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PHOTOCHROMIC AND THERMOCHROMIC SPIROPYRANS. 22*. SPIROPYRANS OF THE 4-OXO-3,4-DIHYDRO-3H-1,3-BENZOXAZINE SERIES CONTAINING π-ACCEPTING SUBSTITUENTS AT POSITION 8'

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New spiropyrans of the benzoxazinone series were synthesized by modification of the formyl group in compounds containing an asymmetric spiro carbon atom. It was shown that ^{1}H NMR identification of the spiropyrans containing π-accepting hydrazone substituents must be conducted at elevated temperatures by following the presence of and degree of subsequent "recovery". According to X-ray crystallographic analysis, crystal solvates can form, depending on the solvent used for crystallization of the hydrazones of the spiropyrans.

Keywords: benzoxazinone, crystal solvate, spiropyran.

A fairly well studied method for the production of spiropyran structures from compounds not containing a carbon spiroatom in general form is condensation of the methylene bases of nitrogen heterocycles or their precursors with *ortho*-hydroxy aromatic aldehydes [2].

Of particular interest is the synthesis and investigation of the photochemical and crystallographic characteristics in a series of compounds containing a nonindoline fragment as hetaryl component [3]. The photochromic characteristics of spiropyrans are determined not only by the contribution from the heteroarene fragment but to a greater degree by the substituent in the 2H-chromene part of the molecule. As concerns the method using modification of spiropyrans on the basis of already prepared spirocyclic structures, they have been used extremely rarely. (The halogenation, nitration, and azocoupling of 1,3,3-trimethylindolinospiropyran at position 6 are known [4].) With the exception of reduction of a nitro group to an amino group [5], the reactions of functional substituents have not been used. It seemed of interest to use π-accepting substituents other than the nitro group, since their effect on the photochromic characteristics of the spiropyrans have so far been insufficiently investigated [2]. The valuable characteristics of spiropyrans containing a π-accepting formyl group at position 8' [1, 6] have stimulated interest in the production of their derivatives. Spiropyrans with a formyl group have previously been preparatively inaccessible and have as a result been studied little.

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* For Communication 21, see [1].

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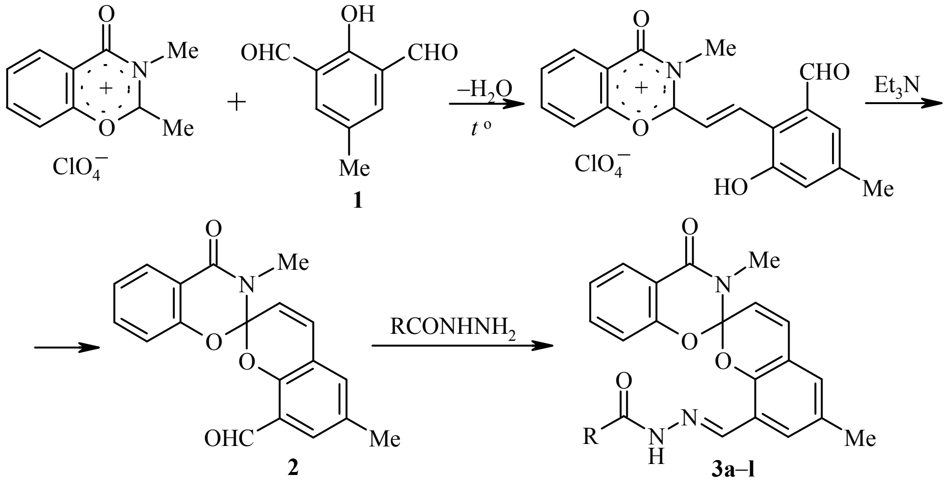
In this connection from 2,6-diformyl-4-cresol (**1**) by the previously developed method [7] we synthesized 8'-formyl-3,6-dimethyl-4-oxo-3,4-dihydrospiro-2H-1,3-benzoxazine-2,2'-[2H]chromene (**2**) with a free formyl group at position 8', which exhibits photochromic characteristics in solutions and in the adsorbed state [1]. From it, by reactions of the formyl group, we obtained compounds **3** (Table 1), which retained the spiropyran ring and contained nontraditional bulky π-accepting substituents at position 8' – derivatives of aliphatic, aromatic, and phenoxyacetic acids.



