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PHOTO- AND THERMOCHROMIC SPIRANES 30*. COMPARATIVE STUDY BY X-RAY STRUCTURAL ANALYSIS OF THE STRUCTURE OF SPIROPYRANS OF THE INDOLINE SERIES CONTAINING A CONDENSED FURAN FRAGMENT

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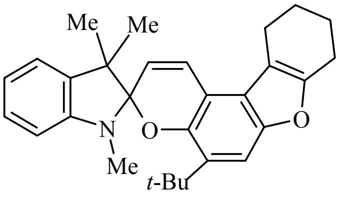
The structure of an indoline spiropyran of molecular formula $C_{29}H_{33}NO_2$ has been studied by X-ray crystallographic analysis. Structural parameters have been determined for this spiropyran, containing a condensed furan fragment with a tert-butyl group, in comparison with the structure of other spiropyrans of this series. The observation in the absorption spectrum of a photoinduced cis-cis isomer is linked with its stabilization by the steric effect of the bulky tert-butyl group and the strength of barriers at 77 K.

Keywords: indoline, spiropyran, condensed furan fragment, X-ray structural analysis.

The present work is devoted to the X-ray structural investigation of spiropyran **1** in comparison with spiropyrans **2a-c** and continues the comparative study of the structure of indolinespiropyrans containing a condensed furan fragment.



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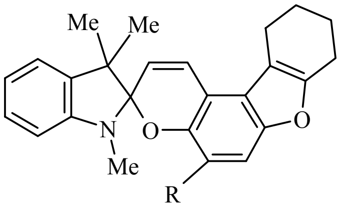

2a-c

2a R = H, **b** R = Br, **c** R = NO_2

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* For Communication 29 see [1].

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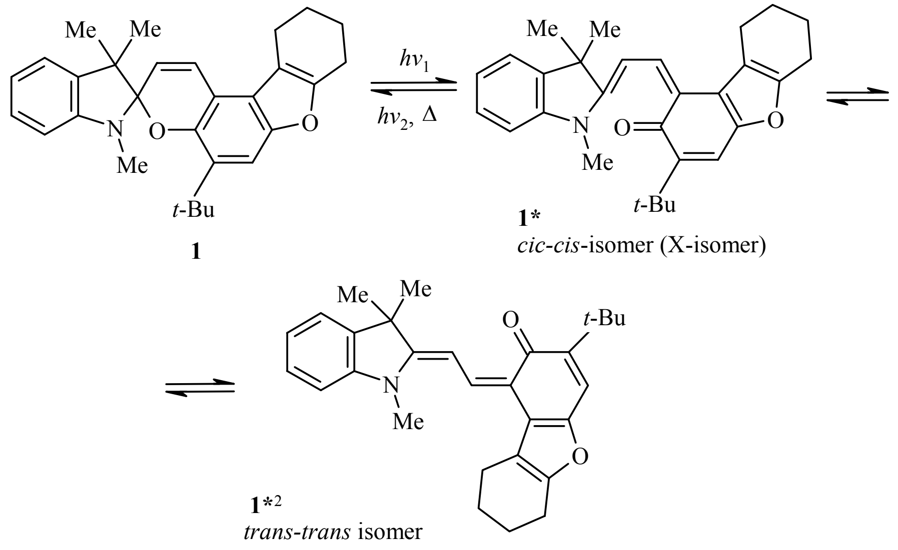
Compounds **1** and **2** were synthesized by brief boiling in alcohol of equimolar amounts of 1,2,3,3-tetramethylindolenilium perchlorate, the appropriate 3-R-2-hydroxy-6,7,8,9-tetrahydrodibenzofuran-2-carbaldehyde and piperidine [2].

As our previous experiments [2] showed, on irradiating spiropyrans **1, 2** with UV light in the stationary mode photochromic properties were displayed in solutions at low temperatures (150 K) with the appearance in the spectra of an absorption band with a maximum in the 585-625 nm region, characteristic of noncyclic transoid isomers. Spiropyran **2c** also displayed these properties in the solid phase, in thin films obtained by vacuum thermal spraying onto glass or quartz supports [2]. Unexpectedly it turned out that at lower temperatures (77 K) only in the case of compound **1** was the appearance observed of an absorption band with a maximum at 471 nm, which on prolonged irradiation is transformed into an absorption band with a maximum at 585 nm [3]. The spectral changes observed are linked with the formation in the first stage of the *cis-cisoid* X-isomer **1***, formed directly after fission of the C$_{\text{spiro}}$–O bond, subsequent photoisomerization of which leads to the appearance of the *trans-trans* isomer **1***^{2}.



