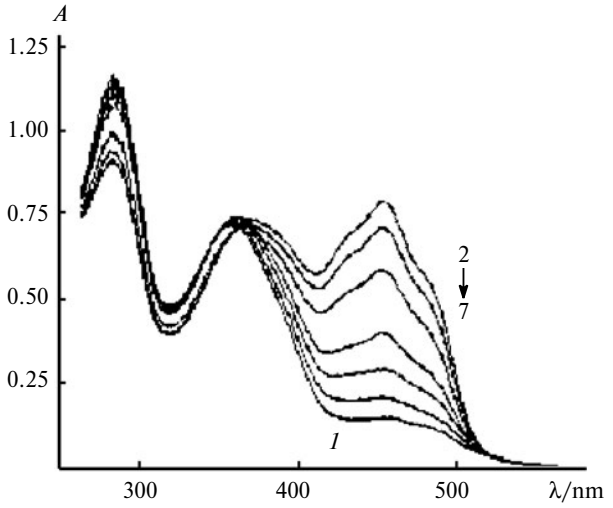


Fig. 1. Absorption spectra of a solution of compound **2** in DMSO before (*1*) and after (*2—7*) UV irradiation with the wavelength 313 nm.

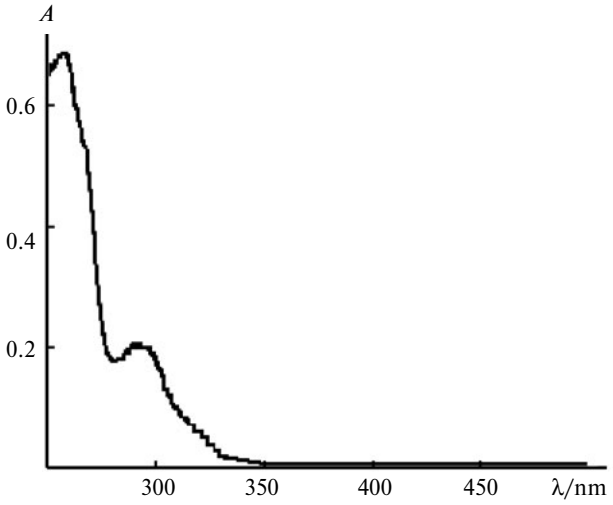


Fig. 2. Absorption spectra of a solution of compound **1** in MeCN before UV irradiation.

(see Table 1). When the polar solvent (DMSO, ε = 48.9) is replaced by a less polar one (MeCN, ε = 36.1), the absorption bands at 362 and 453 nm undergo the hypsochromic shift by 8—11 nm (see Table 1), which, as in the case of spirooxazines,[5] indicates the quinoid character of the merocyanine form of compound **2**. The photoinduced change in the absorbance increases to $\Delta D^{ph} = 0.76$ (see Table 1). It should be mentioned that the absorption band at 362 nm experiences insignificant photoinduced changes.

The introduction of the acceptor substituent NO_2 (compound **3**) into the imine moiety results in the bathochromic shift of the long-wavelength absorption bands of the spiropyran and merocyanine forms by 13 and 53 nm, respectively (see Table 1). The photoinduced change in the absorbance remains rather high ($\Delta D^{ph} = 0.47$).

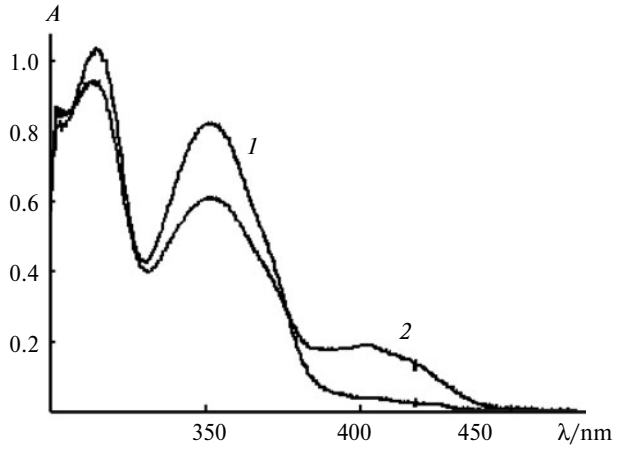


Fig. 3. Absorption spectra of a solution of compound **5** in DMSO before (*1*) and after (*2*) UV irradiation with the wavelength 313 nm.