3 a R = C_5H_{11}, **b** R = C_9H_{19}, **c** R = $C_{13}H_{27}$, **d** R = $C_{17}H_{35}$, **e** R = Ph, **f** R = 4-C_6H_4Me,
g R = 4-C_6H_4OMe, **h** R = 4-$C_6H_4NO_2$, **i** R = 3-C_6H_4Br, **j** R = $PhOCH_2$,
k R = 4-C_6H_4(Me)OCH_2, **l** R = 2,4-$C_6H_3(Br)_2OCH_2$

TABLE 1. Spiropyrans **3**

Compound	Empirical formula	Found, % / Calculated, % C	H	N	Br	mp, °C, DMF	Yield, %
3a	$C_{22}H_{27}N_3O_4$	66.29 66.49	6.65 6.80	16.22 16.12	—	217	72
3b	$C_{26}H_{35}N_3O_4$	68.77 68.87	7.64 7.72	14.10 13.57	—	230	60
3c	$C_{30}H_{43}N_3O_4$	70.83 70.72	8.51 8.44	12.44 12.57	—	235	48
3d	$C_{34}H_{51}N_3O_4$	72.09 72.21	8.88 9.09	7.49 7.43	—	233	40
3e	$C_{26}H_{21}N_3O_4$	70.91 71.05	4.99 4.78	9.63 9.56	—	228	84
3f	$C_{27}H_{23}N_3O_4$	71.39 71.51	4.93 5.07	9.32 9.26	—	248	82
3g	$C_{27}H_{23}N_3O_5$	68.95 69.07	4.82 4.90	9.03 8.95	—	228	79
3h	$C_{26}H_{20}N_4O_5$	64.57 64.46	4.29 4.13	11.43 11.56	—	256	75
3i	$C_{26}H_{20}BrN_3O_4$	60.12 60.24	3.95 3.86	7.98 8.10	15.27 15.41	223	71
3j	$C_{26}H_{23}N_3O_5$	68.15 68.27	4.92 5.03	9.04 9.19	—	223	73
3k	$C_{27}H_{25}N_3O_5$	68.66 68.78	5.22 5.30	8.99 8.91	—	228	75
3l	$C_{26}H_{21}Br_2N_3O_5$	50.61 50.73	3.50 3.41	6.90 6.82	25.77 26.01	231	68

These compounds are of undoubted interest, since they provide the potential possibility of stabilizing the open-chain colored forms through the chelation of metal ions.

In the IR spectra of compounds **3**, together with the absorption band at 1670 cm^{-1} (the stretching vibrations of the carbonyl group in the $–CO–N(CH_3)–$ fragment in the oxazine ring of the initial compound **2**), there are two absorption bands characteristic of the stretching vibrations of the CO (amide-1) and NH groups in the NH–CO fragment of compounds **3** (Table 2).

It is difficult to make an unambiguous assignment of all the signals in the ^1H NMR spectra of the hydrazones containing the spiropyran fragment. The complex form of the spectrum of the spiropyran **3a** (Fig. 1*a*) gives reason to suppose the presence of *syn-anti* isomers and hydrogen bonds. On heating to 120°C (Fig. 1*b*) the spectrum corresponds to structure **3a**. Cooling to 30°C – "recovery" – leads to a spectrum identical with that shown in Fig. 1*a*. The *syn-anti* isomerization process must be rejected since it has a high barrier and is irreversible. In this connection it is necessary to assume that only forms with hydrogen bonds are present. All the forms and also their possible superimpositions are observed in the spectra at 20°C (Fig. 1*a*) and in the recovery spectrum. Only one form **3a** with completely broken hydrogen bonds is observed in the spectrum at 120°C (Fig. 1*b*). Thus, ^1H NMR spectroscopic identification of the spirans containing a hydrazone fragment must be conducted at elevated temperatures while following the presence and degree of subsequent recovery.

X-ray crystallographic investigations were carried out on a single crystal of the spiropyran **3a** and its crystal solvate **3a'** with dioxane in order to determine the effect of the structure of the spiropyrans on their photochromic characteristics (Figs. 2 and 3, Table 3). According to x-ray crystallographic analysis, as in the previously investigated indoline and benzoxazine derivatives of spiropyrans [1, 8], in the molecules the benzopyran and benzoxazine fragments in **3a** and **3a'** are approximately orthogonal with each other and are not individually planar. In compound **3a** the benzoxazine fragment is bent along the N(3)···O(1) line by an angle φ of 34.7°, while in compound **3a'** φ is 34.2°; the benzopyran fragment is bent along the C(3')–O(1') and C(4')–O(1') lines by $\alpha = 22.6°$, $\beta = 7.5°$ and $\alpha = 23.1$, $\beta = 12.9°$ for **3a** and **3a'** respectively. The O(1), C(4), N(3), and O(2) atoms lie in the plane of the benzene ring C(5)C(6)C(7)C(8)C(9).

