Russian Chemical Bulletin, Vol. 47, No. 6, June, 1998

Structures and photochromic properties of substituted spiroindolinonaphthoxazines

S. M. Aldoshin,[a]* *I. I. Chuev*,[a] *O. S. Filipenko*,[a] *A. N. Utenyshev*,[a]
V. Lokshin,[b] *P. Laregenie*,[b] *A. Samat*,[b] *and R. Guglielmetti*[b]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: sma@icp.ac.ru
[b]*Mediterranean University at Luminy, ERS 158 CNRS,**
Case 901, 13288, Cedex 9, France

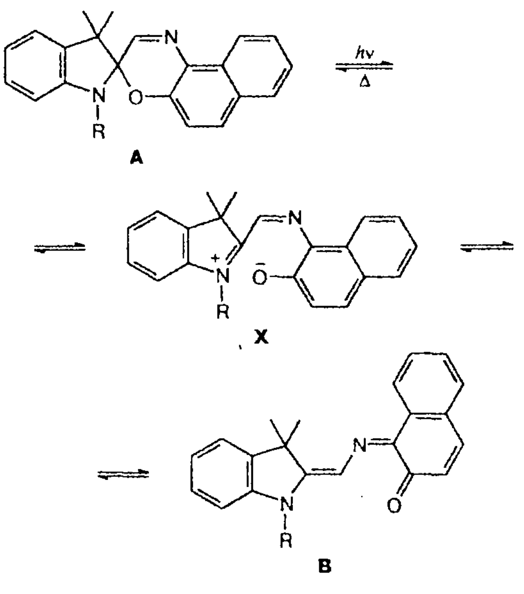
Six indolinospironaphthoxazines were studied by X-ray diffraction analysis. It was demonstrated that the electronic nature of the substituents in the naphthoxazine and indoline fragments has no substantial effect on the C_{spiro}—O and C_{spiro}—N bond lengths. Photocolorability of the compounds under study depends only slightly on the above-mentioned bond lengths and correlates mainly with the energy of steric strain of the oxazine ring. The stability of the open forms of spiroindolinonaphthoxazines that formed upon photoirradiation is determined to a large extent by the electronic and steric nature of the substituents. The exception is the compound that contains the NO_2 group in the indoline fragment. In the last-mentioned case, the cleavage of the ring occurs through a substantially different pathway.

Key words: spirooxazines, X-ray diffraction analysis, photochemistry in solutions, structure—property relationship.

The increased interest in the synthesis and studies of new photochromic spirooxazines in recent years is due to their improved performance compared to spiropyrans.[1—3] This fact aroused interest in studies of the effect of the structural characteristics of these compounds on their photochromic properties. X-ray diffraction studies[4—7] demonstrated that spirooxazines and spiropyrans have similar structures. Photochemical conversions of spirooxazines (Scheme 1) involve heterolytic cleavage of the C—O bond in the oxazine ring (**A**→**X**) followed by *cis—trans* isomerization to form a colored form (**B**).[8] Therefore, a two-stage process occurs upon photoirradiation. At the first stage, the electron density is shifted from the indoline group to the naphthoxazine fragment (**B**), and at the second stage, rehybridization of the C_{spiro} atom leads to the reverse shift of the electron density.

In the indolinospiropyrans[9] as well as in the spirooxazines[4—7] studied previously, the structure of the spiro center of the molecule is favorable for interaction between the lone electron pair of the N(2) atom and the σ^* orbital of the C_{spiro}—O bond, which affects the efficiency of heterolysis of the C_{spiro}—O bond. When spirooxazines adopt the above-mentioned conformation, the n(lone electron pair) orbital of the N(2) atom and the $\sigma^*(C_{spiro}$—O) orbital overlap, which leads to the shortening of the C(1)—N(2) bond and to the elongation of the C(1)—O bond compared to the values observed in the five- and six-membered rings (C—N, 1.47—1.48 Å; and C—O, 1.41—1.43 Å).[10] The efficiency of this interaction depends substantially on the

Scheme 1



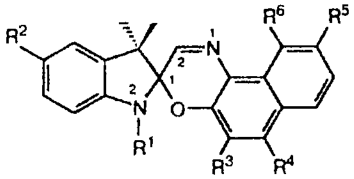
---

* Universite'de la Mediterranee, Faculte des Sciences de Luminy, ERS 158 CNRS, Case 901, 13288 Marseille, Cedex 9, France.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1121—1128, June, 1998.

electronic state of the N(2) and O atoms. For spiropyrans,[9] it was demonstrated that electron-withdrawing substituents in the benzopyran fragment strengthen this interaction, while electron-donating substituents weaken this interaction owing to strengthening or weakening of conjugation between the lone electron pair of the O atom and the π system of the phenyl fragment, respectively.

In this connection, it was of interest to study the effect of substituents in spirooxazines on their structures and photochemical properties. In this work, we studied new substituted spiro[indoline-2,3′-[3*H*]-naphtho-[2,1-*b*][1,4]oxazines] (**1—6**).



1—7

Compound	R1	R2	R3	R4	R5	R6
1	Me	OMe	H	CN	H	H
2	Me	H	OH	H	H	H
3	Me	H	H	SO_2Ph	H	H
4	Me	NO_2	H	H	H	H
5	Me	H	H	H	*	*
6	$CH_2CH=CH_2$	H	H	H	OMe	H
7	Me	H	H	H	H	H

* R5,R6 =

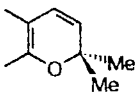
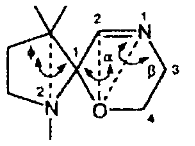


Table 1. Principal geometric parameters of the oxazine (α, β/deg) and indoline (ϕ/deg) rings

Compound		ϕ	α	β
	**1**	37.7	8.6	3.0
	2	39.9	21.4	12.4
	3	(28.0; 26.7)	15.0	7.5
	4	34.1	19.4	7.2
	5	35.0	13.8	5.7
	6	33.8	15.0	7.2

Results and Discussion

The configurations of spirooxazines **1—7** under consideration are similar to those of spirooxazines[4—7] and spiropyrans[9] studied previously. The spiro unit has a tetrahedral structure. The indoline and naphthoxazine fragments, like those in indolinospiropyrans, are almost perpendicular to each other. The indoline ring in spirooxazines is nonplanar and adopts an envelope conformation. The folding angles along the N(2)...$C(CH_3)_2$ line are in the range 33.8°—39.9° (Table 1).

