Photochromic dihetarylethenes

4.* The molecular and crystal structures of 1,2-bis(2-ethyl-5-ethylsulfonylthien-3-yl)perfluorocyclopentene and 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene

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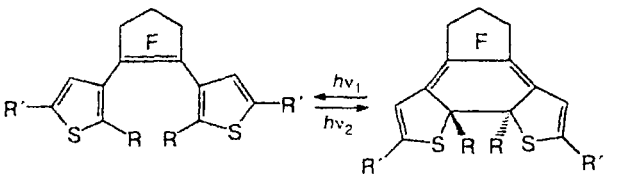
The structures of two hetarylethene photochromes, *viz.*, 1,2-bis(2-ethyl-5-ethylsulfonylthien-3-yl)perfluorocyclopentene and 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene, were established by X-ray diffraction analysis. The conformational parameters of the title compounds are considered. The cyclopentene ring in the former compound is planar and this ring in the latter compound adopts an envelope conformation. There are no overall conjugated systems in the molecules under study. In both structures, the dihetaryl fragments are rotated with respect to the perfluorocyclopentene fragments by ~55°. The thiophene and benzoxazole rings in 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene are coplanar.

Key words: dithienylethenes, 1,2-bis(2-ethyl-5-ethylsulfonylthien-3-yl)perfluorocyclopentene, 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene, photochromes, X-ray diffraction analysis, conformation.

With the aim of preparing promising organic photochromes based on dithienylperfluorocyclopentenes, we studied the effect of substituents of different nature in the thiophene rings on the spatial structure of these compounds and their photochemical properties.

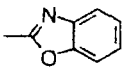
Previously,[2] we have established the molecular and crystal structure of 1,2-bis(2-ethylthiothien-3-yl)perfluorocyclopentene (**1**) and found that the alkylthio groups at positions 2 and 2′ of the thiophene rings are responsible for the formation of stable "open" form **A**, which does not exhibit photochromic properties under UV irradiation, *i.e.*, it does not undergo cyclization to form **B**. To our knowledge, data on the structures of compounds analogous to **A** are lacking in the literature. The only exception is the study[3] in which mention was made of the determination of the crystal structure of 1,2-bis(5-formyl-2-methylthien-3-yl)perfluorocyclopentene. However, the geometric and conformational parameters of the latter compound were not reported.[3] These data are also unavailable in the Cambridge Structural Database.[4]

In the present work, we performed X-ray diffraction study of 1,2-bis(2-ethyl-5-ethylsulfonylthien-3-yl)perfluorocyclopentene (**2**) and 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene (**3**). The syntheses of the title compounds have been reported previously.[1,5]



A **B**

1: R = SEt, R′ = H
2: R = Et, R′ = SO_2Et

3: R = Me, R′ = 

When irradiated with UV light (λ = 313 nm), a colorless ethanolic solution of compound **2** developed a dark-violet color, *i.e.*, dithienylethene **2**, unlike compound **1**, exhibits photochromic properties.[5] In the crystal, molecule **2** (Fig. 1)* has the symmetry C_2. The molecular axis passes through the C(7) atom and the

* For Part 3, see Ref. 1.

* The atomic numbering scheme used in the figures and tables differs from the chemical one and corresponds to that used in the program packages for X-ray diffraction analysis.