TABLE 2. The Spectral Characteristics of the Initial Spiropyran **2** and the Spiropyrans **3**

Compound	IR spectrum, ν, cm^{-1}			UV spectrum, ν_{max}, nm (log ε) (in 2-propanol)*
	NH	C=O	C=N	
2	—	1692, 1638*[2]	—	238 (4.52); 265 (5.14); 294 sh (3.55); 340 (3.58)
3a	3234	1715, 1674*[3]	1634	298 (4.52); 345 (3.91); 451 (3.77)
3b	3247	1717, 1674*[3]	1624	298 (4.51); 359 (3.95); 456 (3.80)
3c	3300	1720, 1660*[3]	1620	301 (4.50); 344 (3.97); 451 (3.74)
3d	3314	1715, 1662*[3]	1620	291 (4.42); 370 (3.92); 464 (3.67)
3e	3268	1726, 1660*[3]	1625	298 (4.52); 345 sh (3.91); 451 (3.77)
3f	3268	1720, 1690*[3]	1632	291 (4.51); 368 (3.94); 452 (3.45)
3g	3230	1723, 1662*[3]	1620	301 (4.60); 350 sh (3.93); 451 (3.74)
3h	3300	1720, 1660*[3]	1610	291 (4.42); 370 (3.93); 464 (3.67)
3i	3284	1715, 1680*[3]	1625	291 (4.49); 359 (3.89); 456 (3.64)
3j	3247	1687, 1660*[3]	1634	255 (4.44); 340 (3.42); 357 (3.29)
2k	3260	1700, 1660*[3]	1620	260 (4.02); 292 (3.93); 326 (2.01); 340 (3.40)
3l	3300	1700, 1665*[3]	1618	272 (5.46); 340 (4.19); 357 (4.02)

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* λ_{max} of the photoinduced form of spiropyran **2** 426, 556 nm.

*[2] $\nu_{C=O}$ of the formyl group.

*[3] $\nu_{C=O}$ of the hydrazone fragment.