1

1*
cic-cis-isomer (X-isomer)

1*^{2}
trans-trans isomer

To clarify the effect of the structure of spiropyran **1** on photochromic properties, X-ray structural investigations were carried out on a monocrystal. The general shape of the compound **1** molecule is represented in Fig. 1.

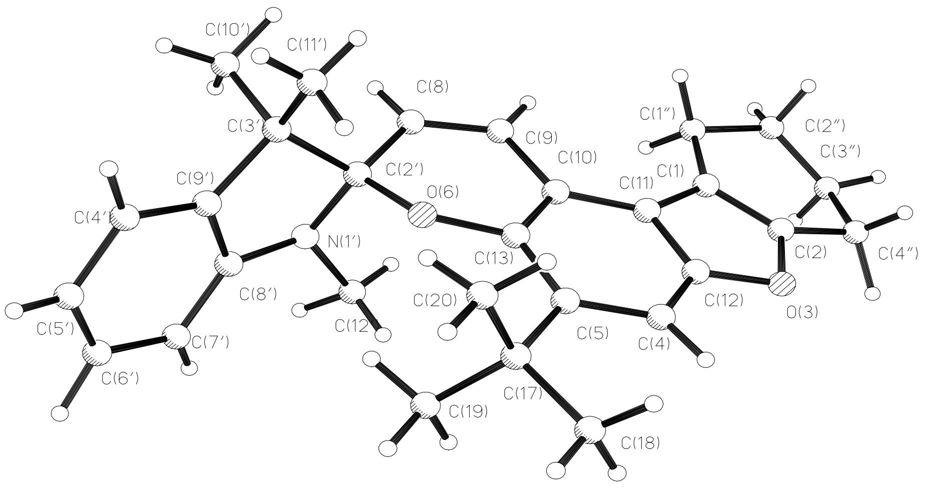


Fig. 1. General shape of the compound **1** molecule. The main crystallographic data for compounds **1** and **2a-c** and the overall values of the crystal lattice energies are given in Table 1.

TABLE 1. Main Crystallographic Characteristics for Compounds **1, 2**

Compound	**2a**	**2b**	**2c**	**1**
Empirical formula	$C_{25}H_{24}NO_2$	$C_{25}H_{24}BrNO_2$	$C_{25}H_{26}N_2O_4$	$C_{29}H_{33}NO_2$
M	369.44	450.36	418.39	427.56
Space group	*C* 2/*c*	*P*-1	*P*-1	*P*2(1)/*n*
a, Å	23.274(5)	17.935(4)	6.970(1)	18.520(8)
b, Å	6.881(1)	8.025(2)	11.063(2)	10.232(5)
c, Å	25.066(5)	7.835(2)	14.153(3)	12.803(5)
α,deg.	90	73.61(3)	75.89(3)	90
β, deg.	102.00(3)	86.50(3)	89.41(3)	106.13(3)
γ, deg.	90	78.02(3)	79.90(3)	90
V, Å^3	3927(1)	1058.29(4)	1041.4(3)	2330.6(2)
Z	8	2	2	4
D, g/cm^3	1.250	1.413	1.373(3)	1.219
Crystal lattice energy *E*, kcal/mol	-36.5	-35.0	-38.3	-39.6

