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Structure and properties of 3,6´-dimethyl-2,3-dihydrospiro[naphtho[1,3]oxazine-2,2´-[2*H*]-chromen]-4-ones

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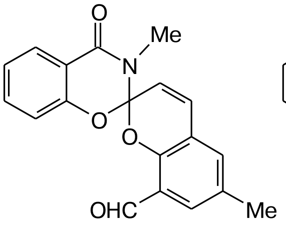
New spiropyrans of the naphthoxazinone series containing structurally different hetarene moieties were synthesized. The structures of all resulting compounds were preliminary investigated by IR and ^{1}H NMR spectroscopy. The structures of some of the newly synthesized spiropyrans were completely characterized by X-ray diffraction. An analysis of the structures and photochromic properties of the spiropyrans led to the conclusion about the influence of the aldehyde group on the photochromic characteristics of spiropyrans.

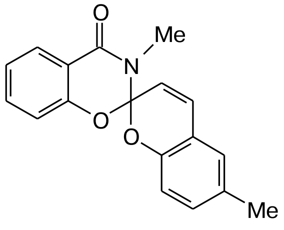
Key words: spiropyran, photochromism, naphthoxazinone, X-ray diffraction study.

Spiropyrans belong to one of the most promising classes of photochromic compounds, whose electronic absorption spectra can undergo reversible changes under activating radiation.[1,2] These compounds have attracted interest due to high sensitivity of their photochromic characteristics to structural variations, as well as because of wide ranges in which the corresponding spectral and photodynamic parameters may vary.[3] Hence, these compounds are attractive for the design of new functional materials. There is an increasing need in the synthesis and investigation of new systematic series of spiropyrans with the aim of revealing structural units, whose modifications can be used to efficiently control the photochemical behavior of spiro systems.

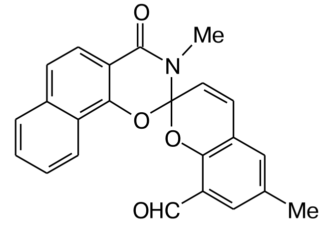
Although the photoisomerization of spiropyrans is described mainly by structural changes in the benzopyran moiety, the photodynamic and spectral characteristics of these compounds depend on the structures of both the 2*H*-chromene and hetarene parts. To analyze the effect of π-acceptor substituents on the photochromic properties of spiro systems, we have studied[4,5] spiropyrans of the benzoxazine series **1a** and **1b** containing the methyl group in position 6´ of the benzopyran moiety of the molecule. To investigate the influence of the conjugation system in the oxazine moiety on the photochemical properties of spiropyrans, we synthesized compound **1c**.[6,7]



1a



1b



1c

In continuation of investigations on the combined influence of the benzannulation in the oxazine moiety and a set of substituents in the benzopyran moiety on the photochromic properties of spiropyrans, in the present study we synthesized analogs of compounds **1a—c**, *viz.*, 3,6´-dimethyl-2,3-dihydrospiro[naphtho[1,3]oxazine-2,2´-[2*H*]-chromen]-4-ones **2a—c**.

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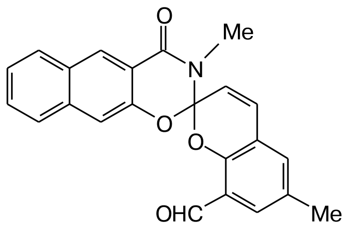
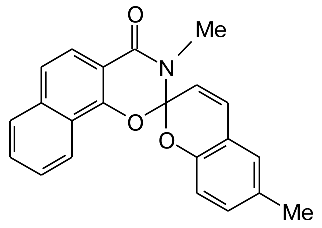
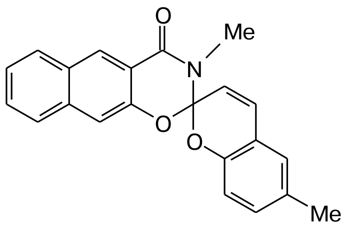


2a



2b



2c

Results and Discussion

Spiropyrans **2a—c** were synthesized by the reaction of 2-formyl-4-methylphenols **3** with 2,3-dimethyl-4-oxo-2,3-dihydronaphtho[1,3]oxazinium perchlorates **4** in acetic acid followed by the treatment of styrene-substituted salts **5** with triethylamine (Scheme 1).