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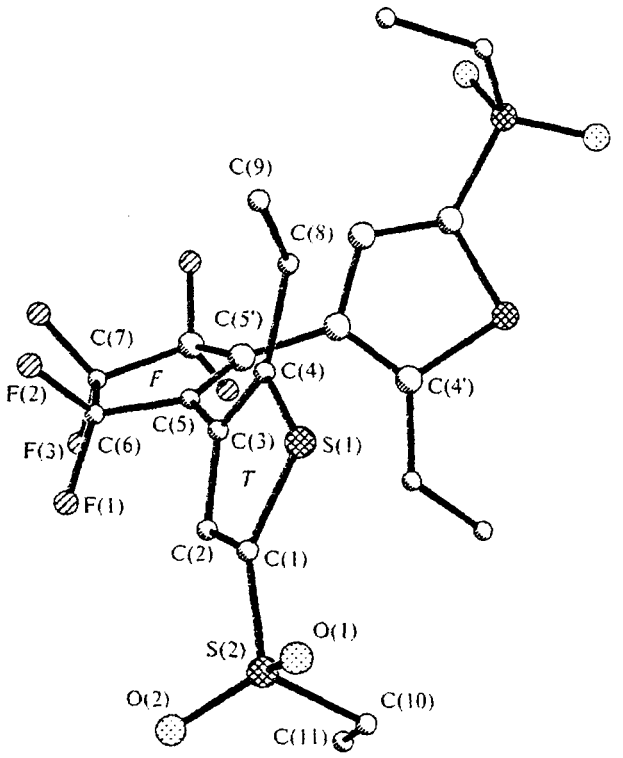

Fig. 1. Structure of molecule **2** (the hydrogen atoms are omitted). The atoms generated from the basis atoms by the symmetry operation $-x, y, -z + 3/2$ are primed.

center of the ethylene bond and coincides with the crystallographic twofold axis. The perfluorocyclopentene fragment (*F*) and the thiophene rings (*T*) are planar to within 0.006 Å. The dihedral angle between their planes is 56.2° (Table 1), which differs only slightly from the analogous angle in the structure of **1**. The dihedral angle between the symmetrical thiophene rings in molecule **2** is 23° smaller than the average value of the analogous angles in the structure of **1** (74.4°). As a result, the C(4)...C(4′) distance between the reaction centers is substantially shorter (3.45 Å) than that in molecule **1** (3.97 Å), *i.e.*, this distance is more favorable for intramolecular cyclization. The ethyl substituents at positions 2 of the thiophene rings are in *trans* orientations with respect to the *F* ring. The sulfonyl group is located asymmetrically relative to the plane of the *T* ring. The O(1)—S(2)—C(1)—S(1) and O(2)—S(2)—C(1)—S(1) dihedral angles are 16.1° and 145.4°, respectively. The O(1) and O(2) atoms deviate from the plane of the *T* ring by 0.133 and 0.635 Å, respectively. The S(1)....O(1) distance (3.046 Å) is close to the normal contact (3.08 Å). The thienylsulfonyl fragment in the thienylsulfonyl derivative of oxathiazol-2-one has an analogous structure.[6] All bond lengths and bond angles in molecule **2** have virtually standard values.[7]

In the crystal structure, molecules **2** are packed in stacks along the *b* axis in a "head-to-head" fashion. No shortened intermolecular contacts are observed.

The structure of compound **3** is of particular interest because, according to the published data,[1] cyclization of this compound in an ethanolic solution is completely photoreversible. The crystal structure of compound **3** consists of two independent molecules **3a** (Fig. 2) and **3b**, which differ only in the conformational parameters, *viz.*, in the angles of rotation of the benzoxazole fragments (B^1 and B^2) with respect to the thiophene rings (T^1 and T^2) (see Table 1) and in the conformational angles in the *F* ring (Table 2). The T^1, T^2, B^1, and B^2 rings in both molecules are planar to within 0.003 Å. In molecule **3a**, the B^1 and B^2 rings differ in the angle of rotation about the thiophene—benzoxazole bond by ~180°. Noteworthy is the conformation of the *F* ring. This ring in compound **3**, unlike those in the structures of **1** and **2**, adopts an envelope conformation with the C(4) atom at the flap, which deviates from the plane through the remaining four atoms by 0.315 and 0.409 Å in **3a** and **3b**, respectively. The torsion angles in molecules **3a** and **3b** differ by no more than 7—8° (see Table 2). Interestingly, the *F* ring in the "closed" form of the photochrome bis(4-chlorobenzoate)-1,2-bis(5-hydroxymethyl-2-methylthien-3-yl)hexafluorocyclopentene[8] also adopts an envelope conformation and the