A comparative analysis of the details of the structure makes it possible to draw the conclusion that in the **1** and **2a-c** molecules the benzopyran and indoline fragments, as in the previously investigated [2] indoline spiropyranes and benzoxazine derivatives of spiropyrans, are disposed approximately orthogonally to one another and individually are nonplanar. In compound **2a** the indoline fragment has a twist along the $N_{(1')}\cdots C_{(3')}$ line by an angle $\varphi = 25.0$, in compound **2b** by 29.6, and in compounds **2c** and **1** by 25.7 and 32.1° respectively. The $N_{(1')}$ and $C_{(3')}$ atoms are disposed in the plane of the benzene ring with a precision of 0.02, 0.016, 0.013, and 0.040 Å in the molecules of compounds **2a-c**, **1** respectively (all geometric details of the structure of the molecules will subsequently be given in this sequence). Twists along the lines passing through the $O_{(6)}C_{(9)}$ and $O_{(6)}C_{(8)}$ atoms were 7.5 and 11.5, 11.0 and 23.0, 8.1 and 13.3, and 15.5 and 10.2° respectively. The twist of 23.0^o along the $O_{(6)}C_{(8)}$ line in **2b** attracts attention, being formally equal to 157^o. In other words the mutual orientation of the two fragments relative to the $O_{(6)}C_{(8)}$ line in the molecules of compounds **2a, 2c**, and **1**, in which the benzopyran fragment is bent back towards the N-methyl substituents, is different from that in **2b**, where a twist towards the geminal carbon atoms occurs. On the whole the geometric structure of the C_{spiro} unit and the benzopyran fragment in compounds **2a-c**, **1** is analogous to the structure in the indoline and benzoxazine spiropyrans studied previously. The emergence of the $N_{(1')}$ atom from the plane of the coordinating atoms $C_{(2')}C_{(8')}C_{(12')}$ is –0.30, 0.27, -0.30, and –0.26 Å, the sum of the valence angles at the $N_{(1')}$ atom is equal to 347.3, 349.3, 347.3, and 349.2° respectively. The appreciable *sp*^{3}-hybrid character of the orbitals of the $N_{(1')}$ atom leads, apart from a twist at the $C_{(3')}\cdots N_{(1')}$ line of the indoline ring, to a torsional turn of the $C_{(2')}$ atom around the $C_{(8')}$-$N_{(1')}$ bond (angle $C_{(9')}–C_{(8')}–N_{(1')}–C_{(2')}$ is equal to 18.8, -20.6, 17.4, and 19.2^o) and a simultaneous turn of the methylene group ($C_{(12')}$ atom) around this bond (angle $C_{(9')}–C_{(8')}–N_{(1')}–C_{(12')}$ equals 159.7, -165.0, 159.1, and 161.3^o). In difference to the benzoxazine analogs the absence of amide conjugation assists the interaction of the unshared electron pair of atom $N_{(1')}$ with the σ*-orbital of the $C_{(2')}–O_{(6)}$ bond, and in addition the geometric disposition of the $C_{(2')}–O_{(1')}$ bond relative to the coordination plane of the $N_{(1')}$ atom becomes more favorable for orbital *n*-σ* interactions. It is characteristic of spiropyrans of this type that under conditions of domination of orbital *n*-σ*-interactions of the unshared electron pair of the $N_{(1')}$ atom with the σ*-orbital of the $C_{(2')}–O_{(6)}$ bond at the spirocenter of the molecule, the shortening of the bond of the N atom with the C_{spiro} atom and lengthening of the $O_{(6)}–C_{spiro}$ bond will be appreciable in comparison with standard values for similar bond lengths. The $C_{(2')}–O_{(6)}$ bond lengths are equal to 1.462(3), 1.483(8), 1.476(4), and 1.467(3) Å, but the $N_{(1')}–C_{(2')}$ bonds at 1.463(4), 1.451(8), 1.444(5), and 1.446 Å are within the range of bond lengths for the previously studied indoline spiropyrans displaying photochromic properties (1.438-1.497 and 1.434-1.453 Å respectively).

It should be noted that replacement of a π-donor by the condensed furan fragment did not change the main picture of electronic interactions characteristic of indoline spiropyran molecules. The degree of conjugation of the $O_{(6)}$ atom with the π-orbital of the benzene ring was analogous to the previously investigated spiropyrans, the $O_{(6)}$–$C_{(13)}$ bond length was 1.382(4) Å. The presence in position 5 of the compounds **2b** and **2c** molecules of a strongly electron-withdrawing substituent, as in the benzoxazinone spiropyrans, leads to a change in the electronic state of the oxygen atom of the spirocenter and a strengthening of the degree of conjugation of the $O_{(6)}$ atom with the benzene fragment. As a result the $O_{(6)}$–$C_{(13)}$ bond in compounds **2b** and **2c** is shortened and is 1.354(7) and 1.352(3) Å, which is accompanied by lengthening of the C_{spiro}–$O_{(6)}$ bond to 1.483(8) and 1.476(4) Å.

The introduction of a bulky *tert*-butyl substituent into the **1** molecule leads, on the one hand, to the the formation of a crystal with lower density (Table 1), and on the other, to the formation of an isotropic crystal structure (Fig. 2).