The naphthoxazine fragment in spirooxazines is flexible as was observed previously in the case of the benzopyran fragment in spiropyrans. This conformation can be characterized by the folding angles along the O(1)...C(2) and O(1)...N(1) lines (see Table 1).

The introduction of the π-electron-withdrawing substituent (R^4 = CN) at the *para* position with respect to the N(1) atom and of the π-electron-donating substituent (R^2 = OMe) at the *para* position with respect to the N(2) atom in compound **1** (Fig. 1) has virtually no effect on its structure compared to unsubstituted spirooxazine **7**. The N(1)—C(3) and O(1)—C(4) bond lengths (1.410(3) and 1.371(3) Å, respectively) in compound **1** agree (to within the experimental error) with the analogous bond lengths in compound **7** (1.416(3) and 1.362(3) Å, respectively). This is indicative of the fact that in compound **1** the conjugation of the π-system of the naphthalene ring with the azomethine π-bond and the lone electron pair of the oxygen atom, and consequently, the n-σ*-orbital interactions, remain unchanged. Because of this, the C(1)—O(1) and C(1)—N(2) bond lengths (1.456(3) and 1.430(3) Å, respectively) in **1**

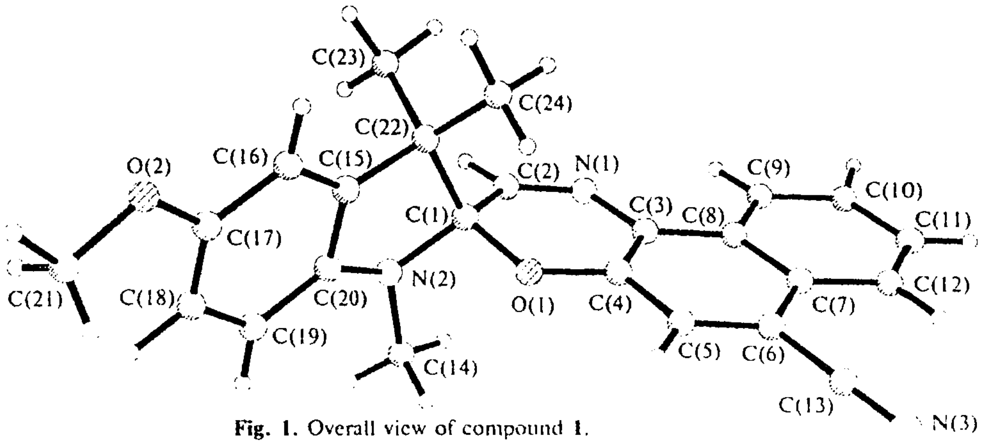


Fig. 1. Overall view of compound **1**.

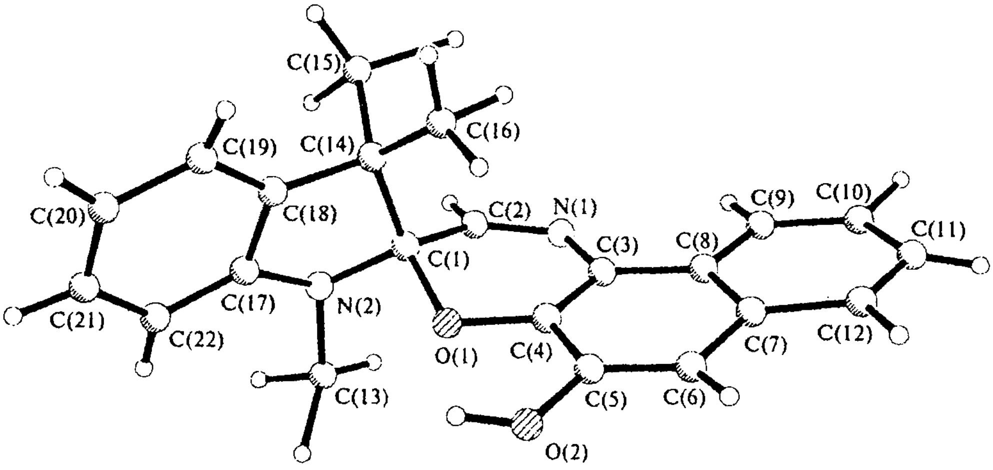


Fig. 2. Overall view of compound **2**.

coincide with the corresponding bond lengths in compound **7** (1.454(3) and 1.436(3) Å, respectively).

The introduction of the OH group into the naphthalene ring at the *ortho* position with respect to the O(1) atom of the oxazine ring in compound **2** (R^3 = OH) (Fig. 2) leads to an insignificant elongation of the C(1)—O(1) bond (1.471(4) Å) compared to the corresponding bonds in **1** and **7**, while the O(1)—C(4) and C(1)—N(2) bond lengths (1.373(5) and 1.434(4) Å, respectively) remain unchanged. Apparently, the elongation of the C(1)—O(1) bond in compound **2** is due to the participation of the O(1) atom in the O(1)...H(O)O(2) intramolecular hydrogen bond rather than to a change in the n-σ* interaction resulting in an increase in the polarity of the C(1)—O(1) bond. The O(1)C(4)C(5)O(2) and C(4)C(5)O(2)H(O) torsion angles are 1.2° and 10°, respectively. The length of the O(1)...H(O) intramolecular hydrogen bond is 2.35(1) Å. The O(1)H(O)O(2), H(O)O(1)C(4), and H(O)O(1)C(1) angles are 103°, 81°, and 150°, respectively. The H(O) atom is involved in a bifurcated intramolecular hydrogen bond forming the second intramolecular hydrogen bond with the oxygen atom of the water molecule (H(O)...O_W, 1.91(5) Å; O(2)...O_W, 2.81(1) Å; and the angle at the H atom is 165°).

Table 2. Absorption of the open form (λ_{max}), photocolorability (A_0), constants of dark decoloration (k_Δ), and strain energies of the oxazine ring (E) in compounds **1**—**7**

Compound	λ/nm	A_0	k_Δ/s^{-1}	E /kcal mol^{-1}
1	659	0.90	0.20	25.4
2	590	1.09	0.21	27.4
3	642	1.17	0.13	25.3
4	555	6.0	0.27	25.8
5	593	1.75	3.04	32.5
6	580	0.79	0.22	25.6
7	594	1.08	0.54	27.0

Therefore, the substituents in compounds **1** and **2** have no effect on the efficiency of specific orbital interactions. The photochemical properties of the spirooxazines under study are also similar as evidenced by the fact that the values A_0 for the photoinduced open forms of **1** (0.9) and **2** (1.09), which characterize the photoactivity of the compounds, are virtually identical to the analogous value for **7** (1.08) (Table 2). At the same time, the position of the maximum of the absorption band (λ_{max}) of the photoinduced open form of **1** (λ_{max} = 659 nm) is changed substantially compared to those of compound **2** (λ_{max} = 590 nm) and unsubstituted compound **7** (λ_{max} = 594 nm) (Table 2). The constants of dark decoloration k_Δ, which characterize the stability of the open photoform (0.20 and 0.21 s^{-1} for **1** and **2**, respectively), are almost half as large as that for **7** (0.54 s^{-1}). Apparently, in the case of compound **1**, this is due to the electron-withdrawing properties of the CN groups, and in the case of **2**, this is due to formation of an intramolecular hydrogen bond with the hydroxyl group.