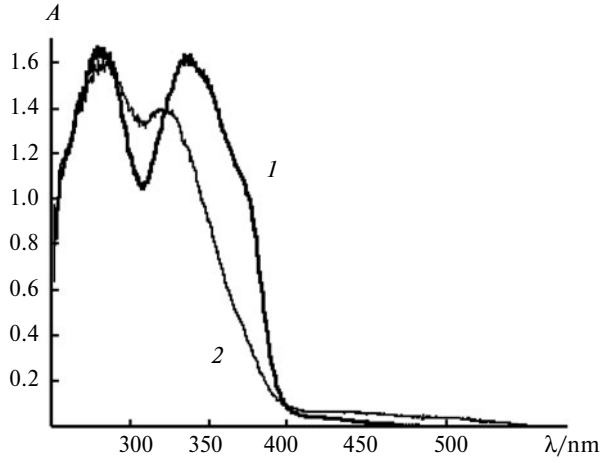


Fig. 4. Absorption spectra of a solution of compound **8** in DMSO before (*1*) and after (*2*) UV irradiation with the wavelength 313 nm.

Unlike the above considered photochromic spiropyrans, other compounds studied are characterized by the high rate of thermal decoloration. Therefore, they are characterized by substantially lower values of photoinduced changes in the absorbance, which do not exceed $\Delta D^{ph} = 0.18$ (see Table 1).

Unlike the spectra of compounds **2** and **3**, the absorption spectrum of the spiropyran form of compound **1** exhibits no long-wavelength absorption band (see Fig. 2). This is due, most likely, that compound **1** contains no imine moiety absorbing at 360—380 nm. Probably, this is a reason for the sharp hypsochromic shift of the absorption band maximum of the photoinduced open form to 400 nm and for the acceleration of spontaneous decoloration (see Table 1).

Unlike all the compounds studied, two absorption bands of the photoinduced form were observed for spiropyran **4**: at 450 and 587 nm (see Table 1).

The photochromic transformations of isomeric compounds **5** and **6** differ substantially when they are compared with each other and also for comparison with other compounds (see Table 1). The photoinduced change in the absorption spectra of compound **5**, unlike the spectra of compounds **2** and **3**, appears a sharp decrease in the intensity of the long-wavelength absorption band of the cyclic form at 350 nm (see Fig. 3). The least efficient photochromic transformations were observed for compound **9** (see Table 1). It should be mentioned that, as in the case of compound **2**, the replacement of more polar DMSO by less polar MeCN results in the hypsochromic shift, whereas the bathochromic shift of the absorption bands of both the spiropyran and merocyanine forms is observed for compound **7** (see Table 1).

Similar photoinduced spectral changes were observed for bis(spiropyrans) **7—9**. The photoinduced spectral changes for compound **8** are shown in Fig. 4.

The replacement of the C=O group (compound **7**) by the C=S group (compound **8**) induces the bathochromic shift of the long-wavelength absorption band of the initial spiropyran form and the hypsochromic shift of the absorption band of the photoinduced merocyanine form. In addition, compound **8** is characterized by the high rate of dark decoloration compared to that of spiropyran **7**, which decreases the photoinduced change in the absorbance at the equilibrium state (see Table 1).

Thus, the study of spiropyrans of the 1,3-benzoxazinone series **1—9** showed that all of them manifest the photochromic transformations. The data of the study of solvatochromism show that the photoinduced merocyanine form of these compounds has the quinoid structure.

Due to the high rate of dark decoloration of the photoinduced form, at 20 °C the photoinduced change in the absorbance in the visible region is low for the most part of compounds. The exception is spiropyrans bearing imine moieties as substituents, which, most likely, impede *cis—trans*-isomerization and, hence, decrease the rate of spontaneous relaxation of the photoinduced merocyanine form to the initial spiro form.

Experimental

The IR spectra of the compounds studied were recorded in a Nujol suspension on a Varian Scimitar spectrometer in the region from 400 to 4000 cm^{-1}. The ^1H NMR spectra were measured in a DMSO-d_6 solution at 20 °C on a Bruker AM-300 instrument using Me_4Si as the internal standard. Spectral studies were carried out using a USB2000 optical-fiber spectrometer (Ocean Optics).

