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PHOTO- AND THERMOCHROMIC SPIRANES. 24*. NOVEL PHOTOCHROMIC SPIROPYRANS FROM 2,4-DIHYDROXYISOPHTHALALDEHYDE

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Novel series of photochromic indoline and benzoxazine spiropyrans containing ortho-placed formyl and hydroxyl groups in the benzene ring of the chromene part of the molecule have been prepared. X-ray analysis has shown that, depending on the structure of the heterocyclic component in the spiro cyclization reaction different, nonequivalent formyl groups of 2,4-dihydroxyisophthalaldehyde can participate. The synthesized compounds were used as original analogs of salicylaldehyde. The novel photochromic bispyropyrans prepared contain two different asymmetric spiro carbon atoms.

Keywords: 2,4-dihydroxyisophthalaldehyde, benzoxazinone, indoline, spiropyran, photochromism.

The photochromic properties of spiropyrans are determined not only by a contribution from the heterene fragment but to a greater extent by the substituents in the 2H-chromene part of the molecule. We have prepared the novel spiropyrans **4** and **6** which are original analogs of salicylaldehyde. The spiropyrans **7** have been prepared from compound **4** and they contain two different spirocyclic centers and hence two asymmetric carbon atoms. The structures of the synthesized compounds **4, 6, 7** were confirmed by elemental analysis (Table 1) and by IR and ^{1}H NMR spectroscopy (Table 2). The IR spectra of compounds **4, 6** show absorption bands at 1584-1633 and 912-996 cm^{-1} ($\nu_{C=C}$ and ν_{C-O} in the 2H-chromene fragment respectively) and in the spiropyrans **4** and **7** there are also carbonyl stretching bands from the benzoxazinone fragment at 1673-1686 cm^{-1}. In the IR spectra of the spiropyrans **4** and **6** the absorption bands for the formyl and hydroxyl groups are absent. Evidently this is connected with a strong intramolecular hydrogen bond (IHB). The ^{1}H NMR spectrum of compound **4a** in deuterochloroform shows signals for the 3' and 4' protons as an AB-spectrum with δ (3') = 5.97 and δ (4') = 6.93 ppm ($J_{3'4'}$ = 9.8 Hz). The N–CH_3 methyl group signal at position 3 of the oxazinone fragment, the formyl proton, and the OH proton placed *ortho* to it in the benzene ring of the 2H-chromene fragment appear as singlets at 3.17, 10.22, and 11.69 ppm respectively.

In the indoline spiropyrans of series **6** the *gem*-dimethyl groups in position 3 are a convenient diastereotopic marker reflecting the spiropyran structure of the compound. The presence in the ^{1}H NMR spectrum of two singlet signals for the *gem*-dimethyl groups (*gem* $(CH_3)_2$) at δ = 1.15 and 1.25 ppm (in the case of compound **6a**) is due to the presence in the molecule of an asymmetric carbon atom and confirms the

* For Communication 23 see [1].

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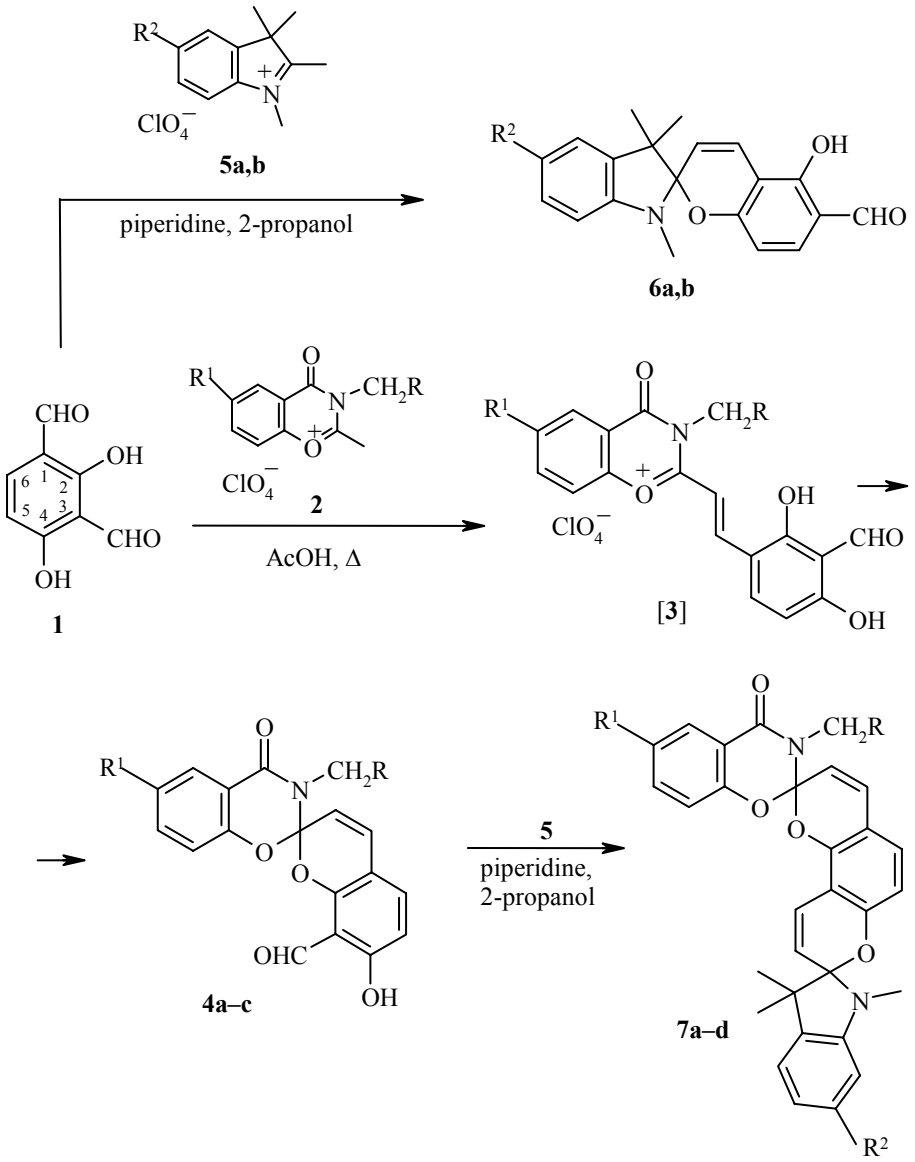


