Molecular structure of 1′,3′,3′-trimethyl-6-trifluoromethylsulfonyl-spiro-(indoline-2,2′-benzo[*b*]pyran)

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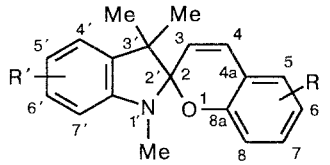
Photochromic 1′,3′,3′-trimethyl-6-trifluoromethylsulfonyl-spiro(indoline-2,2′-benzo[*b*]pyran) (**1**) was studied by X-ray diffraction analysis. In compound **1**, the C_{spiro}—O bond (1.49(1) Å (average)), broken on photoexcitation, is the longest of all the indoline spiropyrans studied.

Key words: molecular structure, photochromism, n-σ*-interaction, 1′,3′,3′-trimethyl-6-trifluoromethylsulfonyl-spiro(indoline-2,2′-benzo[*b*]pyran).

It has been established by an X-ray diffraction study of indoline spiropyrans[1–5] that in all the photochromic spiropyrans of this class, the C_{spiro}—O bond broken on photoexcitation is elongated even in the ground state. The elongation of this bond is explained in terms of specific orbital interactions of the lone electron pair of the N atom of the indoline heterocycle with the antibonding σ*-orbital of C_{spiro}—O.[6,7] The efficiency of this interaction depends on the geometric position and the electronic state of the heteroatom in the spiro unit.



1–9

It has been shown[1–3] that the electron-withdrawing NO_2 group in position 6 of the benzopyran fragment exhibits the greatest effect on the electronic state of the O heteroatom and the efficiency of the n-σ*-interaction. To study the effect of another strong electron-withdrawing substituent, CF_3SO_2, on the structure of the indoline spiropyran, we studied 1′,3′,3′-trimethyl-6-trifluoromethylsulfonyl-spiro(indoline-2,2′-benzo[*b*]pyran) (**1**) by X-ray diffraction analysis.

Experimental

The principal crystallographic parameters for **1**: $C_{20}H_{18}NO_3SF_3$, crystals are monoclinic, a = 25.204(5), b = 11.090(2), c = 29.336(6) Å, β = 107.88(3)°, V = 7803.7((2) Å^3, Z = 16, d_{calc} = 1.394(3) g/cm^3, space group is $C2/c$. Intensities of 3019 independent reflections with $I > 3\sigma(I)$ were measured on an automated DAR-UM diffractometer (CuK_α-radiation, dimensions of the crystal are 0.10×0.15×0.20 mm). The structure was solved by the direct method using the SHELXS-86 program package.[8] Atomic coordinates for hydrogen atoms were determined from the difference Fourier synthesis, except for the methyl H atoms, the coordinates of which were calculated geometrically. The least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms was performed using the SHELXTL-76 program package. The atomic coordinates given in Table 1 correspond to the final values of the R factors: R = 0.058, R_w = 0.061.

Results and Discussion

The crystal structure of **1** contains two independent molecules, which differ mainly in the orientation of the CF_3SO_2 groups in position 6 of the benzopyran fragment (Fig. 1). In the first independent molecule (**A**), the CF_3SO_2 group has the transoid orientation with respect to the *N*-methyl group, whereas in the second molecule (**B**), these groups are in cisoid orientation. The principal geometric parameters of both molecules compared to those of previously studied spiropyrans of the indoline series (**2**—**9**)[5] are presented in Table 2.

The indoline and benzopyran fragments of **1**, as in all studied spiropyrans, are nearly orthogonal to each other. The dihedral angles between the C(22′)C(3′)N(1′) and C(22′)C(3)O planes are 91° and 89° in molecules **A** and **B**, respectively. The five-membered ring of the indoline fragment in molecules **A** and **B** adopts a flattened envelope conformation with folding angles about the N(1′)...C(3′) line of 24.1° and 24.4°, respectively.