Compound **3** that contains the SO_2Ph substituent (R^3 = SO_2Ph) at the *para* position with respect to the N(1) atom (Fig. 3) is of interest from the viewpoint of the photochemical properties (Table 2). In addition to the fact that the photocolorability of this compound, A_0 = 1.17, is somewhat higher than those of compounds **1**, **2**, and **7**, it appeared that its open form is the most stable one in the series of the compounds under study, k_Δ = 0.13 s^{-1} (Table 2). It is difficult to carry out crystal-chemical analysis of this compound because of the fact that the indoline fragment is statistically disordered relative to the C(1)C(2)O(1) plane. However, the bond lengths in the oxazine ring (C(1)—O(1), 1.464(3); O(1)—C(12), 1.365(3); N(1)—C(3), 1.403(3) Å) are identical to the corresponding values in compounds **1** and **2**.

The introduction of the electron-withdrawing NO_2 substituent into the indoline fragment at the *para* position with respect to the N(2) atom (R^2 = NO_2) (Fig. 4)

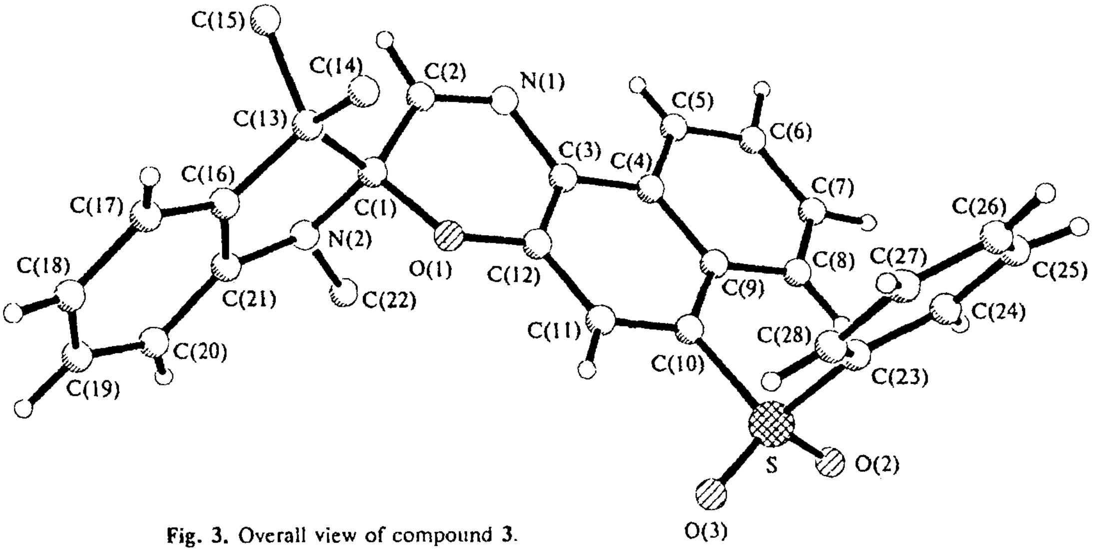


Fig. 3. Overall view of compound 3.

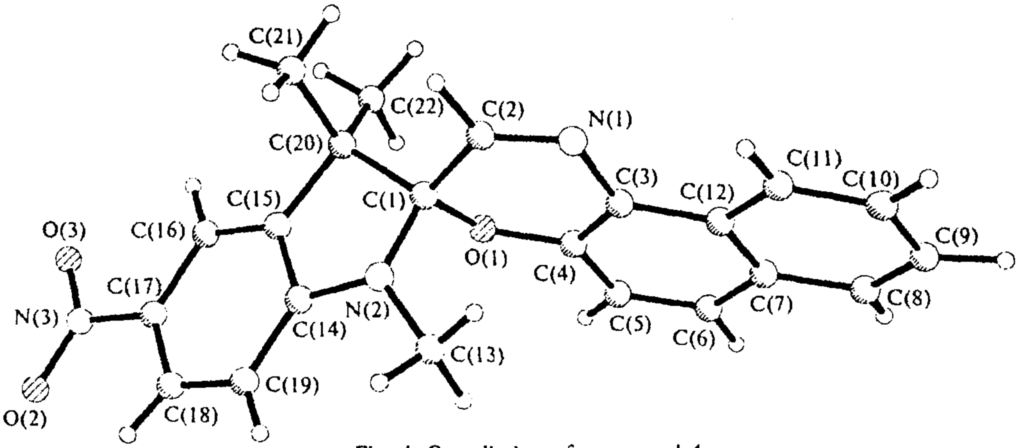


Fig. 4. Overall view of compound 4.

leads to a substantial increase in the value of A_0 (6.00) for compound **4** (Table 2) compared to those for compounds **1** and **2** (0.90 and 1.09, respectively). The C(1)—O(1) and C(1)—N(2) bond lengths (1.451(5) and 1.437(5) Å, respectively) are similar to the corresponding bond lengths in the spiro centers of compounds **1**, **2**, and **7**. The introduction of the NO_2 substituent leads to an increase in the conjugation between the lone electron pair of the N(2) atom and the π-system of the phenyl ring. This is evidenced by the decrease in the N(2)—C(14) bond length to 1.378(5) Å compared to the analogous values in compounds **1**, **2**, and **7** (1.409(3), 1.413(5), and 1.414(3) Å, respectively). Apparently, the electron-withdrawing effect of the NO_2 substituent causes flattening of the pyramidal structure of the N(2) atom. In compound **4**, the deviation of the N(2) atom from the plane through the atoms bonded to N(2) decreases to 0.16 Å compared to the corresponding values in spirooxazines **1**—**3** and **7** (0.26—0.32 Å), and the sum of the bond angles at the N(2) atom increases to 356.1° compared to 345—350° in spirooxazines **1**—**3** and **7**. The above-mentioned flattening leads to a change in the orientation of the lone electron pair of the N(2) atom with respect to the C_{spiro}—O bond (in compound **4**, the $O(1)C(1)N(2)C_{Me}$ torsion angle is 71.7°, while in compounds **1**—**3** and **7**, the corresponding values are in the range of 50—58°). The change in the orientation of the lone electron pair and the σ*-orbital can affect substantially the n-σ* interaction in the electronically excited state of spirooxazine **4**. However, as was demonstrated previously for indolinospiropyrans,[11] the mechanism of cleavage of the oxazine ring in compound **4** that contains the NO_2 substituent is substantially different, which makes it impossible to compare the values of A_0 and the structure of compound **4** with the corresponding characteristics of **1**—**3**.