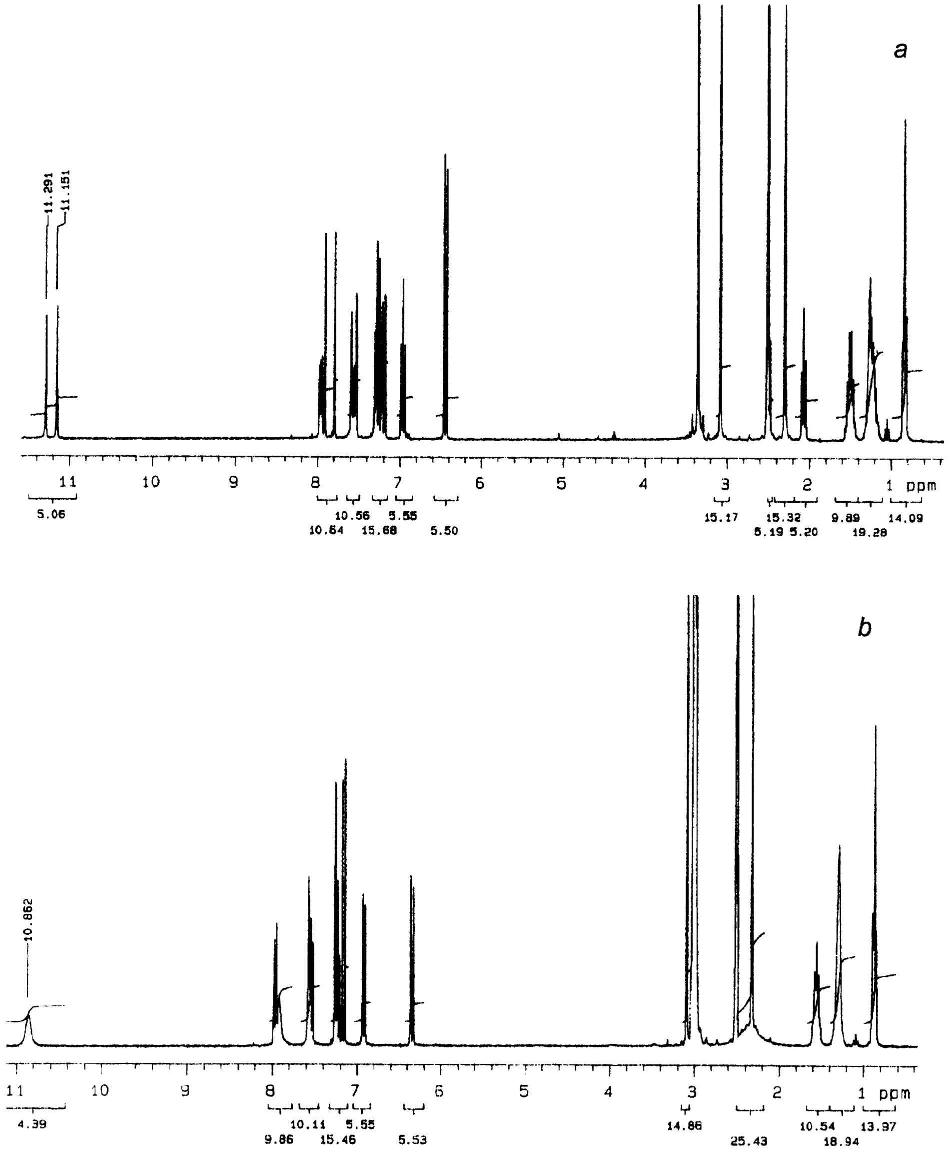

Fig. 1. The ^{1}H NMR spectrum of the spiropyran **3a** in DMSO-d$_6$ at 20 (*a*) and 120°C (*b*).

Thus, the geometric structure of the C$_{spiro}$ unit and the benzopyran fragment in compounds **3a** and **3a'** is similar to the structure of the indoline spiropyrans. However, the inclusion of the C(4)=O(2) carbonyl group in the benzoxazine fragment leads to substantial change in the electronic and geometric pattern of the structure of

TABLE 3. The Basic Values of the Bond Lengths in the Benzoxazine and Hydrazide Fragments of Compounds **3a** and **3a'**

Bond	*d*, Å		Bond	*d*, Å	
	3a	**3a'**		**3a**	**3a'**
$N_{(3)}$–$C_{(4)}$	1.367(2)	1.378(4)	$O_{(1')}$–$C_{(8A')}$	1.379(4)	1.392(3)
$C_{(4)}$–$O_{(2)}$	1.224(2)	1.234(4)	$C_{(3')}$–$C_{(4')}$	1.309(4)	1.310(3)
$C_{(4)}$–$C_{(10)}$	1.465(2)	1.459(5)	$C_{(4')}$–$C_{(4A')}$	1.459(4)	1.452(3)
$O_{(1)}$–$C_{(9)}$	1.379(2)	1.394(3)	$C_{(10')}$–$C_{(8')}$	1.469(4)	1.461(2)

the N(3) unit. The projection of the N(3) atom from the plane of the coordinating atoms C(2'2)C(4)C(12) amounts to 0.06 Å, and the sum of the bond angles at N(3) is 356.2 and 355.9° in **3a** and **3a'** respectively. In spite of the bending of benzoxazine ring along the O(1)···N(3) line and the torsional rotation of the C(2'2) atom about the C(4)–N(3) bond (the torsion angle O(2)–C(4)–N(3)–C(2'2) is 13.5 for **3a** and 10.5° for **3a'**), such a structure for the N(3) unit is due at the same time to rotation of the methylene group C(12) about this bond. (The torsion angle O(2)–C(4)–N(3)–C(12) is 15.1 for **3a** and 12.3° for **3a'**.) The angle between the O(2)C(4)C(10)N(3) and N(3)C(2'2)C(12) planes amounts to 19.2 and 16.7° for structures **3a** and **3a'** respectively. Thus, the vectors of the electron clouds of C(4) and O(2), participating in the formation of the C(4)=O(2) π bond, are not parallel to the unshared electron pair of the N(3) atom. Nevertheless, the length of the amide bond N(3)–C(4) of 1.367(2) for **3a** and 1.378(4) Å for **3a'** indicates appreciable conjugation between the unshared electron pair of the N(3) atom and the π bond of the carbonyl group.