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Table 1. Atomic coordinates ($\times 10^4$, for hydrogen atoms $\times 10^3$) in the crystal structure of **1**

Atom	*x*	*y*	*z*
	Molecule **A**		
S(1)	1075(1)	393(3)	5906(1)
O(1)	1385(3)	−816(6)	7899(2)
O(2)	1041(3)	−661(6)	5625(2)
O(3)	1428(3)	1356(6)	5865(2)
N(1′)	1859(3)	−2281(7)	8442(3)
F(1)	5(3)	203(7)	5704(3)
F(2)	276(3)	1451(7)	5270(2)
F(3)	317(2)	1901(6)	5975(2)
C(22′)	1326(4)	−2029(9)	8088(3)
C(3)	1179(5)	−2943(8)	7678(4)
C(4)	1107(5)	−2674(9)	7230(4)
C(4a)	1159(4)	−1460(8)	7090(4)
C(5)	1083(4)	−1143(9)	6623(3)
C(6)	1163(4)	42(9)	6488(3)
C(7)	1322(4)	880(8)	6854(4)
C(8)	1390(4)	605(9)	7313(3)
C(8a)	1318(4)	−567(9)	7445(4)
C(9)	370(5)	1020(10)	5696(5)
C(3′)	943(4)	−1970(9)	8393(3)
C(4′)	1168(4)	−1318(9)	9282(4)
C(4a′)	1266(4)	−1677(8)	8863(3)
C(5′)	1586(7)	−1144(9)	9699(4)
C(6′)	2105(7)	−1330(10)	9679(4)
C(7′)	2229(5)	−1670(10)	9291(5)
C(7a′)	1817(4)	−1870(8)	8865(3)
C(8′)	2331(6)	−2200(10)	8293(6)
C(9′)	472(6)	−1060(10)	8175(5)
C(10′)	576(7)	−2960(10)	8337(5)
H(3)	112(2)	−375(3)	782(2)
H(4)	96(2)	−319(3)	698(2)
H(5)	96(2)	−165(3)	639(2)
H(7)	136(2)	150(3)	675(2)
H(8)	161(2)	112(3)	756(2)
H(4′)	83(2)	−147(3)	917(2)
H(5′)	167(2)	−101(3)	1009(2)
H(6′)	240(2)	−119(3)	999(2)
H(7′)	257(2)	−170(3)	926(2)
H(8.1′)	261(2)	−168(3)	833(2)
H(8.2′)	266(2)	−245(3)	857(2)
H(8.3′)	245(2)	−258(3)	814(2)
H(9.1′)	59(2)	−29(3)	819(2)
H(9.2′)	32(2)	−137(3)	775(2)
H(9.3′)	24(2)	−71(3)	841(2)
H(10.1′)	16(2)	−401(3)	827(2)
H(10.2′)	64(2)	−326(3)	866(2)
H(10.3′)	82(2)	−366(3)	835(2)
	Molecule **B**		
S(1)	3900(1)	−116(3)	4072(1)
O(1)	3602(3)	−941(5)	5935(2)
O(2)	3711(3)	−1122(6)	3765(2)
O(3)	3745(3)	1079(6)	3904(2)
N(1′)	3907(3)	−2194(7)	6608(3)
F(1)	4846(3)	−1271(6)	4376(2)
F(2)	4904(2)	626(6)	4506(2)
F(3)	4779(3)	−4(6)	3800(2)
C(22′)	3519(4)	−2153(9)	6132(3)
C(3)	3598(4)	−3126(8)	5817(4)
C(4)	3686(4)	−2949(9)	5398(3)
C(4a)	3701(3)	−1746(8)	5211(3)
C(5)	3781(3)	−1500(9)	4781(3)
C(6)	3803(3)	−341(8)	4612(3)
C(7)	3759(3)	581(8)	4915(3)
C(8)	3683(4)	364(8)	5350(3)
C(8a)	3659(4)	−797(9)	5500(3)
C(9)	4659(5)	−240(10)	4196(4)
C(3′)	2963(4)	−2070(10)	6245(4)
C(4′)	2781(6)	−1210(10)	6982(6)
C(4a′)	3089(4)	−1594(9)	6713(4)
C(5′)	299(1)	−840(10)	7417(8)
C(6′)	354(1)	−930(10)	7638(4)
C(7′)	3873(6)	−1350(9)	7394(5)
C(7a′)	3646(5)	−1694(8)	6923(4)
C(8′)	4480(5)	−2070(10)	6670(5)
C(9′)	2701(6)	−3410(10)	6279(5)
C(10′)	2521(5)	−1390(10)	5773(5)
H(3)	353(2)	−391(3)	595(2)
H(4)	375(2)	−358(3)	522(2)
H(5)	383(2)	−201(3)	461(2)
H(7)	375(2)	126(3)	479(2)
H(8)	363(2)	97(3)	551(2)
H(4′)	250(2)	−93(3)	680(2)
H(5′)	278(2)	−48(3)	759(2)
H(6′)	367(3)	−73(4)	797(2)
H(7′)	419(2)	−134(3)	743(2)
H(8.1′)	454(2)	−242(3)	638(2)
H(8.2′)	466(2)	−249(3)	690(2)
H(8.3′)	459(2)	−100(3)	681(2)
H(9.1′)	295(2)	−269(3)	625(2)
H(9.2′)	251(2)	−323(3)	592(2)
H(9.3′)	275(2)	−389(3)	601(2)
H(10.1′)	274(2)	−87(3)	612(2)
H(10.2′)	250(2)	−179(3)	605(2)
H(10.3′)	231(2)	−114(3)	594(2)