From the viewpoint of stabilization of the open form, the behavior of the NO_2 substituent in compound **4**

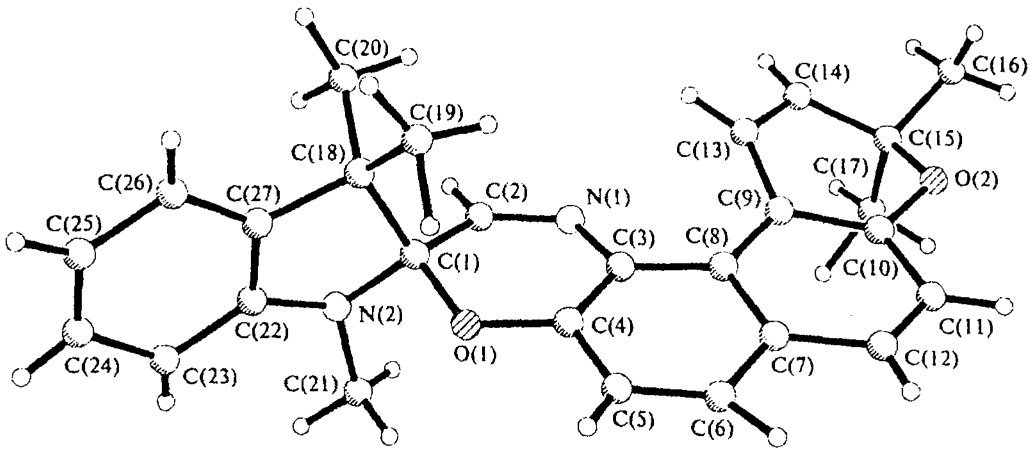
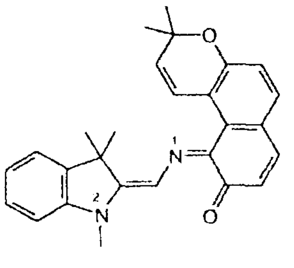


Fig. 5. Overall view of compound 5.

(k_Δ = 0.27 s^{-1}) is analogous to that of the substituents in compounds **1** (k_Δ = 0.20 s^{-1}) and **2** (k_Δ = 0.21 s^{-1}) (see Table 2).

Annelation of the second potentially photochromic chromene ring (Fig. 5) has also virtually no effect on the structure of compound **5**. The C(1)—O(1) and C(1)—N(2) bond lengths (1.448(8) and 1.424(8) Å, respectively) agree (to within the experimental error) with the analogous values in **1** and **7**. However, the short intramolecular contact between the vinyl group of the annelated pyran ring and the N(1) atom (C(13)...N(1), 2.858(2) Å) in compound **5** leads to an increase in the energy of steric strain of the oxazine ring (E = 32.5 kcal mol^{-1}), which is maximum in the series of compounds under study (see Table 2). Previously,[12] using photochromic compounds of the chromene class as examples, we have found a correlation between the energy (E) of steric strain of the pyran ring and the colorability (A_0). Evidently, this relationship is also true for spirooxazines on condition that the structures of the indoline fragments are identical, which accounts for the increase in the value A_0 for compound **5** (1.75) compared to those in compounds **1**, **2**, and **7**. On the other hand, the value k_Δ for the open form of **5** (3.04) is substantially higher than those for the open forms of compounds **1**, **2**, and **7**. This is indicative of the fact that in the case of compound **5**, the dark reaction of closure of the ring proceeds faster and thus the stability of the open form of **5** is lower. In the case of the *trans*-cisoid conformation of the open form of **5**, analogous steric interactions between the N(1) atom and the vinyl group of the pyran ring, which lead to an increase in the efficiency of the photoreaction, destabilize the photoproduct thus accelerating the reverse dark reaction.



In the case of compound **6**, the introduction of the MeO group into the naphthalene ring (R^5 = OMe) has virtually no effect on conjugation between the lone electron pair of the O(1) atom and the π-system of the naphthalene fragment. The O(1)—C(4) bond length (1.369(2) Å) is identical to the corresponding values in compounds **1** and **5** (1.371(3) and 1.374(8) Å, respectively). The C(1)—O(1) bond length (1.446(2) Å) also coincides with the corresponding values in compounds **1**, **5**, and **7** (1.456(3), 1.448(8), and 1.454(3) Å, respectively), while the C(1)—N(2) bond length in **6** (1.456(2) Å) is longer than those in compounds **1**, **5**, and **7** (1.430(3), 1.424(8), and 1.436(3) Å, respectively) The elongation of this bond is due to steric repulsions between the C(24) atom of the terminal vinyl group and the C(1) and C(2) atoms. The intramolecular distances between these atoms remain shortened even if the C(1)—N(2) bond is elongated (C(24)...C(1) and C(24)...C(2) are 3.064 and 2.940 Å, respectively). Steric repulsions between these atoms hinder the n-σ* interaction in the ground and excited states. It is not inconceivable that it is these structural features of compound **6** that cause an increase in the photocolorability (A_0 = 0.79) compared to those of **1**—**3** and **7**, while the stabilities of the open forms of **1**—**3** and **6** are identical (k_Δ(**6**) = 0.22 s^{-1}) (Table 2).