The structures of the resulting compounds were confirmed by IR and ^{1}H NMR spectroscopy.

The IR spectra of spiropyrans **2a—c** show C=C stretching bands of the pyran ring at 1605—1635 cm^{-1} and C=O stretching bands of the naphthoxazine moiety at 1662—1665 cm^{-1}, as well as absorption bands characteristic of the C_{Sp}—O bond at 970—975 cm^{-1}.

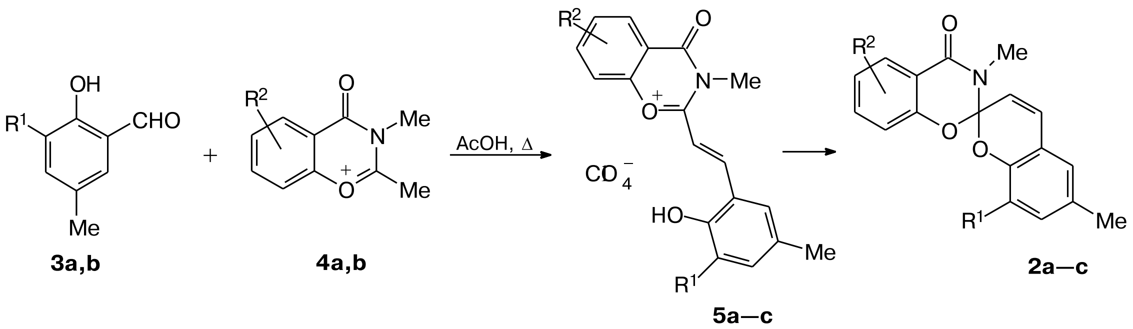
The assignment of the signals in the ^{1}H NMR spectrum is based, in part, on the analogy with the earlier investigations.[6,7] The ^{1}H NMR spectra of compounds **2a—c** show three-proton singlets of NMe groups at δ_H 3.2 and of the methyl group of the benzopyran moiety at δ_H 2.3. The characteristic doublets for the H(3´) protons at δ_H 6.0—6.2 are indicative of the *cis* configuration of the corresponding vinyl group in the molecules and confirm their spirocyclic structure.

We performed photochemical studies of the newly synthesized compounds. Spiropyrans **2a—c**, like compound **1c** synthesized earlier, do not exhibit photochromic properties under irradiation of their ethanolic solutions in a steady-state mode at low (−70 °C) temperatures regardless of the wavelength of activating radiation. In experiments performed in toluene at 20 °C, solutions of spiropyrans **1a**,**c** and **2a** containing the formyl group in position 8´ of the benzopyran moiety display photochromic properties. Under irradiation at λ_{max} = 365 nm, long-wavelength absorption maxima are observed at λ_{max} = 600 (**1c**) and 605 nm (**2a**), which is indicative of the formation of the open merocyanine isomers (Fig. 1, Table 1).

Formyl-substituted compounds **1c** and **2a** exhibit photochromic properties only in solution, whereas they do not show these properties in the solid state, like related spiropyran **1a**.[4] The lifetime of the photoinduced form of spiropyran **1c** is two times longer than that of compound **2a**. On the whole, the additionally annulated benzene ring in the hetarene moiety leads to an increase in the rate of reverse thermal bleaching reactions and, consequently, to a decrease in the lifetime of the photoinduced form regardless of the annulation position.

Unlike compound **1b** studied earlier, its benzo analogs **2b**,**c** do not exhibit photochromic activity in solution regardless of the experimental conditions. Taking into account this behavior, it is of interest to study in detail their structures, including by means of X-ray diffraction. The investigation of the geometric parameters of the C_{Sp}—O bond and the environment of the spirocyclic carbon atom can provide additional information on the influence of the structure of the oxazine and benzopyran moieties on the efficiency of photoisomerization.