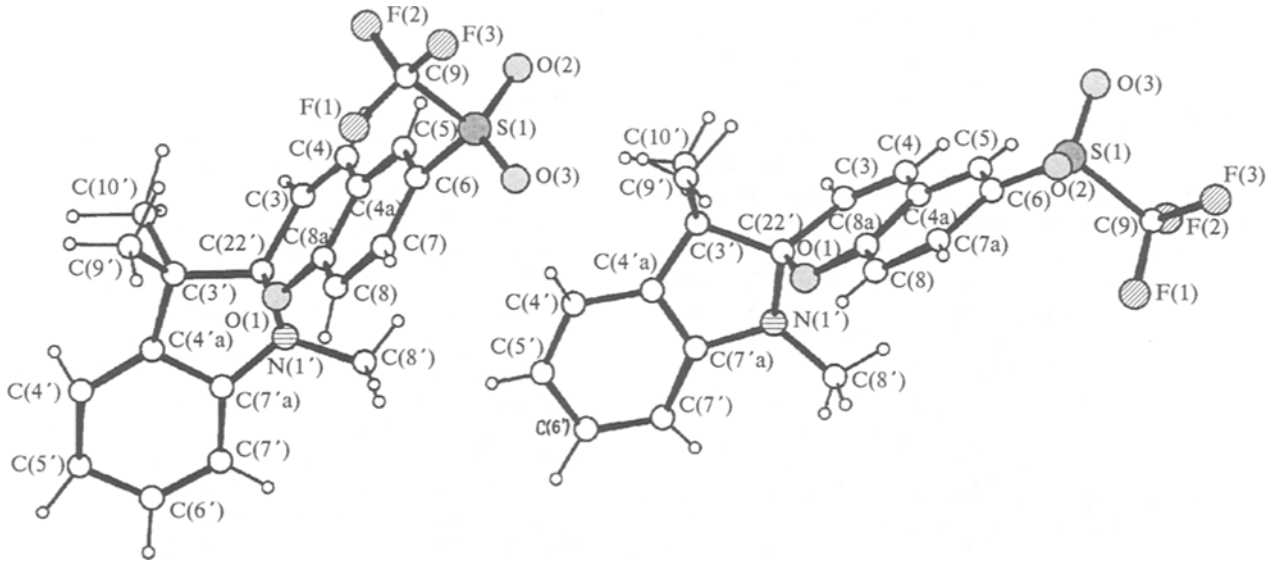


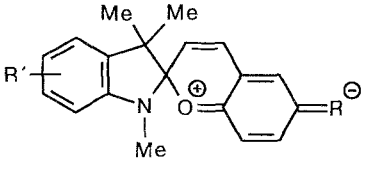
Fig. 1. The overall view of two independent molecules **A** and **B** in the crystal structure of spiropyran **1**.

Table 2. Principal geometric parameters of compound **1** and other indoline spiropyrans[5]

Spiro-pyran	R, R′	C(22′)—O(1)	C(22′)—N(1′)	O(1)—C(8a)	C(6)—R
1A	6-SO_2CF_3	1.50(1)	1.44(1)	1.34(1)	1.694(9)
1C		1.48(1)	1.45(1)	1.32(1)	1.698(9)
2	6-NO_2, 8-Br	1.496	1.453	1.342	1.473
3A	6-NO_2	1.485	1.451	1.359	1.460
3B		1.487	1.437	1.354	1.467
4	6-NO_2, 8-Br	1.486	1.434	1.333	1.448
5	4-Cl, 6-NO_2	1.479	1.438	1.343	1.476
6	4′,5′-Benzo, 6-NO_2	1.478	1.438	1.336	1.459
7	7-OCH_3	1.471	1.442	1.370	1.366
8	*N*-Ph, 5,6-nitrobenzo	1.460	1.450	1.372	1.473
9	5′-NO_2	1.452	1.453	1.361	—

The N(1′) atom adopts the pyramidal configuration and is displaced from the coordination plane by 0.24 Å (**A**) and 0.26 Å (**B**). In both molecules of **1**, the benzopyran fragment is nearly planar; the quite insignificant deviation from planarity in molecule **A** is characterized by folding angles about the O(1)...C(3) and O(1)...C(4) lines of 4.4° and 3.5°, respectively. The CF_3SO_2 group is nearly orthogonal to the plane of the benzopyran fragment. The C(5)C(6)SC(9) torsion angles are 98.7° and −83.1° in molecules **A** and **B**, respectively.