4 a R = R^1 = H, **b** R = Ph, R^1 = H, **c** R = Ph, R^1 = Cl; **5 a** R^2 = H, **b** R^2 = Cl; **6 a** R^2 = H, **b** R^2 = Cl; **7 a** R = R^1 = R^2 = H, **b** R = R^1 = H, R^2 = Cl, **c** R = Ph, R^1 = R^2 = H, **d** R= Ph, R^1 = H, R^2 = Cl

spirocyclic structure of compound **6**. The 3' and 4' proton signals form an AB spectrum with δ (3') = 5.68 and δ (4') = 7.25 ppm, $J_{3',4'}$ = 10.5 Hz and the signals at δ = 9.63 and 11.78 ppm characterize the presence of the formyl and hydroxyl groups respectively.

The ^{1}H NMR spectra of the bispyropyrans **7a-d** show signals for all of the proton containing groups which in chemical shifts and integrated intensities are fully in agreement with the structure discussed. The prochirality of the methylene group in the benzyl radical in compounds **7c,d**, controlling by the spiropyran system, leads to a diastereotopic splitting of the signals for the indicated group protons. If in compound **4b** the benzyl group methylene protons are seen as an AB spectrum with δ = 4.7 and 5.9 ppm and J_{AB} = 15.9 Hz then the introduction of a second asymmetric spiro carbon atom markedly distorts the proton signals for the diastereotopic benzyl group and complicates the overall picture as a result of splittings of other signals (Fig. 1 for compound **7d**).