Amide conjugation significantly weakens the interaction between the unshared electron pair of the N(3) atom and the σ^*-orbital of the C(2'2)–O(1') bond. Moreover, the geometric position of the C(2'2)–O(1') bond in relation to the coordination plane of the N(3) atom – C(2'2)C(4)C(12) – becomes less favorable for the orbital n–σ^*interactions.

In addition, the substitution in the 8'-formyl group substantially reduced the electron-accepting effect of this group on the O(1') atom. This is demonstrated by the increase in the length of the O(1')–C(8a') bond to 1.379(4) and 1.392(3) Å for the crystals of **3a** and **3a'** respectively, compared with 1.439(2) Å for the analogous C(2'2)–O(1') bond in the spiropyrans [2]. The weakening of the electron-accepting effect of the substituent at position 8' reduces the polarity of the C(2'2)–O(1') bond and further weakens the n–σ^* interaction compared with those in the spiropyrans [1]. As a result of this the lengths of the bonds C(2'2)–O(1') 1.421(2) for **3a** (1.424(2) for **3a'**) and C(2'2)–O(1) 1.415(2) for **3a** (1.425(2) Å for **3a'**) are practically identical, and the investigated spiropyrans **3** do not exhibit photochromic characteristics.

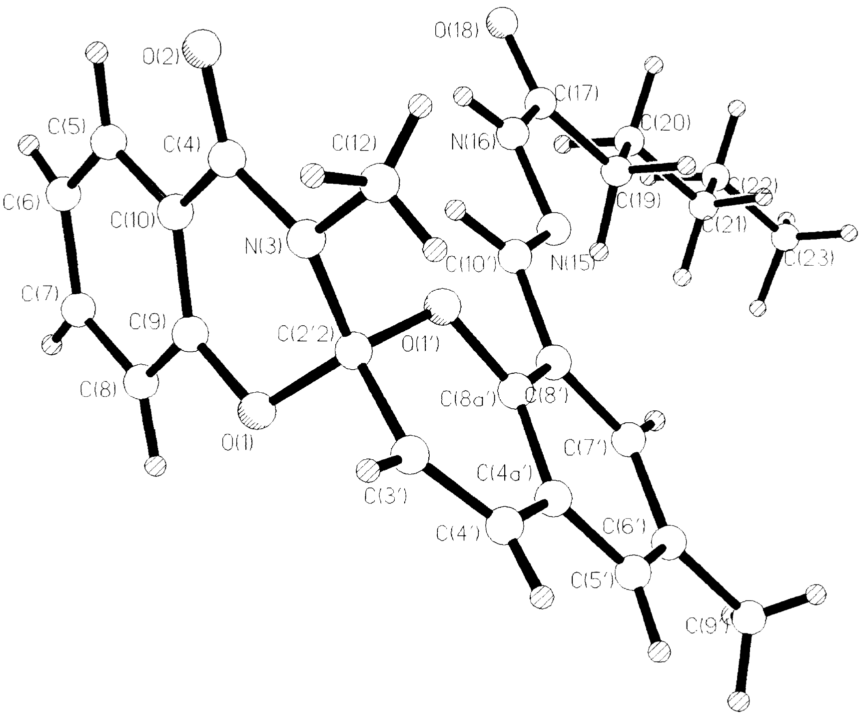

Fig. 2. The general appearance of the molecule of spiropyran **3a** in the crystal.

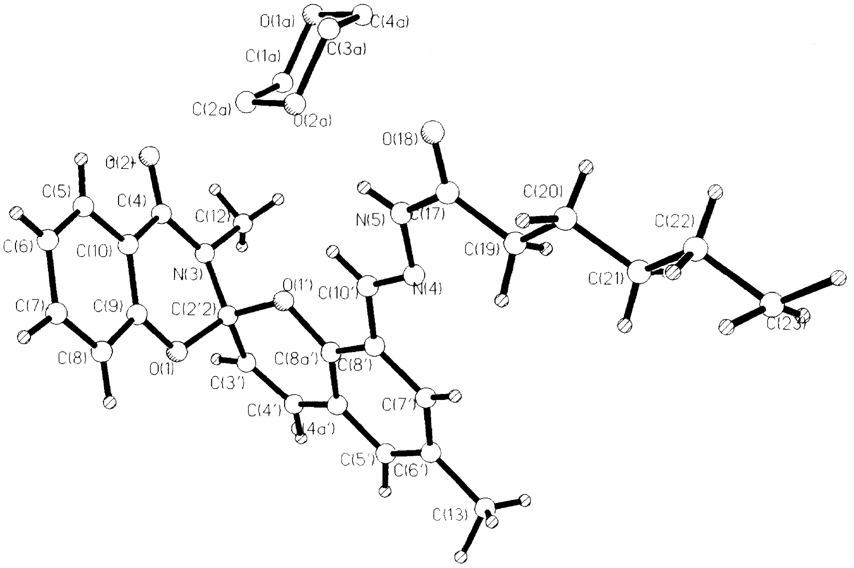

Fig. 3. The general appearance of the molecule of spiropyran **3a** and the solvent molecule in the crystal solvate **3a'**.