Therefore, the results of our studies demonstrated that the electronic nature of the substituents in the naphthoxazine and indoline fragments of spirooxazines under study has no substantial effect on the C_{spiro}—O and C_{spiro}—N bond lengths and hence, on the efficiency of the n-σ* interaction in the spiro center of the molecule. These bond lengths are more substantially affected by secondary interactions, namely, by the participation of the O atom in a weak intramolecular hydrogen bond and by steric repulsions in the spiro center, which

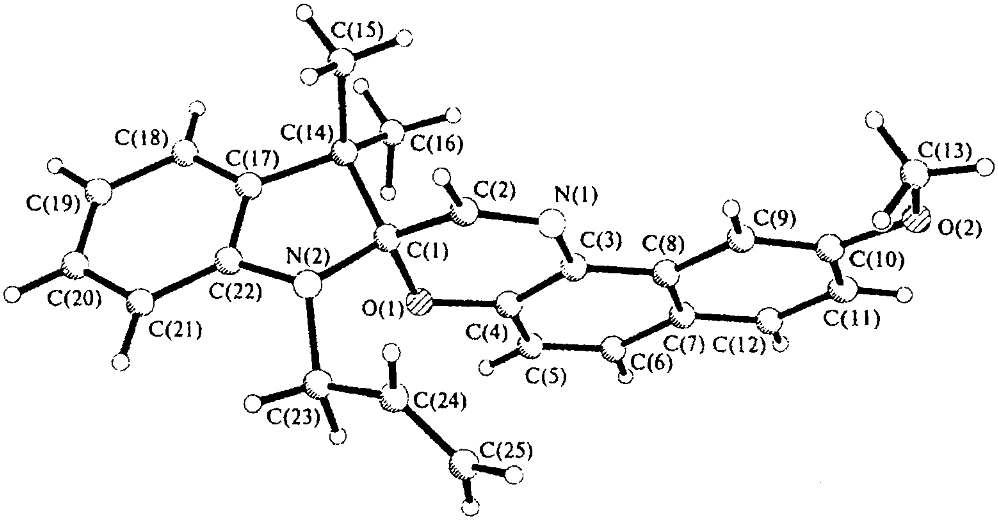


Fig. 6. Overall view of compound **6**.

is additional evidence for the lability of the C_{spiro}—O and C_{spiro}—N bonds in spirooxazines and spiropyrans.

Insignificant changes in the lengths of these bonds have no pronounced effect on photocolorability of spirooxazines under study. Their photocolorability is most substantially affected by the steric strain in the oxazine ring. The correlation between the photocolorability A_0 and the energy of steric strain of the ring (E) was confirmed.

The electronic and steric nature of the substituents affects substantially the stability of the open forms of spirooxazines. The exception is spirooxazine that contains the NO_2 substituent in the indoline fragment. In the last-mentioned case, the mechanism of cleavage of the ring is substantially different.

Experimental

The synthesis of compounds **1**,[13] **2**,[14] **3**,[15] **4**,[16] **5**, [14] and **6** [16] was reported in the literature. Crystals of **3** were prepared by crystallization from a 4 : 1 EtOH—Et_2O mixture. Crystals of the other compounds were prepared by crystallization from heptane.

Photochemical studies were carried out by flash photolysis.[17] The absorption of the open form A_0 (λ_{max}) immediately after photoirradiation (photocolorability) was taken as the characteristic of the photochromic properties along with the thermal stability (the constant of dark decoloration k_Δ/s^{-1}) and the position of the maximum of the long-wavelength absorption (λ_{max}) of the open form (**B**).

The strain energies of the pyran rings were calculated by molecular mechanics (MM2).[18]

The details of X-ray diffraction studies are given in Table 3.

Table 3. Principal crystallographic data for compounds **1**—**6**

Parameter	**1**	**2**	**3**	**4**	**5**	**6**
Molecular formula	$C_{24}H_{21}N_3O_2$	$C_{22}H_{20}N_2O_2 \cdot H_2O$	$C_{28}H_{24}N_2O_3S$	$C_{22}H_{19}N_3O_3$	$C_{27}H_{26}N_2O_2$	$C_{25}H_{24}N_2O_2$
M	383.45	362.43	468.58	373.41	410.52	384.48
a/Å	17.420(2)	29.989(2)	15.800(3)	8.462(3)	8.105(4)	8.736(1)
b/Å	8.772(3)	8.120(7)	15.571(2)	15.370(6)	12.981(3)	10.692(3)
c/Å	6.668(3)	15.909(1)	9.483(3)	14.363(7)	21.548(9)	12.275(1)
α/deg	94.86(3)	90.0	90.0	90.0	90.0	66.41(3)
β/deg	83.95(3)	108.33(3)	90.0	94.08(3)	97.85(3)	86.68(3)
γ/deg	98.48(3)	90.0	93.07(3)	90.0	90.0	75.83(3)
Z	2	8	4	4	4	2
d_{calc}/g cm^{-1}	1.211	1.309	1.336	1.331	1.214	1.262
Space group	$P\bar{1}$	$C2/c$	$P2_1/b$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Crystal dimensions /mm mm mm	0.15×0.15×0.20	0.10×0.15×0.25	0.25×0.10×0.20	0.10×0.15×0.20	0.15×0.10×0.15	0.20×0.10×0.15
Radiation	MoKα	CuKα	CuKα	CuKα	MoKα	CuKα
Number of reflections (I > 2σ)	1423	1232	3095	1557	1026	2524
R factor	0.037	0.049	0.048	0.051	0.036	0.043

Table 4. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **1**

Atom	*x*	*y*	*z*
O(1)	7196(2)	2435(3)	5899(2)
O(2)	9345(3)	7152(3)	11161(2)
N(1)	7499(2)	934(2)	2033(2)
N(2)	7861(2)	4643(3)	4472(2)
N(3)	4494(2)	−1902(3)	8626(3)
C(1)	7890(2)	3038(3)	4637(3)
C(2)	7921(1)	2172(3)	2584(3)
C(3)	6908(2)	312(3)	3466(3)
C(4)	6761(2)	1066(3)	5315(3)
C(5)	6143(2)	526(2)	6695(3)
C(6)	5682(2)	−822(2)	6193(2)
C(7)	5815(2)	−1693(2)	4318(2)
C(8)	6433(2)	−1092(3)	2932(3)
C(9)	6563(2)	−1918(3)	1037(3)
C(10)	6114(3)	−3297(3)	591(2)
C(11)	5514(3)	−3894(2)	1989(2)
C(12)	5358(3)	−3102(2)	3789(2)
C(13)	5025(2)	−1405(3)	7590(2)
C(14)	7202(2)	5126(3)	3643(3)
C(15)	8616(2)	4569(3)	7060(3)
C(16)	9001(2)	5152(2)	8717(3)
C(17)	8940(2)	6652(3)	9496(3)
C(18)	8504(2)	7529(3)	8616(3)
C(19)	8103(2)	6960(3)	6943(3)
C(20)	8174(2)	5469(3)	6174(2)
C(21)	9199(2)	8577(3)	12181(2)
C(22)	8616(2)	3038(3)	5826(2)
C(23)	9369(1)	3133(3)	4360(2)
C(24)	8554(2)	1631(3)	7070(2)
H(2)	832(1)	264(1)	155(1)
H(5)	604(1)	114(1)	789(1)
H(9)	698(1)	−146(1)	1(1)
H(10)	629(1)	−384(1)	−84(1)
H(11)	521(1)	−483(1)	165(1)
H(12)	492(1)	−347(1)	480(2)
H(14)	708(1)	439(1)	261(1)
H(141)	674(1)	502(1)	484(2)
H(142)	726(1)	617(2)	352(1)
H(16)	930(1)	451(2)	926(1)
H(18)	844(1)	867(1)	914(1)
H(19)	775(1)	758(1)	640(2)
H(21)	942(1)	933(1)	1138(2)
H(211)	869(1)	860(2)	1248(1)
H(212)	955(1)	878(2)	1377(1)
H(23)	986(1)	330(2)	512(1)
H(231)	941(1)	399(2)	355(1)
H(232)	941(1)	210(2)	349(1)
H(24)	905(1)	165(1)	772(1)
H(241)	806(1)	155(2)	796(1)
H(242)	854(1)	66(2)	607(1)