Table 1. Dihedral angles (φ) and the conformation of the perfluorocyclopentene fragment in compounds **1**—**3**

Angle, ring	φ/deg				
	1a	**1b**	**2**	**3a**	**3b**
T^1/F	57.8	54.0	56.2(1)	55.2(1)	53.1(1)
T^2/F	59.8	59.4	56.2(1)	55.1(1)	51.1(1)
T^1/T^2	75.7	73.2	51.4(1)	60.8(1)	55.8(1)
B^1/T^1	—	—	—	3.38(7)	6.7(1)
B^2/T^2	—	—	—	17.4(2)	3.06(7)
F	Planar	Planar	Planar	Envelope	Envelope

Note. **1a** and **1b** are independent molecules in the structure of **1**; **3a** and **3b** are independent molecules in the structure of **3**.

Table 2. Torsion angles (τ) in the *F* ring of compound **3**

Angle	τ/deg	
	3a	**3b**
C(1)—C(2)—C(3)—C(4)	−12.2(3)	−16.5(3)
C(2)—C(3)—C(4)—C(5)	18.7(3)	24.9(3)
C(3)—C(4)—C(5)—C(1)	−18.7(3)	−24.6(3)
C(4)—C(5)—C(1)—C(2)	12.3(3)	15.7(3)
C(5)—C(1)—C(2)—C(3)	0.03(3)	0.54(3)

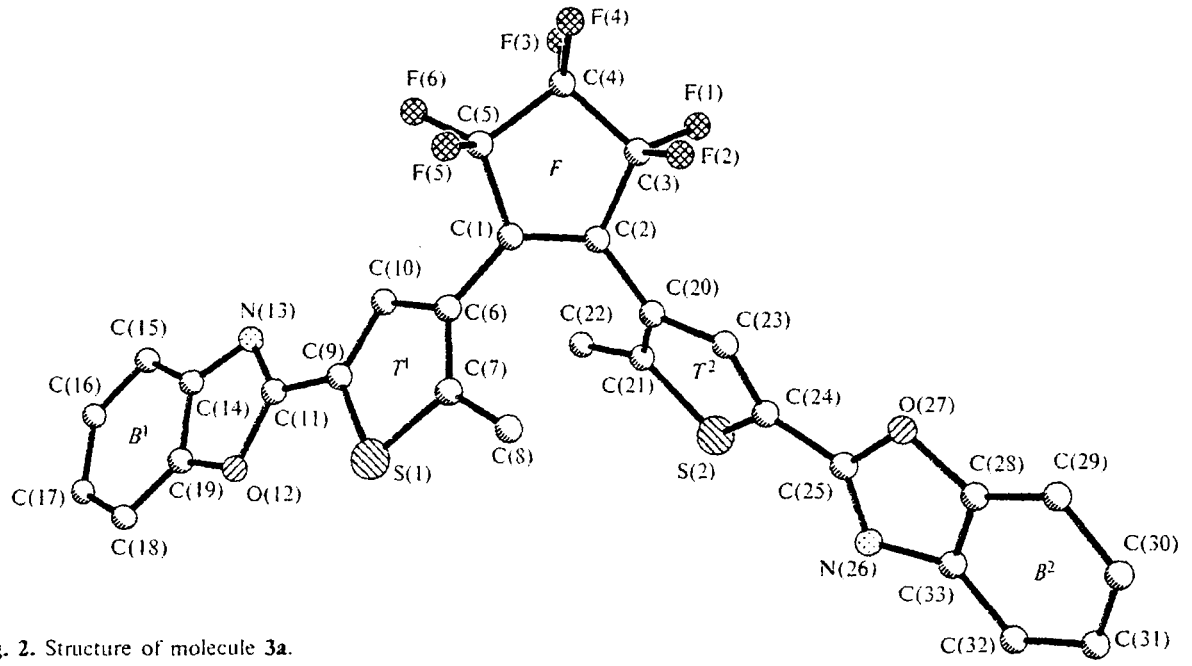

Fig. 2. Structure of molecule **3a**.

torsion angles are close to the corresponding angles in molecule **3b**.