Scheme 1



3a: R^1 = —CHO;
3b: R^1 = —H;

4a: R^2 = 6,7-benzo;
4b: R^2 = 7,8-benzo;

5a, **2a:** R^1 = —CHO; R^2 = 6,7-benzo;
5b, **2b:** R^1 = —H; R^2 = 7,8-benzo;
5c, **2c:** R^1 = —H; R^2 = 6,7-benzo

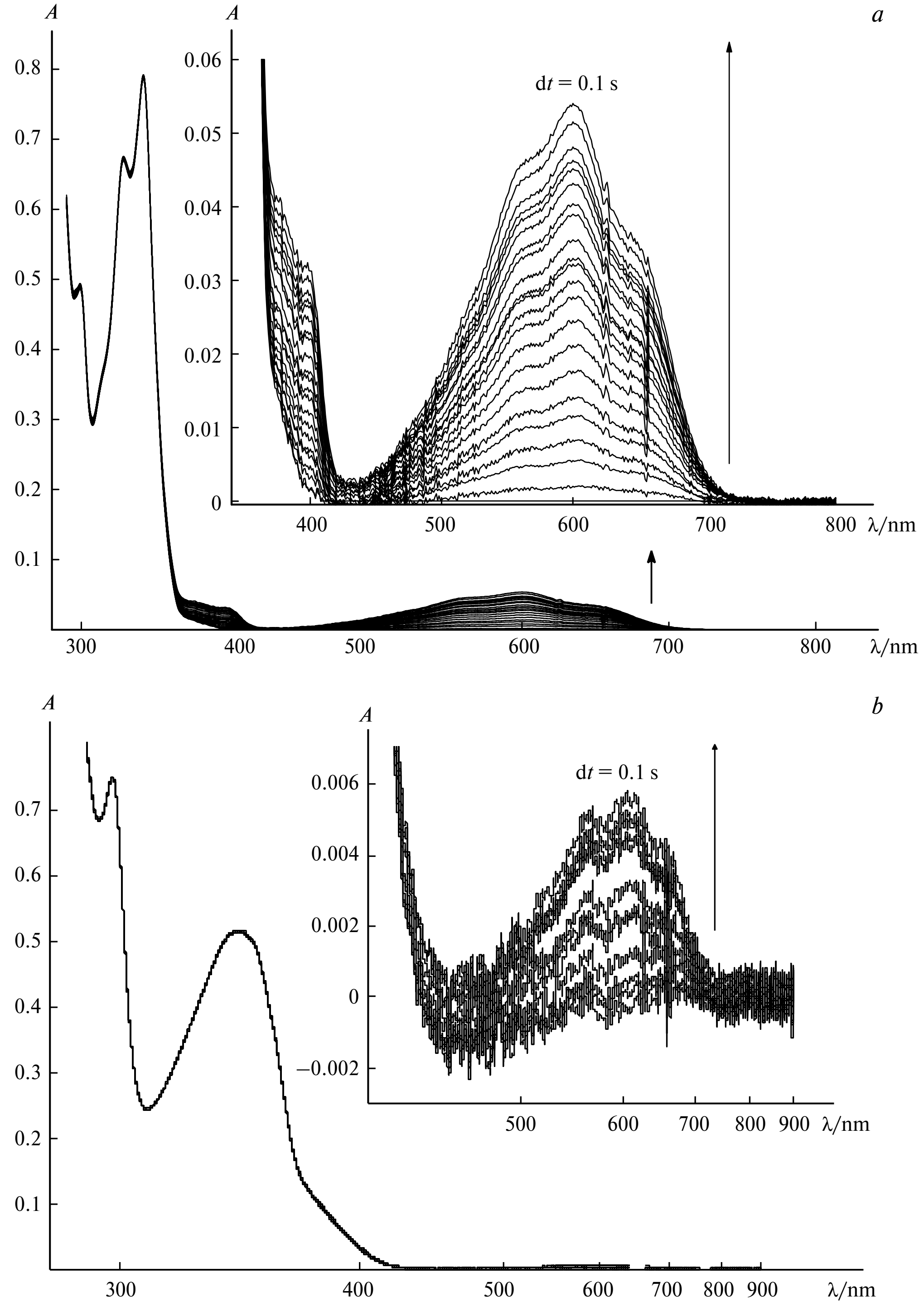


Fig. 1. UV absorption spectra of spiropyrans **1c** (*a*) and **2a** (*b*) in toluene before and after steady-state irradiation at λ_{max} = 365 nm and T = 20 °C; the direction of an increase in the intensity of the long-wavelength absorption maximum under irradiation is indicated by arrows.