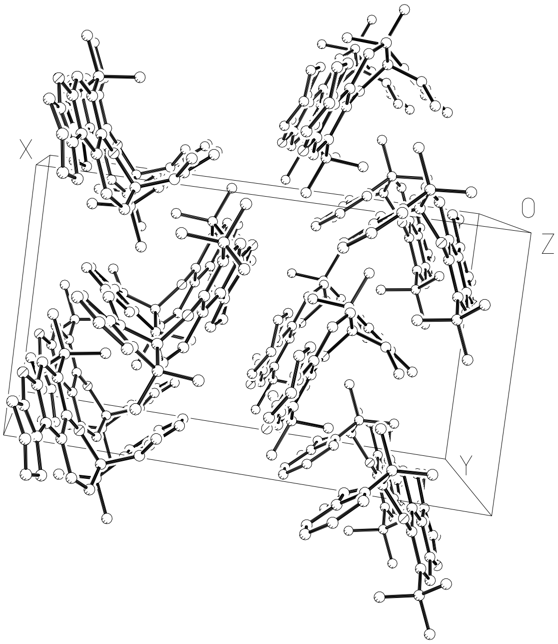


Fig. 2. Projection of the crystal structure of compound **1** on the XY0 plane.

The main contribution to the energy of crystal structure **2a** is introduced by the twin intermolecular interactions of -8.3 kcal/mol between the molecules translationally bonded in the direction X (Fig. 3) and the energy of the twin intermolecular interactions between the centrosymmetrically bonded molecules of -12.4 (0 1 1), -14.6 (1 0 1), and -10.2 kcal/mol (1 1 1). A projection of the crystal structure of **2a** is represented in Fig. 3.

The main contribution to the energy of crystal structure **2b** is introduced by the twin intermolecular interactions of -6.9 kcal/mol between translationally linked molecules and also by the bonded center of inversion (2 0 1) at -11.42 kcal/mol and with the symmetry element 0.5 + *x*, 0.5 + *y*, *z* (1 -1 0 and 1 0 1) at -12.6 and -10.7 kcal/mol respectively. A projection of the crystal structure of **2b** is represented in Fig. 4.

The main contribution to the energy of crystal structure **2c** is introduced by the twin intermolecular interactions -5.1, -5.6, -9.9 kcal/mol between the translationally linked molecules, and also by those linked with the center of inversion at -10.1 kcal/mol. A projection of the crystal structure of **2c** is represented in Fig. 5.

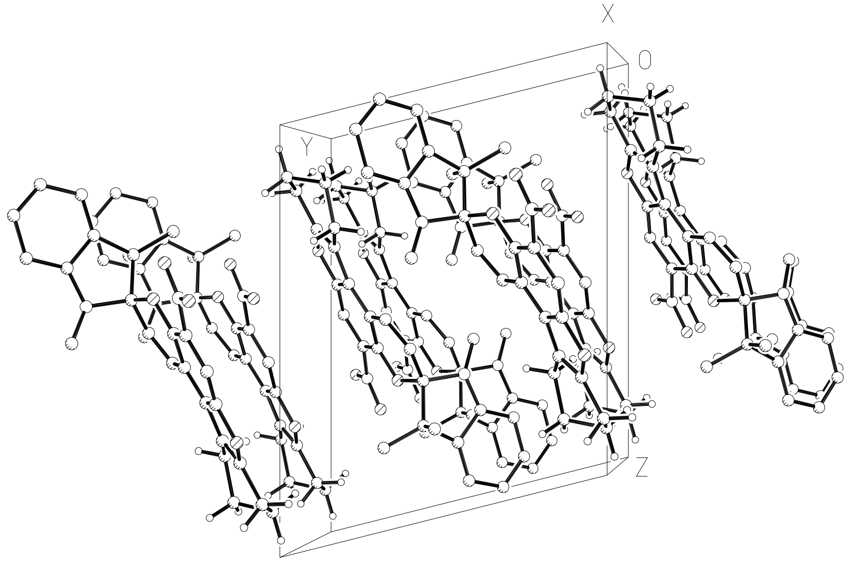


Fig. 3. Projection of the crystal structure of compound **2a** on the Y0Z plane.