A CARY UV 50 spectrophotometer (Varian) was used to study the kinetics of photochromic transformations of the compounds. The solvents used were DMSO and MeCN (Aldrich). The working concentration of solutions was $2 \cdot 10^{-4}$ mol L^{-1}. A 0.2-cm quartz cell was used for measurements. Irradiation was carried out by the filtered light from a DRSh-250 lamp.

Bis(hydrazones), 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] with carbohydrazide (**7**) and thiocarbohydrazide (**8**), were synthesized according to a known procedure.[6] Compounds **1—6** and **9** were synthesized as described below.

8′-Methoxy-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (1) was synthesized by a procedure published earlier.[7] The yield was 74%, m.p. 152—153 °C. Found (%): C, 69.50; H, 4.30; N, 5.07. $C_{18}H_{15}NO_4$. Calculated (%): C, 69.99; H, 4.85; N, 4.52. IR, ν/cm^{-1}: 1680 (C=O), 1656 (C=C, chromene), 1612 (C=C, arom.), 1374 (C—N), 988, 935, 766 (C_{spiro}—O). ^1H NMR, δ: 7.91 (dd, 1 H, H(5), J = 7.7 Hz, J = 1.6 Hz); 7.49 (ddd, 1 H, H(7), J = 8.0 Hz, J = 7.5 Hz, J = 1.6 Hz); 7.17 (dd, 1 H, H(6), J = 7.7 Hz, J = 7.5 Hz); 7.07 (d, 1 H, H(4′), J = 9.7 Hz); 6.82—6.98 (m, 4 H, H(8), H(5′), H(6′), H(7′)); 6.17 (d, 1 H, H(3′), J = 9.70 Hz); 3.60 (s, 3 H, OMe); 3.07 (s, 3 H, NMe).

7′-Hydroxy-8′-(2-hydroxyphenyliminomethyl)-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (2). A solution of 2-aminophenol (0.1 g, 0.001 mol) in ethanol (5 mL) was added to a solution of 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene][7] (0.32 g, 0.001 mol) in ethanol (10 mL). The mixture was refluxed for 2.5 h. The orange precipitate formed was filtered off, washed with hot methanol, and recrystallized from an ethanol—MeCN mixture. The yield was 0.12 g (25%), m.p. 225 °C. Found (%): C, 69.90; H, 3.70; N, 6.30. $C_{24}H_{18}N_2O_5$. Calculated (%): C, 69.58; H, 4.34; N, 6.75. IR, ν/cm^{-1}: 3500 (OH′, anyl), 2800—3100 (OH, chromene), 1664 (C=O), 1647 (C=C, chromene), 1609, 1602 (C=C, arom.), 1590 (C=N), 1320 (C—N). ^1H NMR, δ: 14.47 (s, 1 H, OH); 9.86 (s, 1 H, OH″); 8.40 (s, 1 H, CH=N); 7.98 (dd, 1 H, H(5), J = 7.7 Hz, J = 1.3 Hz); 7.57 (ddd, 1 H, H(7), J = 8.1 Hz, J = 7.7 Hz, J = 1.3 Hz); 7.47 (d, 1 H, H(5′), J = 8.6 Hz); 7.31 (dd, 1 H, H(6), J = 7.7 Hz, J = 7.7 Hz); 7.18 (d, 1 H, H(4′), J = 9.7 Hz); 7.09 (dd, 1 H, H(3″), J = 7.9 Hz, J = 7.7 Hz); 7.02 (d, 1 H, H(8), J = 8.1 Hz); 6.90 (d, 1 H, H(1″), J = 8.0 Hz); 6.77 (dd, 1 H, H(2″), J = 8.0 Hz, J = 7.7 Hz); 6.65 (d, 1 H, H(6′), J = 8.5 Hz); 6.52 (d, 1 H, H(4″), J = 7.9 Hz); 6.30 (d, 1 H, H(3′), J = 9.7 Hz); 3.13 (s, 3 H, NMe).