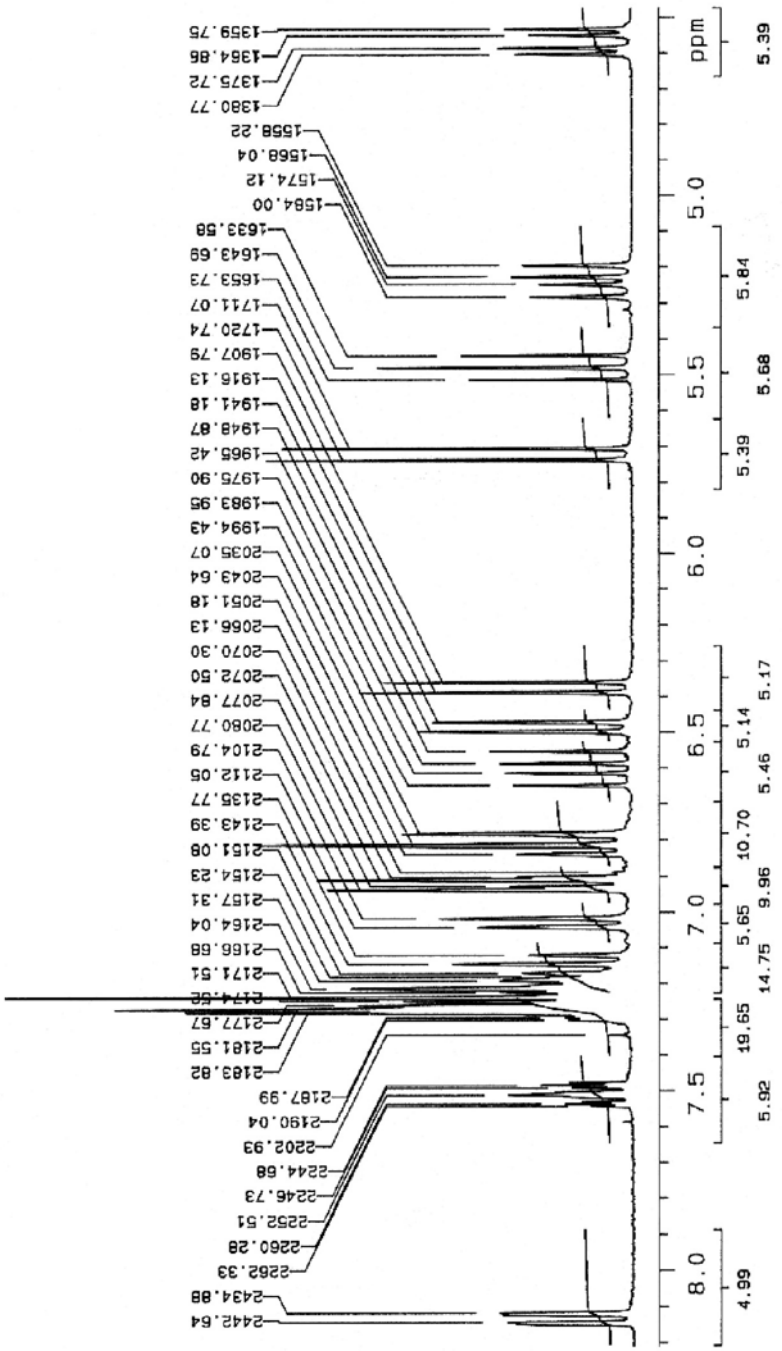


Fig. 1. ^{1}H NMR spectrum of spiropyran **7d** in $CDCl_3$ at 20°C.

TABLE 1. Characteristics of Compounds **4, 6 ,7**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yield, %
		C	H	N	Cl		
4a	$C_{18}H_{13}NO_5$	67.02 / 66.87	3.90 / 4.05	4.11 / 4.33	—	155	48
4b	$C_{24}H_{17}NO_5$	71.92 / 72.17	4.04 / 4.29	3.43 / 3.51	—	140	46
4c	$C_{24}H_{16}ClNO_5$	66.28 / 66.44	3.63 / 3.72	3.34 / 3.23	8.02 / 8.17	138	42
6a	$C_{20}H_{13}NO_3$	74.86 / 74.75	5.83 / 5.96	4.43 / 4.36	—	147	57
6b	$C_{20}H_{12}ClNO_3$	67.63 / 67.51	4.95 / 5.10	4.01 / 3.94	10.04 / 9.96	162	53
7a	$C_{30}H_{26}N_2O_4$	75.56 / 75.30	5.74 / 5.48	5.62 / 5.85	—	210	60
7b	$C_{30}H_{25}ClN_2O_4$	70.31 / 70.24	4.85 / 4.91	5.53 / 5.46	6.89 / 6.91	226	62
7c	$C_{36}H_{30}N_2O_4$	78.12 / 77.96	5.41 / 5.45	4.96 / 5.05	—	122	59
7d	$C_{36}H_{29}ClN_2O_4$	73.24 / 73.40	4.85 / 4.96	4.91 / 4.76	6.09 / 6.02	125	44

For a more detailed study of the structure of the synthesized spiropyrans the experimental choice of solvent allowed the growth of monocrystals of spiropyrans **4a** and **6a** and hence their X-ray investigation. Only the X-ray method made it possible to determine the structure of the spiropyrans **4** and **6** obtained and unambiguously to determine the position of the formyl and hydroxyl groups in the benzene ring of the [2H]-chromene fragment (Figs. 2 and 3, Table 3).

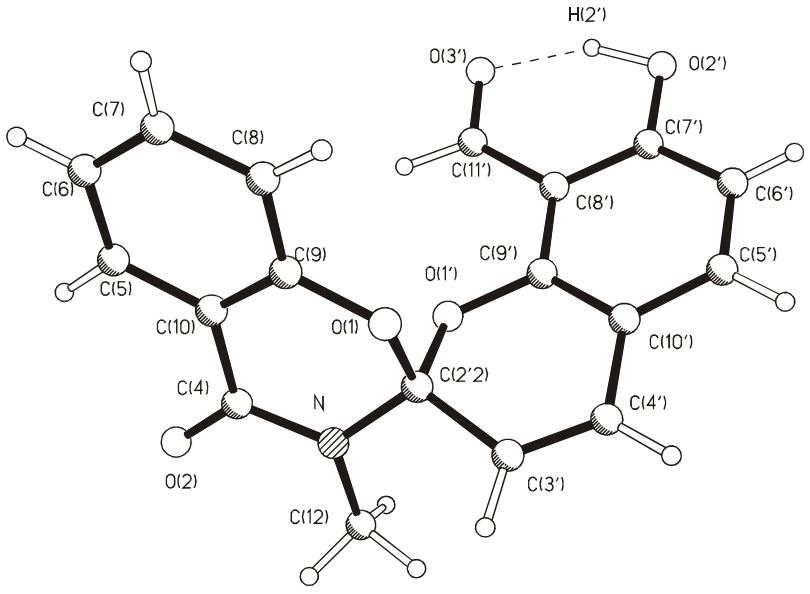


Fig. 2. X-ray structure of spiropyran **4a**. Hydrogen bond length 1.625 Å.