The molecular structures of compounds **2b** and **2c** are shown in Figs 2 and 3, respectively. In all the above-mentioned compounds, the benzopyran and naphthoxazine moieties are approximately orthogonal to each other and are individually nonplanar. The naphthoxazine moieties in these compounds are bent along the N(3)—O(1) line by 31.4° and 38.3°, respectively. The benzopyran moiety is bent along the C(3´)...O(1´) and C(4´)...O(1´)

Table 1. Characteristics of the absorption spectra of spiropyrans **2a—c** in toluene at 20 °C compared with the spectra of compounds **1a—c** synthesized earlier

Compound	Substituent	Closed cyclic form		Photoinduced open form	
		λ_{max}/nm	ε/L mol^{-1} cm^{-1}	λ_{max}/nm	τ/s
1a[a]	6´-Me	346	4360	594	3.00
	8´-CHO	336	4020	564	—
1b[b]	6´-Me	335	4450	—[c]	—
1c	6´-Me	329	6710	600	0.89
	8´-CHO	342	7940	—	—
2a	6´-Me	297	7430	605	0.50
	8´-CHO	343	5340	—	—
2b[d]	6´-Me	300	6190	—[c]	—
2c[d]	6´-Me	298	9390	—[c]	—

[a] The compound exhibits photochromic properties both in the solid state and in solution at −70 °C.

[b] The compound exhibits photochromic properties only in solution at −70 °C.

[c] Is not observed in the experimental conditions.

[d] The compound does not show photochromic properties regarldess of the experimental conditions.

lines by 18.3° and 9.9°, respectively, in compound **2b** and by 19.5° and 9.3° in compound **2c**. The O(1), N(3), C(4), and O(15) atoms in both molecules lie in the planes of the corresponding naphthalene moieties.

The deviation of the nitrogen atom N(3) from the plane passing through the C(2´2), C(4), and C(16) atoms is 0.15 and 0.18 Å in compounds **2b** and **2c**, respectively. This parameter is at the lower limit of the range of the corresponding values (0.34—0.12 Å) for the indoline spiropyrans (ISP) containing the methyl substituent at the nitrogen atom studied earlier.[8] The sum of the bond angles at the nitrogen atom N(3) is 356.0 and 355.5° in compounds **2b** and **2c**, respectively. These values are indicative of a slight pyramidalization of the nitrogen atoms N(3) and the weaker sp^3 character of its lone pair (LP). Similar values of the above-mentioned parameters are observed for compound **1b**: the deviation of the nitrogen atom from the corresponding plane is 0.16 Å, the sum of the bond angles at the nitrogen atom is 355.8°. The LP—N(3)—C(2´2)—O(1´) torsion angle is 1.2 and 5.8° in compounds **2b** and **2c**, respectively (3.7° in compound **1b**), which attests that the lone pair of the nitrogen atom is located almost parallel to the σ* orbital of the C(2´2)—O(1´) bond. Due to this mutual arrangement, the orbital interaction between the n-lone pair of the nitrogen atom N(3) and the antibonding orbital of this bond becomes possible. This should lead to the strengthening of the C(2´2)—N(3) bond and the loosening of the C(2´2)—O(1´) bond. As mentioned earlier,[5] the efficiency of this interaction depends mainly on the following two factors: the mutual orientation of the heteroatoms in the spiro unit and the electronic state of these heteroatoms. Unlike indoline analogs, in which the lone pair of the nitrogen atom is conjugated with the π system of the benzene ring ($N—C_{Ph}$ = 1.393—1.416 Å), the lone pair of the nitrogen atom N(3) in compounds **2b**,**c**, as well as in compound **1b**, is involved in the more efficient amide conjugation with the carbonyl group C(4)=O(15), whose π* orbital is lower in energy than the π* orbital of the phenyl group. This conjugation results in the shortening of the N(3)—C(4) bond in compounds **2b** and **2c** to 1.346(6) and 1.372(2) Å, respectively (1.370(2) Å in compound **1b**) and to a decrease in the efficiency of the n—σ* interaction between the lone pair of the nitrogen atom N(3) and the σ* orbital of the C(2´2)—O(1´) bond in molecules **2b**, **2c**, and **1b** compared with the indoline analogs.