7′-Hydroxy-8′-(2-hydroxy-5-nitrophenyliminomethyl)-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (3) was synthesized similarly to compound **2**. The red precipitate formed from the reaction mixture was filtered off, washed with hot methanol, and recrystallized from dioxane. The yield was 45%, m.p. >290 °C. Found (%): C, 79.70; H, 5.30; N, 12.10. $C_{24}H_{17}N_3O_7$. Calculated (%): C, 80.24; H, 4.73; N, 11.69. IR, ν/cm^{-1}: 3400 (OH′, anyl), 2900—3100 (OH, chromene), 1670 (C=O), 1642 (C=C, chromene), 1615, 1603 (C=C, arom.), 1585 (C=N), 1320 (C—N). ^1H NMR, δ: 13.63 (s, 1 H, OH); 10.53 (s, 1 H, OH″); 8.49 (s, 1 H, CH=N); 7.96 (d, 1 H, H(5), J = 7.5 Hz); 7.69 (d, 1 H, H(1″), J = 2.5 Hz); 7.60 (dd, 1 H, H(3″), J = 8.2 Hz, J = 2.5 Hz); 7.54 (dd, 1 H, H(7), J = 7.8 Hz, J = 8.0 Hz); 7.42 (d, 1 H, H(5′), J = 8.5 Hz); 7.28 (dd, 1 H, H(6), J = 7.8 Hz, J = 7.5 Hz); 7.09 (d, 1 H, H(4′), J = 9.8 Hz); 6.92 (d, 1 H, H(8), J = 8.0 Hz); 6.69 (dd, 1 H, H(4″), J = 7.6 Hz, J = 2.5 Hz); 6.69 (d, 1 H, H(6′), J = 8.5 Hz); 6.14 (d, 1 H, H(3′), J = 9.8 Hz); 3.14 (s, 3 H, NMe).

7′-Hydroxy-3-methyl-4-oxo-8′-(1,2,4-triazol-4-ylimino-methyl)-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (4). A solution of 4-amino-1,2,4-triazole (0.168 g, 0.002 mol) in ethanol (7 mL) was poured to a solution of 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (0.652 g, 0.002 mol) in ethanol (10 mL), and the mixture was refluxed for 1 h. A yellowish precipitate formed

was filtered off, washed with hot methanol, and recrystallized from an ethanol—dioxane mixture. The yield was 0.46 g (75%), m.p. >260 °C. Found (%): C, 61.30; H, 3.30; N, 17.59. $C_{20}H_{15}N_5O_4$. Calculated (%): C, 61.72; H, 3.85; N, 17.19. IR, ν/cm^{-1}: 2900—3200 (OH, chromene), 1665 (C=O), 1648 (C=C, chromene), 1610 (C=C, arom.), 1590 (C=N), 1320 (C—N). ^{1}H NMR, δ: 10.58 (s, 1 H, OH); 8.62 (s, 1 H, CH=N); 8.46 (s, 2 H, H of triazole); 7.98 (dd, 1 H, H(5), J = 7.3 Hz, J = 1.3 Hz); 7.49 (ddd, 1 H, H(7), J = 8.1 Hz, J = 7.6 Hz, J = 1.3 Hz); 7.37 (d, 1 H, H(5′), J = 8.5 Hz); 7.22 (dd, 1 H, H(6), J = 7.3 Hz, J = 7.6 Hz); 7.06 (d, 1 H, H(4′), J = 9.7 Hz); 6.86 (d, 1 H, H(8), J = 8.1 Hz); 6.65 (d, 1 H, H(6′), J = 8.5 Hz); 6.09 (d, 1 H, H(3′), J = 9.7 Hz); 3.12 (s, 3 H, NMe).

Schiff base of 4-aminoacetoacetanilide and 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (5) was synthesized similarly to compound **2**. The orange precipitate formed from the reaction mixture was separated by filtration, washed with hot methanol, and recrystallized from an ethanol—dioxane mixture. The yield was 56%, m.p. >260 °C. Found (%): C, 68.60; H, 5.10; N, 9.70. $C_{26}H_{21}N_3O_5$. Calculated (%): C, 68.59; H, 4.61; N, 9.23. IR, ν/cm^{-1}: 3340 (NH), 2750—3100 (OH, chromene), 1665 (C=O), 1648 (C=C, chromene), 1600 (C=C, arom.), 1580 (C=N), 1321 (C—N). ^{1}H NMR, δ: 13.71 (s, 1 H, OH); 9.84 (s, 1 H, NH); 8.30 (s, 1 H, CH=N); 7.99 (dd, 1 H, H(5), J = 7.4 Hz, J = 1.3 Hz); 7.51 (d, 2 H, H(3″), J = 8.0 Hz); 7.50 (ddd, 1 H, H(7), J = 8.0 Hz, J = 7.5 Hz, J = 1.3 Hz); 7.35 (d, 1 H, H(5′), J = 8.3 Hz); 7.23 (dd, 1 H, H(6), J = 7.5 Hz, J = 7.4 Hz); 7.07 (d, 1 H, H(4′), J = 9.7 Hz); 6.92 (d, 1 H, H(8), J = 8.0 Hz); 6.74 (d, 2 H, H(2″), J = 8.0 Hz); 6.59 (d, 1 H, H(6′), J = 8.3 Hz); 6.12 (d, 1 H, H(3′), J = 9.7 Hz); 3.13 (s, 3 H, NMe); 2.03 (s, 3 H, C(O)Me).