TABLE 2. Spectroscopic Characteristics of Spiropyrans **4, 6, 7**

Compound	IR spectrum, ν, cm^{-1}			UV spectrum, λ, nm	
	C=O	C=C	C–O	λ_{max} (log ε)	λ_{max} for photoinduced forms
4a	1673	1633, 1600	984, 954, 921	270 (4.32); 364 (3.48)	368, 430 sh.
4b	1686	1639, 1623	996, 919	272 (4.3); 364 (3.49)	392
4c	1686	1633, 1593	961, 912	282 (4.31); 316 sh. (4.17)	465 sh.
6a	—	1633, 1613	950	254 (4.3); 264 (4.43); 296 sh. (3.89)	408, 500
6b	—	1633, 1620	950	258 (4.54); 300 (4.2)	395, 508
7a	1673	1633, 1600, 1584	950, 921	247 (4.57); 273 sh. (4.36); 287 sh. (4.30); 324 sh. (3.49); 540 sh. (3.31)	418 sh., 434, 520, 560
7b	1673	1633, 1600, 1584	950, 921	256 (4.58); 290 sh. (3.99); 342 (3.11)	423, 520, 545
7c	1673	1633, 1594	996, 912	246 (4.58); 277 sh. (4.1); 288 sh. (4.06); 326 sh. (3.27); 343 sh. (3.11)	422, 434, 540, 567 sh.
7d	1673	1633, 1593	950, 927	248 (4.57); 279 sh. (4.01); 348 sh. (3.06)	419, 589

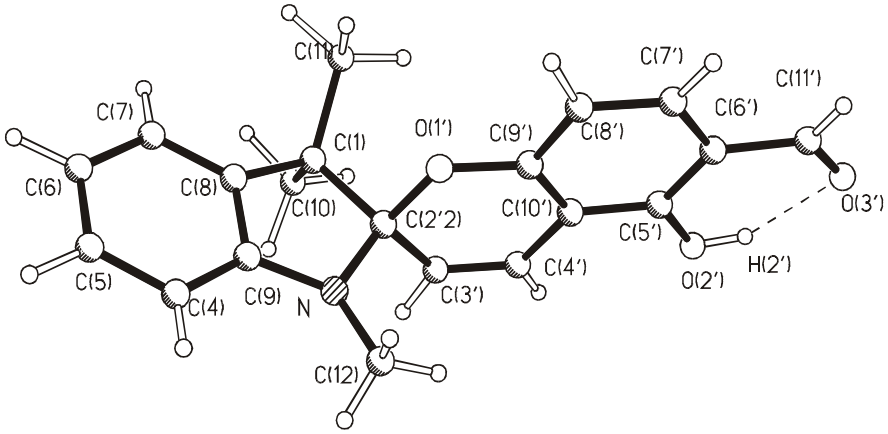


Fig. 3. X-ray structure of spiropyran **6a**. Hydrogen bond length 1.978 Å.

In the investigated compounds molecules the benzopyran and benzoxazinone fragments, as in the previously studied indoline (ISD) and benzoxazinone spiropyran derivatives [3-5], are placed virtually orthogonally to one another and individually nonplanar. The nonplanarity of the benzoxazinone fragment in compound **4a** is due to twisting along the N···O(1) line by an angle of 33.9° and that of the benzopyran fragment caused by twisting along the C(3')···O(1') and C(4')···O(1') lines by angles of 22.6 and 7.5° respectively. The atoms O(1), C(4), N, and O(2) occur in the plane of the benzene ring C(5)C(6)C(7)C(8)C(9). Compound **6a** is an ISD and the angles of twist in the indoline fragment along the N···C(1) line is 6.9° and in the benzopyran