Table 5. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **2**

Atom	*x*	*y*	*z*
O(1)	963(2)	1315(4)	3405(2)
O(2)	455(1)	2044(4)	1714(2)
O(3w)	0	−224(4)	2500
N(1)	1855(2)	2686(4)	4206(2)
N(2)	1012(2)	49(4)	4736(2)
C(1)	1283(2)	433(3)	4163(2)
C(2)	1697(3)	1551(3)	4588(2)
C(3)	1604(2)	2965(4)	3301(2)
C(4)	1167(2)	2316(4)	2932(2)
C(5)	899(2)	2670(3)	2051(3)
C(6)	1082(3)	3618(3)	1553(2)
C(7)	1543(3)	4263(3)	1893(2)
C(8)	1804(3)	3991(3)	2792(2)
C(9)	2254(3)	4730(3)	3143(2)
C(10)	2440(2)	5645(3)	2619(2)
C(11)	2196(3)	5841(3)	1719(2)
C(12)	1757(3)	5178(4)	1352(2)
C(13)	773(3)	1379(4)	5058(2)
C(14)	1407(3)	−1257(4)	3874(3)
C(15)	1847(3)	−1970(3)	4584(2)
C(16)	1490(3)	−1293(3)	2968(2)
C(17)	763(3)	−1418(3)	4415(2)
C(18)	991(2)	−2237(3)	3883(2)
C(19)	804(3)	−3724(3)	3510(2)
C(20)	407(4)	−4365(3)	3648(2)
C(21)	198(3)	−3517(3)	4147(2)
C(22)	372(3)	−2026(4)	4545(2)
H(O)	35(2)	126(2)	203(2)
H(2)	176(2)	144(2)	536(2)
HW(1)	26(2)	−91(2)	267(1)
H(6)	93(1)	384(2)	96(1)
H(9)	241(1)	455(2)	373(1)
H(10)	282(1)	612(2)	289(1)
H(11)	229(1)	669(2)	143(1)
H(12)	153(1)	524(2)	64(1)
H(13)	34(1)	169(2)	467(1)
H(131)	65(1)	82(2)	554(1)
H(132)	102(1)	214(2)	523(2)
H(15)	190(1)	−319(2)	457(2)
H(151)	179(2)	−178(2)	535(2)
H(152)	225(2)	−98(2)	447(1)
H(16)	160(2)	−232(2)	275(1)
H(161)	128(2)	−79(2)	231(1)
H(162)	180(2)	−65(2)	307(1)
H(19)	93(1)	−412(2)	313(1)
H(20)	31(1)	−540(2)	336(1)
H(21)	−5(1)	−404(1)	428(2)
H(22)	23(1)	−141(1)	488(2)

Table 6. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **3**

Atom	*x*	*y*	*z*
S	4662(2)	8322(3)	2130(3)
O(1)	2116(2)	8073(3)	5268(2)
O(2)	5303(2)	7778(3)	1637(2)
O(3)	4866(2)	8926(3)	3233(3)
N	1407(2)	6561(3)	3991(3)
C(1)	1413(2)	7606(3)	5990(2)
C(2)	1046(2)	6893(3)	5045(2)
C(3)	2206(2)	6921(3)	3601(2)
C(4)	2540(3)	7661(3)	4237(2)
C(5)	3310(2)	8048(3)	3784(2)
C(6)	3757(2)	7687(3)	2715(2)
C(7)	3461(2)	6890(3)	2064(2)
C(8)	3913(2)	6455(3)	1009(2)
C(9)	3583(3)	5707(3)	434(2)
C(10)	2786(3)	5358(3)	843(2)
C(11)	2335(3)	5752(3)	1871(2)
C(12)	2664(2)	6522(3)	2517(3)
C(13)	1716(3)	7259(3)	7353(3)
N(13)	1678(3)	7276(3)	7353(3)
C(13A)	2332(3)	6662(3)	7384(3)
C(13B)	2691(3)	6995(3)	7341(3)
C(13C)	1154(3)	6478(3)	7889(3)
C(14)	1597(3)	7953(3)	8372(3)
C(15)	1928(3)	8064(3)	9715(3)
C(16)	1697(3)	8771(3)	10484(3)
C(17)	1164(2)	9347(3)	9943(3)
C(18)	841(2)	9248(3)	8588(3)
C(19)	1066(3)	8540(3)	7813(3)
C(20)	784(3)	8261(3)	6361(2)
N(20)	796(2)	8262(3)	6438(3)
C(20A)	802(2)	9025(3)	5287(3)
C(20B)	−136(2)	7857(3)	6428(3)
C(20C)	402(2)	8797(3)	5395(3)
C(21)	4271(2)	8889(3)	682(3)
C(22)	3962(2)	9690(3)	919(3)
C(23)	3648(2)	10133(3)	−202(3)
C(24)	3645(1)	9782(3)	−1532(2)
C(25)	3962(3)	8993(3)	−1764(3)
C(26)	4285(3)	8535(3)	−648(3)
H(2)	046(1)	665(2)	530(2)
H(5)	353(1)	861(2)	417(1)
H(8)	448(1)	668(2)	69(1)
H(9)	394(1)	541(2)	−26(1)
H(10)	249(1)	478(1)	39(2)
H(11)	183(1)	551(1)	218(1)
H(15)	228(1)	752(2)	1002(1)
H(16)	191(1)	892(2)	1141(2)
H(17)	106(1)	982(1)	1053(2)
H(22)	394(1)	993(1)	184(2)
H(23)	344(1)	1074(2)	−2(1)
H(24)	342(1)	1002(1)	−219(1)
H(25)	396(1)	880(2)	−273(2)
H(26)	452(1)	799(1)	−83(2)