EXPERIMENTAL

The IR spectra were recorded on a prism double-beam Specord IR-71 spectrometer. The instrument was calibrated against polystyrene.

The electronic spectra of the investigated compounds were recorded at room temperature on a Varian Carry spectrometer. The absorption spectra before and after irradiation were recorded on a Specord UV-Vis spectrometer fitted with a special cryostat for low-temperature measurements. The excitation source was a DRSh-250 mercury lamp with light filters isolating light with λ_{max} 313 and 365 nm. The ^{1}H NMR spectra were recorded on Bruker-250 (250 MHz) and Varian Unity 300 (300 MHz) spectrometers.

The crystals of **3a** for X-ray crystallographic analysis were produced by crystallization from isopropyl alcohol, and those of **3a'** were produced by crystallization from dioxane. The X-ray diffraction experiment was conducted on an automatic four-circle KYMA diffractometer at 293 K with MoKα radiation at angles θ in the range of 1.59-25.04° for **3a** and with CuKα radiation at angles θ 3.14-74.94° for **3a'**.

Principal crystallographic data for structure **3a**: ($C_{25}H_{27}N_3O_4$) (Fig. 2), $a = 8.556(4)$, $b = 10.862(4)$; $c = 13.077(7)$ Å, $\alpha = 94.17(4)$, $\beta = 99.66(5)$, $\gamma = 104.01(3)°$; $V = 1154.3(9)$ Å^3; $Z = 2$; P-1 (triclinic); $d = 1.247$ g/cm^3; $F(000) = 460$; M = 433.50. The structure of **3a** was interpreted by the direct method and refined by least-squares treatment in F^2 to $R = 0.047$ ($R_w = 0.084$, Goof = 1.164) in 3253 reflections with $I > 2\sigma(I)$ in anisotropic approximation by the SHELXL-93 software [9]. The hydrogen atoms were revealed in a Fourier difference synthesis, and only the position parameters were refined.

Principal crystallographic data for structure **3a'**: ($C_{29}H_{27}N_3O_6$) (Fig. 3), $a = 10.308(4)$, $b = 15.020(4)$, $c = 10.294(7)$ Å; $\alpha = 76.34(4)$, $\beta = 70.64(5)$, $\gamma = 70.09(3)°$; $V = 1407.6(12)$ Å^3; $Z = 2$; $d = 1.247$ g/cm^3; $F(000) = 460$; M = 513.54. The structure of **3a'** was obtained by direct methods, and the obtained data were then processed and refined by full-matrix least-squares treatment in F^2 to $R = 0.069$ for 2580 reflections with $I > 2\sigma(I)$ in anisotropic approximation using the SHELXL-93 software [9]. For the hydrogen atoms, revealed in the Fourier synthesis, only the position parameters were refined.

The energy of the crystals was calculated by the atom–atom potential method using the PCM software [10] with the 6-exp potentials proposed by A. I. Kitaigorodskii. The crystal lattice energy of the crystal of compound **3a** was $E = -58$ kcal/mol, and that of the crystal of compound **3a'** was $E = -53$ kcal/mol.

The free volume in the unit cell for each molecule amounted to ~189 and ~197 for compounds **3a** and **3a'** respectively.

8'-Formyl-3,6-dimethyl-4-oxo-3,4-dihydrospiro(2H-1,3-benzoxazine-2,2'-[2H]-chromene) (2). The compound was obtained by the method in [1, 7].

Spiropyrans 3. To compound **2** (0.1 g, 0.33 mol) in hot ethanol (1 ml) we added an equivalent amount of the respective acid hydrazide. The mixture was boiled for 15 min and allowed to stand until a precipitate had separated. The precipitate was filtered off, dried, and recrystallized from DMF. The melting points, yields, and elemental analyses are given in Table 1.

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