TABLE 3. Basic Bond Lengths in Compounds **4a** and **6a**

Compound **4a**		Compound **6a**	
Bond	*l*, Å	Bond	*l*, Å
C(2'2)–O(1')	1.454(2)	C(2'2)–O(1')	1.468(2)
O(1')–C(9')	1.369(2)	O(1')–C(9')	1.347(3)
C(9')–C(10')	1.384(2)	C(9')–C(10')	1.396(3)
C(10')–C(4')	1.451(3)	C(10')–C(4')	1.453(3)
C(4')–C(3')	1.322(3)	C(4')–C(3')	1.314(4)
C(3')– C(2'2)	1.493(2)	C(3')– C(2'2)	1.503(2)
C(10')–C(5')	1.407(3)	C(10')–C(5')	1.390(3)
C(5')–C(6')	1.368(3)	C(5')–C(6')	1.407(3)
C(6')–C(7')	1.388(3)	C(6')–C(7')	1.398(3)
C(7')–C(8')	1.403(3)	C(7')–C(8')	1.366(3)
C(8')–C(9')	1.405(2)	C(8')–C(9')	1.400(3)
C(7')–O(2')	1.351(3)	C(5')–O(2')	1.343(3)
O(2')–H(2')	1.06(3)	O(2')–H(2')	0.84(3)
C(8')–C(11')	1.447(3)	C(6')–C(11')	1.446(4)
C(11')–O(3')	1.227(2)	C(11')–O(3')	1.219(4)
O(3')– H(2')	1.62(4)	O(3')– H(2')	1.86(4)
C(2'2)–N	1.432(3)	C(2'2)–N	1.435(3)
N–C(4)	1.362(3)	N–C(9)	1.402(3)
N–C(12)	1.465(2)	N–C(12)	1.410(4)
C(4)–O(2)	1.224(3)	C(8)–C(9)	1.385(3)
C(4)–C(10)	1.473(3)	C(1)–C(8)	1.484(3)
C(10)–C(9)	1.388(3)	C(1)–C(2'2)	1.558(3)
C(9)–O(1)	1.374(2)	C(1)–C(11)	1.576(4)
O(1)–C(2'2)	1.413(2)	C(1)–C(12)	1.410(4)

fragment along the C(3')···O(1') and C(4')···O(1') lines 2.1 and 0.9° respectively. Hence the geometric structure of the C_{spiro} node and benzopyran fragment in compounds **4a** and **6a** are similar to the structure of previously studied indoline and benzoxazine spiropyrans.

The inclusion of the C(4)=O(2) carbonyl group in the benzoxazinone fragment of the spiropyran **4a** causes a marked change in the electronic and geometric picture for the structure of the N-node. The deviation of the N atom from the plane of the coordinated atoms C(2',2) C(4) C(12) in compound **4a** is 0.052 Å and the sum of the valence angles at N 356.1°. The length of the amide bond in compound **4a** N–C(4) of 1.361(3) Å points to a marked conjugation of the unshared electron pair (UEP) of the N atom with the π-bond of the carbonyl group. The amide conjugation is significantly weakened by interaction of the N atom UEP with the σ* orbital of the C(2',2)–O(1') bond. In addition, the geometric positioning of the C(2,2')–O(1') bond relative to the coordination plane of the nitrogen atom C(2',2) C(4) C(12) remains less favourable for *n*-σ* orbitals.

On the other hand, the presence of a formyl group on the C(8') atom increases the electron-acceptor effect on atom O(1') and this is indicated by some shortening of the O(1')–C(9') bond to 1.369(2) Å when compared with analogous compounds (1.379(4) Å). The increase in the electron-acceptor effect of the 8'-substituent increases the polarity of the C(2',2)–O(1') bond and additionally strengthens the n-σ* interaction when compared with indoline spiropyrans [6]. As a result, the bond lengths C(2',2)–O(1') of 1.454(2) and C(2',2)–O(1) 1.414(2) Å in compound **4a** have different values.

In the spiropyran **6a** the N atom UEP is conjugated directly with the benzene ring and so the electronic and geometric picture for the N-node in this compound differs from that found in compound **4a**. The deviation of the N atom from the plane of the coordinated atoms C(2',2)C(9)C(12) in compound **6a** is 0.11 Å and the overall N valence angles 354.7°. The N–C(9) bond length of 1.400(3) Å is markedly larger than in compound **4a** but typical of ISP. The geometric placement of the C(2',2)–O(1') bond in compound **6a** relative to the nitrogen atom coordination plane C(2',2)C(9)C(12) is favorable for *n*-σ* orbital interaction of the N atom UEP with the σ* orbitals of the C(2',2)–O(1') bond. Hence in compound **6a** the electron effects at the spiro center of the molecule can be regarded as classical for spiropyrans with photochromic properties with shortening of the N–C(2',2) bond to 1.437 Å and increase in the O(1')–C(2',2) to 1.473 Å when compared with the values for analogous bonds [6].