Schiff base of 4-methoxybenzhydrazide and 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (6) was synthesized similarly to compound **2**. A yellowish precipitate was filtered off, washed with hot methanol, and recrystallized from an ethanol—dioxane mixture. The yield was 70%, m.p. 244—245 °C. Found (%): C, 66.50; H, 4.90; N, 8.40. $C_{26}H_{21}N_3O_6$. Calculated (%): C, 66.24; H, 4.49; N, 8.91. IR, ν/cm^{-1}: 3277 (NH), 2800—3100 (OH), chromene), 1672 (C=O), 1654 (C=O), 1645 (C=C, chromene), 1600 (C=C, arom.), 1580 (C=N), 1311 (C—N), 964, 950, 768 (C_{spiro}—O). ^{1}H NMR, δ: 12.49 (s, 1 H, OH); 11.94 (s, 1 H, NH); 8.38 (s, 1 H, CH=N); 7.97 (dd, 1 H, H(5), J = 7.7 Hz, J = 1.6 Hz); 7.82 (d, 2 H, H(2″), J = 8.7 Hz); 7.52 (ddd, 1 H, H(7), J = 8.2 Hz, J = 7.7 Hz, J = 1.6 Hz); 7.26 (d, 1 H, H(5′), J = 8.5 Hz); 7.21 (dd, 1 H, H(6), J = 7.7 Hz, J = 7.7 Hz); 7.05 (d, 1 H, H(4′), J = 9.7 Hz); 6.94 (d, 2 H, H(3″), J = 8.7 Hz); 6.91 (d, 1 H, H(8), J = 8.2 Hz); 6.61 (d, 1 H, H(6′), J = 8.5 Hz); 6.04 (d, 1 H, H(3′), J = 9.7 Hz); 3.84 (s, 3 H, OMe); 3.13 (s, 3 H, NMe).

Bis(hydrazone) based on 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] and oxalic acid bis(amidrazone) (9). A hot solution of bis(amidrazone)[8] (0.116 g, 0.001 mol) in ethanol (10 mL) was added to a solution of 7′-hydroxy-8′-formyl-3-methyl-4-oxo-3,4-dihydrospiro[1,3-benzoxazine-2,2′-chromene] (0.652 g, 0.002 mol) in ethanol (10 mL). The mixture was refluxed for 3 h. A dark yellow precipitate formed was separated, washed with boiling methanol, and refluxed for 5 h in anhydrous methanol (20 mL) for further purification. The yield was 0.48 g (62%), m.p. >250 °C. Found (%): C, 62.70; H, 3.80; N, 15.60. $C_{38}H_{28}N_8O_8$. Calculated (%): C, 62.98; H, 3.89; N, 15.46. IR, ν/cm^{-1}: 3504, 3401 (NH), 2600—3100 (OH, chromene), 1679 (C=O), 1649 (C=C, chromene), 1616 (C=C, arom.), 1595 (C=N), 1320 (C—N), 944, 767 (C_{spiro}—O). ^{1}H NMR, δ: 11.74 (s, 2 H, OH); 8.25 (s, 2 H, CH=N); 7.94 (dd, 2 H, H(5), J = 7.78 Hz, J = 1.6 Hz); 7.51 (ddd, 2 H, H(7), J = 8.1 Hz, J = 7.5 Hz, J = 1.6 Hz); 7.29 (d, 2 H, H(5′), J = 8.5 Hz); 7.20 (dd, 2 H, H(6), J = 7.7 Hz, J = 7.5 Hz); 7.05 (d, 2 H, H(4′), J = 9.7 Hz); 6.89 (d, 2 H, H(8), J = 8.2 Hz); 6.61 (d, 2 H, H(6′), J = 8.5 Hz); 6.50 (br.s, 4 H, NH_2); 6.04 (d, 2 H, H(3′), J = 9.7 Hz); 3.10 (s, 6 H, NMe).

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