Table 7. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	4580(2)	3620(1)	823(2)	O(2)	−2426(3)	6227(1)	1432(2)	H(9)	947(1)	28(2)	−143(2)
N(1)	5475(2)	1946(1)	1459(1)	O(3)	−425(3)	6610(1)	2352(2)	H(10)	843(1)	−16(1)	−15(2)
N(2)	2101(2)	3028(1)	1159(1)	N(3)	−1105(2)	6084(1)	1817(2)	H(11)	686(1)	64(1)	77(2)
C(1)	3695(1)	3218(1)	1539(2)	C(14)	1153(1)	3744(1)	1252(2)	H(13)	60(1)	213(1)	57(2)
C(2)	4509(1)	2406(2)	1895(2)	C(15)	1899(1)	4344(2)	1867(1)	H(131)	187(1)	264(1)	−19(2)
C(3)	5917(1)	2275(2)	593(2)	C(16)	1187(2)	5118(2)	2058(1)	H(132)	233(1)	186(1)	70(2)
C(4)	5468(2)	3092(1)	297(2)	C(17)	−322(2)	5275(2)	1610(1)	H(16)	174(1)	552(1)	245(2)
C(5)	5995(2)	3451(1)	−528(2)	C(18)	−1065(2)	4674(1)	1026(1)	H(18)	−205(1)	482(2)	81(1)
C(6)	6942(2)	2966(1)	−1066(1)	C(19)	−347(2)	3908(2)	832(1)	H(19)	−81(1)	348(2)	42(2)
C(7)	7383(2)	2105(1)	−805(1)	C(20)	3445(2)	3951(2)	2280(1)	H(21)	272(1)	401(2)	364(2)
C(8)	8342(2)	1581(1)	−1362(1)	C(21)	3122(2)	3553(1)	3233(1)	H(211)	234(1)	317(2)	321(2)
C(9)	8692(2)	747(2)	−1104(1)	C(22)	4821(1)	4586(2)	2398(1)	H(221)	578(1)	428(2)	265(2)
C(10)	8117(1)	389(2)	−308(2)	H(2)	421(1)	220(1)	256(2)	H(22)	499(1)	493(2)	181(2)
C(11)	7240(2)	879(2)	251(2)	H(5)	567(1)	401(1)	−73(2)	H(212)	409(1)	333(2)	352(2)
C(12)	6848(2)	1745(2)	22(2)	H(6)	733(1)	332(2)	−168(2)	H(222)	461(1)	504(2)	285(2)
C(13)	1716(2)	2349(2)	475(2)	H(8)	873(1)	189(1)	−186(2)				

Table 8. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	383(2)	1748(2)	79(1)	C(16)	−5407(3)	5786(2)	−2805(1)	H(16)	−529(2)	671(2)	−259(1)
O(2)	−5402(2)	4104(2)	−2435(1)	C(17)	−6251(2)	5428(2)	−1774(1)	H(161)	−648(3)	578(2)	−301(1)
N(1)	−867(2)	3605(2)	−483(2)	C(18)	3112(2)	2572(2)	89(1)	H(162)	−494(2)	556(2)	−311(1)
N(2)	1554(2)	2751(3)	909(2)	C(19)	3203(3)	1921(2)	−498(1)	H(17)	−606(2)	617(2)	−157(1)
C(1)	1299(2)	2690(3)	244(1)	C(20)	3892(3)	3655(2)	−5(1)	H(171)	−611(3)	485(1)	−130(1)
C(2)	360(2)	3608(3)	−31(1)	C(21)	115(3)	2732(2)	1249(1)	H(172)	−743(3)	525(1)	−193(1)
C(3)	−1430(2)	2632(3)	−729(1)	C(22)	3021(3)	2232(2)	1136(1)	H(19)	249(2)	114(1)	−36(1)
C(4)	−848(2)	1742(2)	−426(1)	C(23)	3523(3)	1923(2)	1758(1)	H(191)	445(2)	186(1)	−53(1)
C(5)	−1562(2)	795(2)	−583(1)	C(24)	5150(3)	1488(2)	1863(1)	H(192)	237(2)	219(2)	−83(1)
C(6)	−2847(2)	732(2)	−1049(1)	C(25)	6108(3)	1377(2)	1422(1)	H(20)	322(2)	385(2)	−38(1)
C(7)	−3435(2)	1593(2)	−1388(1)	C(26)	5578(2)	1702(2)	810(1)	H(201)	522(2)	343(1)	−16(1)
C(8)	−2699(2)	2601(2)	−1250(1)	C(27)	4001(3)	2097(2)	686(1)	H(202)	393(2)	411(1)	42(1)
C(9)	−3330(3)	3451(2)	−1619(1)	H(2)	76(2)	421(2)	11(1)	H(21)	33(2)	278(1)	173(1)
C(10)	−4736(3)	3304(2)	−2059(1)	H(5)	−114(2)	12(2)	−44(1)	H(211)	−42(2)	205(1)	111(1)
C(11)	−5490(3)	2364(2)	−2177(1)	H(6)	−344(2)	6(1)	−128(1)	H(212)	−47(2)	335(2)	114(1)
C(12)	−4814(3)	1528(2)	−1871(1)	H(11)	−651(2)	233(1)	−250(1)	H(23)	291(2)	201(2)	201(1)
C(13)	−2523(3)	4429(2)	−1630(1)	H(12)	−525(2)	96(1)	−190(1)	H(24)	539(2)	125(2)	227(1)
C(14)	−3321(3)	5236(2)	−1941(2)	H(13)	−136(2)	455(2)	−149(1)	H(25)	716(2)	93(1)	148(1)
C(15)	−5088(3)	5163(2)	−2233(2)	H(14)	−276(2)	574(2)	−185(1)	H(26)	634(2)	138(2)	46(1)