Another distinguishing structural feature of compound **3** is the formation of the planar and extended conjugated thiophene—benzoxazole system. Thus, the angles of rotation of the benzoxazole fragments with respect to the *T* rings in molecule **3b** and of the B^1 fragment with respect to the T^1 ring in molecule **3a** are no larger than 3—6°. A somewhat larger dihedral angle between the B^2 and T^2 fragments (~17°) in molecule **3a** is, apparently, determined by the effect of the crystal field and has no substantial influence on the character of conjugation. This is also confirmed by a noticeable shortening of all C(*T*)—C(*B*) bonds in the conjugated system (on the average, to 1.442 Å) compared to the average value of the C(*F*)—C(*T*) bond lengths (1.470 Å) in the absence of conjugation. The remaining conformational parameters, *viz.*, the T^1/F, T^2/F, and T^1/T^2 dihedral angles, are comparable with the analogous angles in molecule **2**. The C(7)...C(21) distance between the potential reaction centers is 3.643(4) and 3.537(4) Å in molecules **3a** and **3b**, respectively. The bond lengths and bond angles in the structure of **3** have standard values. No shortened intermolecular contacts are observed.

In conclusion, it should be noted that in all dithenylperfluorocyclopentenes **1**—**3** studied in open form **A**, the angle of rotation of the cyclopentene ring with respect to the thienyl fragment is virtually identical (~55°), *i.e.*, this angle is independent of the nature of substituents in the thiophene rings. This is indicative of the absence of a common conjugation system between the ethene fragment and the dihetaryl substituents in the molecules under consideration.

Experimental

X-ray diffraction study of 1,2-bis(2-ethyl-5-ethylsulfonylthien-3-yl)perfluorocyclopentene (2) and 1,2-bis[5-(benzoxazol-2-yl)-2-methylthien-3-yl]perfluorocyclopentene (3). The intensities of reflections were measured on an automated four-circle Syntex $P2_1$ diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique). The structures were solved by the direct method and refined based on F^2 (with the use of all independent reflections) by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the hydrogen atoms were located from difference electron density syntheses and refined isotropically by the least-squares method. Calculations were carried out with the use of the SHELXTL PLUS (Version 5.03+) and AREN-90 program packages. The atomic coordinates, the thermal parameters, and the geometric parameters of molecules **2** and **3** were deposited in the Cambridge Structural Database.

Compound 2. Colorless transparent rhombic crystals of composition $C_{21}H_{22}F_6O_4S_4$ were obtained from an ethanol—chloroform mixture. The unit cell parameters are as follows: a = 15.965(7) Å, b = 16.855(8) Å, c = 9.075(4) Å, V = 2442(2) Å^3, d_{calc} = 1.579 g cm^{-3}, space group *Pbcn*, Z = 4. Intensities of 3185 independent reflections were measured at −60 °C. The reliability factor R_1 was 0.038 using 2839 reflections with $I > 2\sigma(I)$. For all observed reflections, wR_2 = 0.117.

Compound 3. Colorless triclinic crystals of composition $C_{29}H_{16}F_6N_2O_2S_2$ were prepared from a solution in chloroform. At −70 °C, a = 13.065(4) Å, b = 14.131(4) Å, c = 15.743(4) Å, α = 93.54(2)°, β = 98.12(2)°, γ = 113.86(2)°, V = 2609(1) Å^3, d_{calc} = 1.534 g cm^{-3}, space group $P\bar{1}$, Z = 4. A total of 9017 independent reflections were measured. The structure was refined by the least-squares method using 6611 reflections with $I > 2\sigma(I)$ to R_1 = 0.047 and wR_2 = 0.130. The reliability factor R_1 taking into account all measured reflections was 0.079.

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