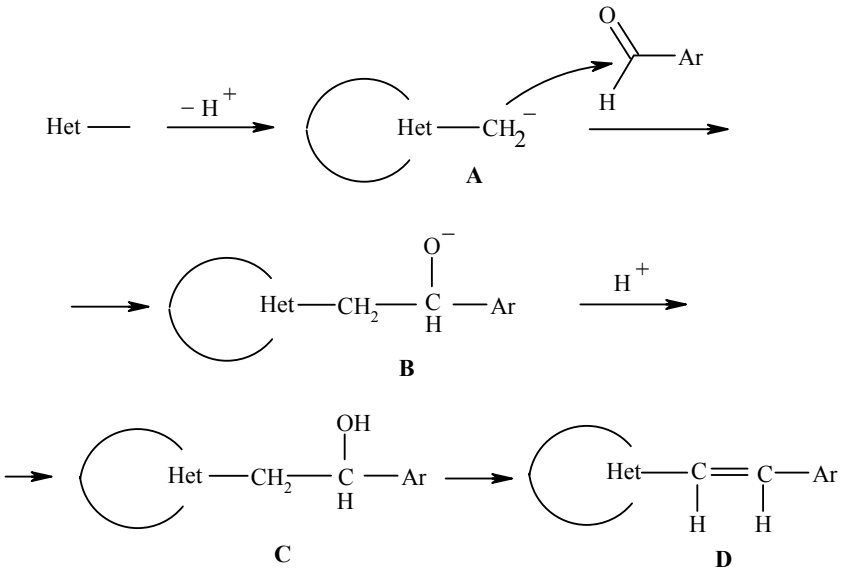
The molecular structure for **4a** and **6a** are characterized by the presence of strong intramolecular bonds between the hydroxyl hydrogen atom and the formyl oxygen atom (Figs. 2 and 3 respectively). The parameters of IHB for compound **4a** are O(3')···H(2') = 1.63(3), O(2')···O(3') = 2.586(3) Å, O(2')H(2')O(3') = 145.6°) (and O(3')···H(2') = 1.86(4), O(2')···O(3') = 2.623(3) Å, O(2')H(2')O(3') = 149.4° for compound **6a**).

From the X-ray results it was found that, despite the similarity in the methods for the synthesis of compounds **4a** and **6a**, the carbonyl and hydroxyl substituents occupy nonequivalent positions (Figs. 2 and 3). Evidently the different heterene components take part differently in spiro cyclization with the nonequivalent formyl groups in the starting aldehyde.

In order to explain the reason for such a selective condensation we carried out quantum chemical calculations. The model mechanism chosen was the Knoevenagel condensation as the most relevant reaction type (Scheme 1).

Analysis of the data obtained has shown that it is impossible to explain the selectivity indicated above from a thermodynamic viewpoint. The key to understanding the problem of the choice of formyl group for attack is the stage **B** → **C**. In this reaction for the benzoxazinium salt **2** the stage of attack at the –CHO group in position 3 of the 2,4-dihydroxyisophthalaldehyde system is obliged to overcome an energy barrier of about 9 kcal/mol but for attack at the formyl group in position 1 the minimum energetic system path is accompanied by a steady, progressive lowering of the energy. A similar picture is seen when considering the reaction with an indolenium salt. When reacting with a formyl group in position 1 the energy barrier at the **B** → **C** stage is about 13 kcal/mol and for condensation with a formyl group at position 3 about 20 kcal/mol, i.e. in both cases the reaction is kinetically controlled.

Scheme 1



EXPERIMENTAL

IR absorption spectra were recorded on a Specord IR-71 prism, double beam spectrometer. Polystyrene was used for calibration.

Electronic spectra for the compounds studied were recorded at room temperature on a Varian Carry (USA) spectrophotometer. The absorption spectra before and after irradiation were recorded on a Specord UV-vis spectrophotometer fitted with a special cryostat for low temperature measurement and a DRS-250 mercury lamp was used as excitation source with a filter giving light with λ_{max} 313 and 365 nm.

Accumulation of the ^{1}H NMR spectra was carried out on a Bruker-250 (250 MHz) spectrometer and a Varian Unity-300 (300 MHz) instrument. Assignment of signals was made relative to the residual proton signal in deuterochloroform at 7.26 ppm.

8'-Formyl-7'-hydroxy-3-methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-[2H]chromene (4a) was prepared from N-methyl-2-hydroxybenzamide [7] and 2,4-dihydroxyisophthalaldehyde. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.17 (H, s, NCH_3); 5.97 (1H, d, *J* = 9.8, H-3'); 6.61 (1H, d, *J* = 8.6, H-6'); 6.88 (1H, d, *J* = 8.3, H-8); 6.93 (1H, d, *J* = 9.8, H-4'); 7.37 (1H, d, *J* = 8.6, H-5'); 7.19 (1H, t, *J* = 7.6, H-6); 7.47 (1H, t, *J* = 7.4, H-7); 8.05 (1H, d, *J* = 7.8, H-5); 10.22 (1H, s, CHO); 11.69 (1H, d, OH).