The energy of the σ* orbitals of the C(2´2)—O(1´) and C(2´2)—O(1) bonds decreases as the polarity increases. The polarity of the above-mentioned bonds and the electronic structure of the O(1) and O(1´) atoms depend on the degree of the involvement of the oxygen lone pairs in the conjugation with the π systems of the aromatic groups. As opposed to compound **1b**, the lone pairs of the oxygen

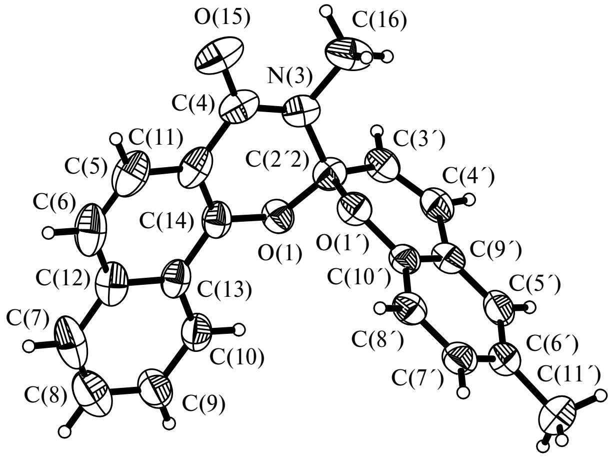


Fig. 2. Molecular structure of compound **2b**.

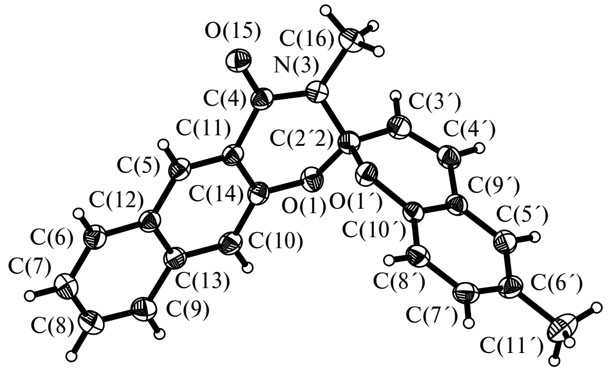


Fig. 3. Molecular structure of compound **2c**.

atoms O(1) in compounds **2b** and **2c** are involved in the conjugation with the π systems of the naphthalene rather than benzene moieties. However, the C(10´)—O(1´) and C(14)—O(1) bond lengths (1.402(4) and 1.370(4) Å, respectively, in **2b**; 1.381(2) and 1.375(2) Å in **2c**) are only slightly different from the corresponding values in **1b** (1.375(2) and 1.370(2) Å). It should be noted that the C(14)—O(1) bond in compound **2b** is shorter than the C(10´)—O(1´) bond and it is equal, within experimental error, to the corresponding bonds in compounds **2c** and **1b**, *i.e.*, the length of this bond is independent of the nature of the aromatic group, whose π system is conjugated with the lone pair of the oxygen atom O(1). The C(2´2)—O(1´) (1.430(4) Å) and C(2´2)—O(1) (1.437(4) Å) bond lengths in **2b** and the C(2´2)—O(1´) (1.428(2) Å) and C(2´2)—O(1) (1.426(2) Å) bond lengths in **2c**, like those in compound **1b** (C(2´2)—O(1´), 1.424(2) Å; C(2´2)—O(1), 1.423(3) Å), are almost equal and substantially deviate from the range of the corresponding C_{Sp}—O bond lengths in ISP (1.485—1.492 Å). The N(3)—C_{Sp} bond lengths in compounds **2b**, **2c**, and **1b** are 1.428(5), 1.449(2), and 1.445(2) Å, respectively, and are in the range of C_{Sp}—N bond lengths for ISP (1.438—1.497 Å). These data indicate that the $n_N—\sigma^*C_{(2´2)—O(1´)}$ interaction in compounds **2b**,**c** and in compound **1b** is weak compared with that in the formyl-substituted spiropyran[4] and ISP and it has virtually no effect on the length and strength of the C(2´2)—O(1´) bond, which, apparently, accounts for the fact that compounds **2b,c** and **1b** do not exhibit photochromic properties.