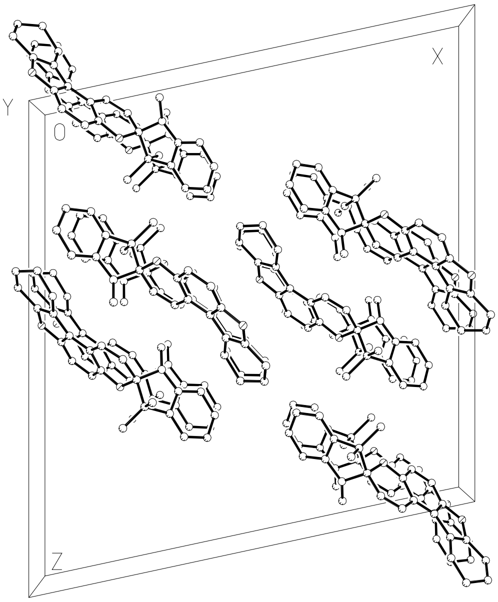


Fig. 4. Projection of the crystal structure of compound **2b** on the X0Z plane.

In comparison with structures **2a-c** the main contribution to the crystal energy of structure **1** is introduced only by the energy of twin intermolecular interactions of –13.5 kcal/mol between molecules linked with the center of inversion. In the other structures denser packing is formed with a large number of intermolecular interactions. The observation in the absorption spectrum of compound **1** at 77 K of the photoinduced *cis-cis* isomer **1*** is linked with its stabilization as a result of the steric effects of the bulky *tert*-butyl group and viscous barriers at low temperature.

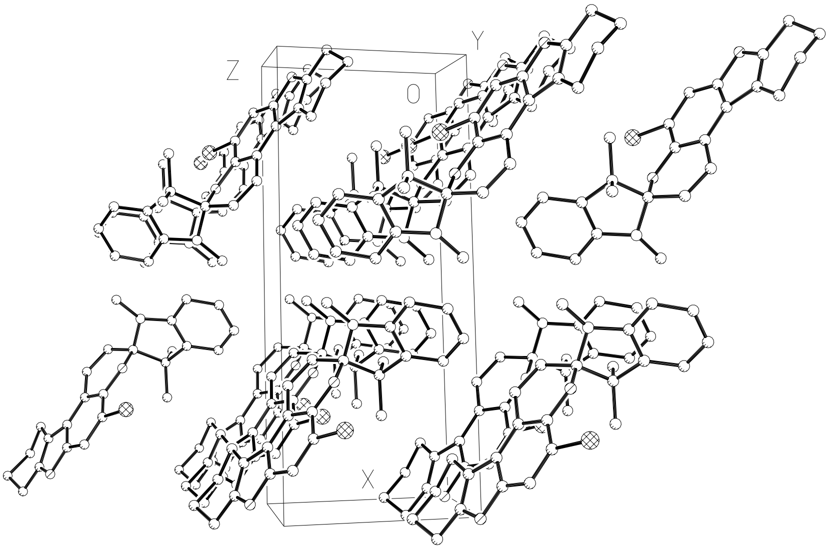


Fig. 5. Projection of the crystal structure of compound **2c** on the X0Z plane.

EXPERIMENTAL

Compound **1** ($C_{29}H_{33}NO_2$) crystallizes in the monoclinic system. The principal crystallographic data for compound **1** are given in Table 1. The collection of the intensities of 4505 reflections ($1.73 < \theta < 26.06$) was obtained by $\omega/2\theta$ scanning on a KUMA-4 four-circle diffractometer (MoKα radiation) at T = 293(2) K. Absorption was not calculated, μ (MoKα) = 0.075 mm^{-1}.

After elimination of systematically quenched reflections the working mass of measured reflections amounted to 2416 with $I > 2\sigma(I)$. The structure was solved by the direct method and refined by the full matrix least squares method in an anisotropic approach for the non-hydrogen atoms with the SHELXL97 set of programs [4]. All hydrogen atoms were determined from a difference synthesis and were further refined in an isotropic thermal vibration approach, except for the H-10A, H-10B, H-11A, and H-11B atoms which were calculated geometrically and for which positional parameters were refined. The final refinement parameters on refinement of 405 parameters were: $R = 0.0484$, $R_\omega = 0.1502$, GOOF = 0.964, $F(000) = 920$, maximum and minimum electron densities were 0.273 and –0.323 eÅ^{-3}.

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