3-Benzyl-8'-formyl-7'-hydroxy-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-[2H]chromene (4b) was prepared similarly from N-benzyl-2-hydroxybenzamide [10] and 2,4-dihydroxyisophthalaldehyde. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.76 and 5.09 (2H, AB-spectrum, *J* = 15.9, NCH_2); 5.83 (1H, d, *J* = 9.9, H-3'); 6.58 (1H, d, *J* = 8.6, H-6'); 6.84 (1H, d, *J* = 8.3, H-8); 6.88 (1H, d, *J* = 9.8, H-4'); 7.17-7.27 (5H, m, C_6H_5); 7.32 (1H, d, *J* = 8.6, H-5'); 7.37 (1H, d, *J* = 8.6, H-6); 7.5 (1H, t, *J* = 7.4, H-7); 8.12 (1H, d, *J* = 7.8, H-5); 9.48 (1H, s, CHO); 11.64 (1H, s, OH).

N-Benzyl-6-chloro-2-hydroxybenzamide (8). A mixture of 5-chlorosalicylic acid (17.25 g, 100 mmol) and $SOCl_2$ (11.9 g, 110 mmol, about 8.4 ml) in benzene (100 ml) was refluxed using a condenser for 3-4 h until evolution of HCl ceased. Benzylamine (20.14 g, 200 mmol, about 21.8 ml) was added to the reaction mixture and left to stand overnight. The precipitate obtained was filtered off, washed several times with water, and dried. Yield 5.5 g (21%); mp 147°C (aqueous methanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.61 (2H, d,

J = 5.6, CH_2); 6.48 (1H, br. s, NH); 6.73 (1H, d, J = 8.6, H-4); 7.24 (1H, s, H-6); 7.26-7.35 (5H, m, C_6H_5); 7.39 (1H, d, J = 8.6, H-3); 12.21 (1H, s, OH). Found, %: C 64.88; H 4.75; Cl 13.39; N 5.21. $C_{14}H_{18}ClNO_2$. Calculated, %: C 64.75; H 4.62; Cl 13.55; N 5.35.

3-Benzyl-6-chloro-8'-formyl-7'-hydroxy-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-[2H]-chromene(4c) was prepared similarly from compound **8** and 2,4-dihydroxyisophthalaldehyde. ^{1}H NMR spectrum, δ, ppm (J, Hz): 4.76 and 5.04 (2H, AB spectrum, J = 15.9, NCH_2); 5.82 (1H, d, J = 9.9, H-3'); 6.58 (1H, d, J = 8.4, H-6'); 6.84 (1H, d, J = 8.6, H-8); 6.88 (1H, d, J = 10.7, H-4'); 7.15-7.24 (5H, m, C_6H_5); 7.32 (1H, d, J = 8.6, H-5'); 7.45 (1H, t, J = 8.8, H-7); 8.08 (1H, d, J = 2.6, H-5); 9.7 (1H, s, CHO); 11.64 (1H, s, OH).

8'-Formyl-7'-hydroxy-1,3,3-trimethylspiroindoline-2,2'-[2H]chromene (6a). Piperidine (0.1 ml, 1.1 mmol) was added dropwise with heating to a solution of aldehyde **1** (166 mg, 1 mmol) and 1,2,3,3-tetramethylindolenium perchlorate **5** (274 mg, 1 mmol) in 2-propanol (5 ml). The reaction mixture was refluxed for 10 min and cooled. The precipitate was filtered off and recrystallized. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.15, 1.25 (6H, 2s, *gem* $(CH_3)_2$); 2.72 (3H, s, NCH_3); 5.68 (1H, d, J = 10.5, H-3'); 6.34 (1H, d, J = 8.7, H-6'); 6.53 (1H, d, J = 7.8, H-5'); 6.85 (1H, t, J = 7.4, H-5); 7.08 (1H, d, J = 7.3, H-4); 7.19 (1H, t, J = 7.6, H-6); 7.25 (1H, d, J = 10.5, H-4'); 7.27 (1H, d, J = 8.4, H-7); 9.63 (1H, s, CHO); 11.78 (1H, s, OH).

5-Chloro-8'-formyl-7'-hydroxy-1,3,3-trimethylspiropindoline-2,2'-[2H]chromene(6b) was prepared similarly to compound **6a** from 1,2,3,3-tetramethylindolenium perchlorate and 2,4-dihydroxyisophthalaldehyde. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.16, 1.26 (6H, 2s, *gem* $(CH_3)_2$); 2.68 (3H, s, NCH_3); 5.66 (1H, d, J = 10.5, H-3'); 6.53 (1H, d, J = 7.8, H-7'); 6.85 (2H, m, H-4,6); 7.08-7.25 (3H, m, H-8',4',7); 9.64 (1H, s, CHO); 11.64 (1H, s, OH).