The introduction of electron-withdrawing substituents into the benzene group of the molecules can increase the degree of conjugation between the lone pair of the oxygen atom and the π system of the benzene ring, resulting in the structural modification of the spiro unit. Actually, as we have shown earlier,[4] the C(2´2)—O(1´) (1.439(2) Å) bond in the benzopyran moiety of compound **1a**, which is the formyl derivative of **1b**, is much longer than the corresponding C(2´2)—O(1) bond in the benzoxazine moiety (1.405(2) Å) due to the introduction of the strong π-acceptor substituent. As a result, compound **1a** displays photochromic properties not only in solution but also in the solid state.[4]

Therefore, a series of new spiropyrans of the oxazinone series were synthesized. These compounds differ both by the set of substituents in the benzopyran moiety of the molecule and the structure of the oxazine ring. In particular, the structures of the resulting products and their photochromic properties depend on the electronic structure of the substituents in position 8´ of the benzopyran moiety of the molecule. The presence of the additionally annulated benzene ring in the oxazine moiety (**1c** and **2a—c**) leads to a decrease in the quantum yield of the phototransformation due to radiationless deactivation of the excited state (in particular, due to the intramolecular energy transfer from the pyran ring to the oxazine moiety) of spiropyran and, as a consequence, results in destabilization of the open form. At the same time, the absence of the electron-withdrawing aldehyde group in compounds **2b**,**c** is an additional factor responsible for a decrease in the efficiency of photoisomerization.[9] The investigation of the newly synthesized compounds compared with spiropyrans **1a—c** synthesized earlier showed the influence of the synchronous variation in the structure of both the oxazine and benzopyran moieties on the photochromic properties. It was confirmed that the introduction of the additionally annulated benzene ring into the oxazine moiety leads to substantial destabilization of the photoinduced open form and, in the case of compounds **2b** and **2c**, results in the complete disappearance of the photochromic properties regardless of the experimental conditions. The linear 6,7-annulation of the benzene group in the benzoxazine component (compound **2a**) is responsible for the twofold decrease in the lifetime of the photoinduced open isomer compared with 7,8-annulation (compound **1c**).

Experimental

The IR absorption spectra were recorded on an Excalibur HE 3100 PC Fourier-transform infrared spectrometer using the attenuated total internal reflection (ATIR) technique. The electronic absorption spectra were measured in toluene solutions on an Agilent 8453 spectrophotometer with the use of a DRSh-250 mercury lamp equipped with a standard kit of light filters as a radiation source. The ^{1}H NMR spectra were recorded on a Bruker 250 radio-frequency spectrometer (250 MHz) in a pulsed Fourier-transform mode in deuteriochloroform. The positions of the signals were determined on the δ scale with respect to the residual signals of the proton of $CDCl_3$ as the deuterio solvent.

2,6-Diformyl-4-methylphenol (**3a**) was synthesized according to a known procedure.[10]

2,3-Dimethyl-4-oxo-2,3-dihydronaphtho[3,2-*e*][1,3]oxazinium perchlorate (**4a**) was synthesized from 2,3-hydroxynaphthoic acid according to a procedure completely analogous to that used for the synthesis[6] of **4b** and was introduced into the reactions without the preliminary identification.