The electronic effect of the electron-withdrawing CF_3SO_2 group in position 6 of the benzopyran fragment is similar to that of the electron-withdrawing 6-NO_2 group in spiropyrans **2—4**.[5] In spiropyran **1**, the C_{spiro}—O bond is elongated to 1.49(1) Å (average) (1.50(1) and 1.48(1) Å in molecules **A** and **B**, respectively), and the O(1)—C(8a) bonds (1.34(1) and 1.32(1) Å) are shortened. Note also the substantial shortening of the S—C(6) bond (1.698(9) and 1.694(9) Å) compared to this bond (1.772(5) Å) in diphenyl sulfone.[9] This distribution of bond lengths in spiropyrans with 6-electron-withdrawing substituents is attributable to the substantial contribution of the quinoid resonance structure:



This is also indicated by the shortening of the C(4a)—C(5) and C(7)—C(8) bonds (1.34—1.37 Å) in the benzene nucleus.

Hence, the introduction of electron-withdrawing substituents in the *para*-position with respect to the O atom causes the enhancement of the conjugation between the π-component of the lone electron pair of the O atom and the benzene nucleus through the additional transfer of electron density from the O atom to the electron-withdrawing substituent. The decrease in the electron density on the O atom causes the further polarization of the C_{spiro}—O bond, which results in a decrease in the energy of the σ*-orbital of the C_{spiro}—O bond and its greater localization on the spiro C atom.[10] This causes the enhancement of the n_N-σ*-interaction and weakening and elongation of the C_{spiro}—O bond.

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