3-Methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-2H,8H-pyrano[2,3-*f*]chromene-8'-spiro-2'',1'',3'',3''-trimethylindoline (7a). Piperidine (0.1 ml, 1.1 mmol) was added dropwise with stirring to a solution of the spiropyran **4a** (0.323 g, 1 mmol) and 1,2,3,3,-tetramethylindolenium perchlorate (0.274 g, 1 mmol) in 2-propanol (5 ml). The reaction mixture was refluxed for 10 min and cooled. The precipitate was filtered off and recrystallized. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.08 (3H, s, 3''-CH_3); 1.21 (3H, s, 3''-CH_3); 2.64 (3H, s, 1''-CH_3); 3.18 (3H, s, 3-CH_3); 5.50 (1H, d, J = 8.7, H-9'); 5.87 (1H, d, J = 9.7, H-3'); 6.30-7.60 (11H, m, H-4',10', arom); 8.08 (1H, d, J = 7.8, H-8).

3-Methyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-2H,8H-pyrano[2,3-*f*]chromene-8'-spiro-5''-chloro-2'',1'',3'',3''-trimethylindoline (7b) was synthesized similarly to compound **7a**. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.08 (3H, s, 3''-CH_3); 1.22 (3H, s, 3''-CH_3); 2.62 (3H, s, 1''-CH_3); 3.18 (3H, s, 3-CH_3); 5.45 (1H, d, J = 8.8, H-9'); 5.87 (1H, d, J = 9.7, H-3'); 6.30-7.60 (10H, m, H-4',10', arom.); 8.08 (1H, d, J = 7.8, H-8).

3-Benzyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-2H,8H-pyrano[2,3-*f*]chromene-8'-spiro-2'',1'',3'',3''-trimethylindoline (7c) was synthesized similarly to compound **7a**. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.08 (3H, s, 3''-CH_3); 1.22 (3H, s, 3''-CH_3); 2.65 (3H, s, 1''-CH_3); 4.58 and 5.24 (2H, AB spectrum, J = 16.0, NCH_2); 5.48 (1H, d, J = 7.9, H-9'); 5.72 (1H, d, J = 9.7, H-3'); 6.30-7.60 (16H, m, H-4',10' arom); 8.08 (1H, d, J = 7.8, H-8).

3-Benzyl-4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2-spiro-2'-2H,8H-pyrano[2,3-*f*]chromene-8'-spiro-5''-chloro-2'',1'',3'',3''-trimethylindoline (7d) was prepared similarly to compound **7a**. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.08 (3H, s, 3''-CH_3); 1.22 (3H, s, 3''-CH_3); 2.65 (3H, s, 1''-CH_3); 4.56 and 5.25 (2H, AB spectrum, J = 15.9, NCH_2); 5.48 (1H, d, J = 7.9, H-9'); 5.72 (1H, d, J = 9.7, H-3'); 6.30-7.60 (15H, d, H-4',10', arom); 8.08 (1H, d, J = 7.8, H-8);

X-ray Structural Investigation of Compounds 4a and 6a. Crystals of **4a** and **6a** for X-ray were prepared by crystallization from isopropyl alcohol. The X-ray experiment was performed on a KYMA automatic, four circle diffractometer (CuKα irradiation) at T = 293 K in the θ angle range from 4.14 to 79.76° for compound **4a** and from 4.26 to 80.0° for compound **6a**.

The basic crystallographic data for **4a** ($C_{18}H_{13}NO_5$): a = 7.302(2), b = 19.115(2), c = 10.867(3) Å; β = 101.08(5)°; V = 1154.3(9) Å^3; $P2_1/c$; Z = 4 (monoclinic); d = 1.443 g/cm^3; F(000) = 672; M = 323.29. The structure of **4a** was solved by a direct method using least squares analysis for F^2 to R = 0.043 (R_w = 0.062 for

2518 reflections, GOF = 1.08, 269 refinement parameters) for 2938 reflections with $I > 2\sigma I$) in the anisotropic approximation with the SHELXL-93 program package [11]. Hydrogen atoms were revealed in Fourier difference synthesis and only the positional parameters were refined.

The basic crystallographic data for **6a** ($C_{20}H_{19}NO_3$): a = 10.886(4), b = 9.672(2), c = 8.522(2) Å; α = 76.67(3), β = 78.01(3), γ = 74.87(3)°; V = 1407(1) Å^3; P-1; Z = 2; d = 1.285 g/cm^3; F(000) = 340; M = 321.36. The structure of **6a** was solved by a direct method using least squares analysis for F^2 to R = 0.071 (R_w = 0.085 for 3225 reflections, GOF = 1.16, 281 refinement parameters) for 2615 reflections with $I > 2\sigma I$) in the anisotropic approximation with the SHELXL-93 program package [11]. Hydrogen atoms were revealed in Fourier difference synthesis and only the positional parameters were refined.

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