8´-Formyl-3,6´-dimethyl-2,3-dihydrospiro[naphtho[3,2-*e*]-[1,3]oxazine-2,2´-[2*H*]-chromen]-4-one (2a). 2,3-Dimethyl-4-oxo-2,3-dihydronaphtho[3,2-*e*][1,3]oxazinium perchlorate (**4a**) (3.25 g, 0.01 mol) was added to a hot solution of 2,6-diformyl-4-methylphenol (**3a**) (1.64 g, 0.01 mol) in acetic acid (15 mL). The reaction mixture was refluxed for 5 min and then cooled. The dark-brown precipitate of salt **5a** that formed was filtered off, washed with diethyl ether (3×15 mL), and placed in anhydrous diethyl ether (50 mL). Then Et_3N (1.5 mL, 0.01 mol) was added dropwise. After 12 h, the diethyl ether was decanted, the solvent was distilled off, and the yellow oily residue was recrystallized from ethanol. The yield was 1.04 g (28%), m.p. 151—153 °C (from EtOH). Found (%): C, 74.44; H, 4.56; N, 3.69. $C_{23}H_{17}NO_4$. Calculated (%): C, 74.39; H, 4.58; N, 3.77. UV, λ_{max}/nm (ε): 297 (7430). IR, ν/cm^{-1}: 1665 (C=O), 1624 (C=C), 971 (C_{Sp}—O). ^{1}H NMR, δ: 2.35 (s, 3 H, C(6´)Me); 3.25 (s, 3 H, N(3)Me); 6.22 (d, 1 H, H(3´), *J* = 9.8 Hz); 7.05 (d, 1 H, H(4´), *J* = 9.8 Hz);

7.24 (s, 1 H, H(10)); 7.34 (s, 1 H, H (5´)); 7.42—7.58 (m, 3 H, H(7), H(8), H(7´)); 7.69 (d, 1 H, H(9), *J* = 8.2 Hz); 7.98 (d, 1 H, H(6), *J* = 8.1 Hz); 8.65 (s, 1 H, H(5)); 9.8 (s, 1 H, CHO).

3,6´-Dimethyl-2,3-dihydrospiro[naphtho[2,1-*e*][1,3]oxazine-2,2´-[2*H*]-chromen]-4-one (2b). 2,3-Dimethyl-4-oxo-2,3-dihydronaphtho[2,1-*e*][1,3]oxazinium perchlorate (**4b**) (3.25 g, 0.01 mol) was added to a hot solution of 2-formyl-4-methylphenol (**3b**) (1.36 g, 0.01 mol) in acetic acid (15 mL). The reaction mixture was refluxed for 5 min and then cooled. The dark-brown precipitate of salt **5b** that formed was filtered off, washed with diethyl ether (3×15 mL), and placed in anhydrous diethyl ether (50 mL). Then Et_3N (1.5 mL, 0.01 mol) was added dropwise. After 12 h, the diethyl ether was decanted and evaporated, and the yellow oily residue was recrystallized from ethanol. The yield was 0.82 g (24%), m.p. 162—163 °C (from EtOH). Found (%): C, 76.89; H, 5.03; N, 4.01. $C_{22}H_{17}NO_3$. Calculated (%): C, 76.97; H, 4.97; N, 4.08. UV, λ_{max}/nm (ε): 300 (6190). IR, ν/cm^{-1}: 1662 (C=O); 1634 (C=C); 972 (C_{Sp}—O). ^{1}H NMR, δ: 2.27 (s, 3 H, C(6´)Me); 3.20 (s, 3 H, N(3)Me); 6.11 (d, 1 H, H(3´), *J* = 9.7 Hz); 6.64 (d, 1 H, H(8´), *J* = 8.2 Hz); 6.92—7.14 (m, 3 H, H(4´), H(7´), H(5´)); 7.4 (т, 1 H, H(9), *J* = 8.1 Hz); 7.5—7.62 (m, 2 H, H(8), H(10)); 7.82 (d, 1 H, H(7), *J* = 8.2 Hz); 7.96 (d, 1 H, H(6), *J* = 8.4 Hz); 8.05 (d, 1 H, H(5), *J* = 8.6 Hz).