Table 9. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in molecule **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	321(2)	5224(2)	6763(2)	C(15)	4179(2)	4590(3)	8500(2)	H(131)	−292(1)	117(2)	1195(1)
O(2)	−2822(3)	−0235(2)	11305(3)	C(16)	3523(2)	3654(3)	7103(2)	H(132)	−132(1)	8(2)	1220(1)
N(1)	−64(2)	3837(2)	9135(2)	C(17)	3490(2)	6237(2)	6481(2)	H(15)	385(1)	544(2)	875(1)
N(2)	1019(2)	6965(2)	7187(2)	C(18)	4836(2)	6412(2)	5808(2)	H(151)	399(1)	371(3)	908(1)
C(1)	1268(2)	5453(2)	7556(2)	C(19)	4912(2)	7768(3)	5054(2)	H(152)	538(1)	441(2)	835(1)
C(2)	741(2)	4782(2)	8772(2)	C(20)	3652(2)	8903(3)	4979(2)	H(16)	470(1)	341(2)	695(1)
C(3)	−582(1)	3409(2)	8324(1)	C(21)	2279(2)	8741(3)	5645(2)	H(161)	321(1)	284(3)	773(1)
C(4)	−392(2)	4107(2)	7168(2)	C(22)	2229(2)	7387(3)	6398(2)	H(162)	283(1)	395(3)	627(1)
C(5)	−950(2)	3720(2)	6349(2)	C(23)	−660(2)	7851(3)	6965(2)	H(18)	568(1)	564(2)	582(1)
C(6)	−1674(2)	2614(2)	6709(2)	C(24)	−1692(1)	7508(3)	7978(1)	H(19)	591(1)	786(2)	459(1)
C(7)	−1907(2)	1875(2)	7881(2)	C(25)	−3154(2)	7282(3)	7965(2)	H(20)	373(1)	983(2)	437(1)
C(8)	−1377(2)	2277(2)	8709(2)	H(2)	114(1)	510(2)	932(1)	H(21)	136(1)	961(2)	555(1)
C(9)	−1666(2)	1575(3)	9885(2)	H(5)	−77(1)	421(3)	555(1)	H(23)	−136(1)	778(2)	625(1)
C(10)	−2450(2)	505(3)	10205(2)	H(6)	−205(1)	233(2)	612(1)	H(231)	−54(1)	883(2)	674(1)
C(11)	−2950(3)	68(3)	9398(3)	H(9)	−132(1)	184(2)	1043(1)	H(24)	−125(1)	747(2)	870(1)
C(12)	−2697(3)	745(3)	8265(3)	H(11)	−351(1)	−67(2)	964(1)	H(25)	−366(1)	726(2)	726(1)
C(13)	−2426(3)	165(3)	12171(3)	H(12)	−302(1)	41(2)	774(1)	H(251)	−382(1)	716(2)	870(1)
C(14)	3155(2)	4931(3)	7412(2)	H(13)	−291(1)	−42(2)	1279(1)				

The structures were solved by direct methods using the SHELX-86 program package[19] and refined anisotropically by the full-matrix least-squares method (SHELX-93).[20] The positions of the hydrogen atoms were located from the difference Fourier syntheses, and only their positional parameters were refined. The atomic coordinates of compounds **1**—**6** are given in Tables 4—9, respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32046) (Russian scientists) and by the ESSILOR International (France) and PPG Industries (USA) (French scientists).

We thank CNRS (France) and the Russian Academy of Sciences for help in collaboration between the Russian and French laboratories (exchange agreement No. 4083).

References

1. N. Y. C. Chu, in *Photochromism, Molecules, and Systems*, Eds. H. Durr and H. Bouas-Laurent, Ch. 10, Elsevier, Amsterdam, 1990.
2. G. Favaro, F. Masetti, V. Mazzucato, G. Ottavi, P. Allegrini, and V. Malatesta, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 333.
3. P. Tardieu, R. Dubest, J. Aubard, A. Kellmann, F. Tfibel, A. Samat, and R. Guglielmetti, *Helv. Chim. Acta*, 1992, 75, 1185.
4. Y. T. Osano, K. Mitsuhashi, S. Maeda, and T. Matsuzaki, *Acta Cryst.*, 1991, **C47**, 2137.
5. R. Millini, G. Del Piero, P. Allegrini, L. Crisci, and V. Malatesta, *Acta Cryst.*, 1991, **C47**, 2567.
6. W. Clegg, N. C. Norman, T. Flood et al., *Acta Cryst.*, 1991, **C47**, 817.
7. J. P. Reboul, A. Samat, P. Lareginie, V. Lokshin, R. Guglielmetti, and G. Pepe, *Acta Cryst.*, 1995, **C51**, 1614.
8. N. Tamai and H. Masuhara, *Chem. Phys. Lett.*, 1992, **191**, 189.
9. S. M. Aldoshin, *Usp. Khim.*, 1990, **59**, 1144 [*Russ. Chem. Rev.*, 1990, **59**, 663 (Engl. Transl.)].
10. *Molecular Structures and Dimensions*, Utrecht, Netherlands, 1972, **A1**.
11. V. A. Barachevskii, G. I. Lashkov, and V. A. Tsekhomskii, *Fotokhromizm i ego primenenie* [*Photochromism and Its Applications*], Khimiya, Moscow, 1977, 280 pp. (in Russian).
12. S. Aldoshin, I. Chuev, A. Utenyshev, O. Filipenko, V. Lokshin, J.-L. Pozzo, and R. Guglielmetti, *Acta Cryst.*, 1996, **C52**, 1834.
13. V. Lokshin, A. Samat, and R. Guglielmetti, *Tetrahedron*, 1997, **53**, 9669.
14. P. Laregenie, *Synthese et etude des proprietes photochromiques de spiro[azacycloalcane-oxazines]*, Ph.D. Thesis, Universite d'Aix-Marseille II, Marseille, 1995.
15. P. Laregenie, V. Lokshin, A. Samat, R. Guglielmetti, and E. Zaballos-Garcia, Pat. France, 1996 (*Chem. Abstr.*, 124:356317, 1996).
16. E. Mencherini-Pottier, *Synthese et structure de spiro[indoline-naphtoxazines] et de spiro[indoline-pyridobenzoxazines] diversement substitutees. Etudes de leurs proprietes photochromiques*, Ph.D. Thesis, Universite d'Aix-Marseille II, Marseille, 1990.
17. J. A. Miler, P. Levoir, J. C. Fontaine, F. Garnier, and J. F. Dubois, *Anal. Chem.*, 1975, **47**, 29.
18. N. L. Allinger and Young Yuh, *Molecular Mechanics, MM2 and MMP2 Programs*, QCPE-395, 1977.
19. G. M. Sheldrick, *SHELX-86; Program for Crystal Structure Determination*, University of Cambridge (England), 1986.
20. G. M. Sheldrick, *SHELXL93; Program for the Refinement of Crystal Structures*, University of Gottingen (Germany), 1993.

Received October 21, 1997;
in revised form December 5, 1997