3,6´-Dimethyl-2,3-dihydrospiro[naphtho[3,2-*e*][1,3]oxazine-2,2´-[2*H*]-chromen]-4-one (2c) was synthesized by analogy with compound **2b** with the use of 2,3-dimethyl-4-oxo-2,3-dihydronaphtho[3,2-*e*][1,3]oxazinium perchlorate (**4a**). The yield was 0.68 g (20%), m.p. 178—179 °C (from EtOH). Found (%): C, 76.99; H, 5.09; N, 4.07. $C_{22}H_{17}NO_3$. Calculated (%): C, 76.97; H, 4.97; N, 4.08. UV, λ_{max}/nm (ε): 298 (9390). IR, ν/cm^{-1}: 1665 (C=O); 1629, 1605 (C=C); 985, 971 (C_{Sp}—O). ^{1}H NMR, δ: 2.29 (s, 3 H, C(6´)Me); 3.19 (s, 3 H, N(3)Me); 6.06 (d, 1 H, H(3´), *J* = 9.6 Hz); 6.63 (d, 1 H, H(8´), *J* = 8.1 Hz); 6.90—7.10 (m, 3 H, H(4´), H(7´), H(5´)); 7.22 (s, 1 H, H(10)); 7.33—7.53 (m, 2 H, H(7), H(8)); 7.67 (d, 1 H, H(9), *J* = 8.5 Hz); 7.94 (d, 1 H, H(6), *J* = 8.1 Hz); 8.64 (s, 1 H, H(5)).

X-ray diffraction study. The unit cell parameters of the crystals of **2b** and **2c** were determined and three-dimensional sets of intensities were measured on a Bruker P-4 automated diffractometer (Mo-Kα radiation, graphite monochromator) at ~20 °C.

Colorless transparent crystals of **2b** are orthorhombic: $C_{22}H_{17}NO_3$, $M = 368.45$; $a = 6.454(1)$ Å, $b = 14.106(2)$ Å, $c = 19.332(3)$ Å, $V = 1760.0(5)$ Å^3, $Z = 4$, $\rho_{calc} = 1.296$ g cm^{-3}, μ(Mo-Kα) = 0.087 mm^{-1}, space group $P2_12_12_1$. The intensities of 2188 reflections were measured in the angle range $2\theta \le 50°$ by the ω/2θ-scanning technique from a single crystal of dimensions 0.42×0.38×0.36 mm. After rejection of the systematic absences and merging of equivalent reflections (R(int) = 0.018), the X-ray data set contained 2012 independent reflections ($F^2(hkl)$ and $\sigma(F^2)$), of which 1038 reflections were with $F^2 > 4\sigma(F^2)$. The structure was solved by direct methods with the use of the SHELXTL program package[11] and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms against F^2 using the SHELXL program package.[11] In the crystal structure of **2b**, all H atoms were located in difference Fourier maps, and then the coordinates and isotropic thermal parameters for all H atoms were refined by the least-squares method using a riding model.[11] The final refinement parameters were $R_1 = 0.034$, $wR_1 = 0.068$, $R_2 = 0.092$, $wR_2 = 0.093$, GOF = 1.021. The maximum and minimum difference electron densities were 0.112 and –0.112 e A^{-3}, respectively.

Colorless transparent crystals of **2c** are monoclinic: $C_{22}H_{17}NO_3$, $M = 343.37$; $a = 6.475(1)$ Å, $b = 25.092(7)$ Å, $c = 10.789(1)$ Å, $\beta = 100.32(1)°$. $V = 1724.5(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.322$ g cm^{-3}, μ(Mo-Kα) = 0.087 mm^{-1}, space group $P2_1/n$. The intensities of 3654 reflections were measured in the angle range $2\theta \le 50°$ using the ω/2θ-scanning technique from a single crystal of dimensions 0.40×0.35×0.35 mm. After rejection of the systematic absences and merging of equivalent reflections, the X-ray data set contained 2796 independent reflections ($F^2(hkl)$ and $\sigma(F^2)$), of which 2097 reflections were with $F^2 > 4\sigma(F^2)$. The structure was solved and refined by analogy with **2c**. In the last cycle of the full-matrix refinement, the absolute shifts of all 236 variable parameters of structure **2c** were smaller than 0.001σ; $R_1 = 0.041$, $wR_2 = 0.10$ based on 2796 observed reflections with $I \ge 2\sigma(i)$; $R_2 = 0.061$, $wR_2 = 0.11$ based on all measured reflections, GOF = 1.042. After the refinement, the maximum and minimum difference electron densities were 0.237 and –0.156 e A^{-3}, respectively.

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