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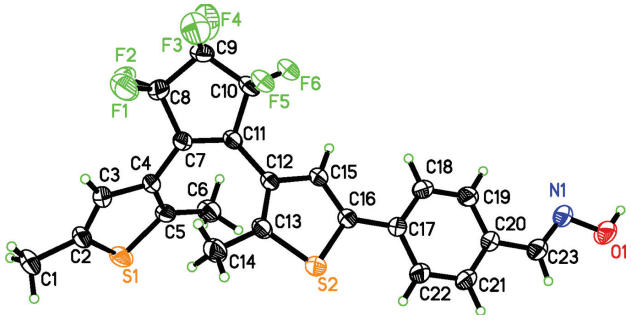
Crystal structure and photochromism of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(benzaldoxime)-3-thienyl] perfluorocyclopentene, $C_{23}H_{17}F_6NOS_2$



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Abstract

$C_{23}H_{17}F_6NOS_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.379(3)$ Å, $b = 11.509(2)$ Å, $c = 12.817(3)$ Å, $\alpha = 71.272(3)°$, $\beta = 81.342(4)°$, $\gamma = 77.553(3)°$, $V = 1138.7(5)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0489$, $wR_{ref}(F^2) = 0.1296$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of materials

To a stirred solution of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(benzaldehyde-4-yl)-3-thenyl)]perfluorocyclopentene [5] (0.24 g; 0.5 mmol) in ethanol (2.5 mL), hydroxylamine hydrochloride (0.035 g; 0.5 mmol) was added and continuously stirred. After refluxing for 5 h, the mixture was cooled to room temperature and concentrated under vacuum. The product was purified by flash chromatography with

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.28 × 0.26 × 0.17 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.30 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5853, 3980, 0.017
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2858
$N(param)_{refined}$:	381
Programs:	Bruker programs [1], SHELX [2–4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
N1	0.9965(4)	0.1385(3)	0.4543(2)	0.0669(8)
O1	1.0967(3)	0.0720(2)	0.3874(2)	0.0886(8)
H1E	1.0990	−0.0029	0.4170	0.133*
S1	0.59918(11)	1.04064(8)	0.82370(8)	0.0677(3)
S2	0.53463(12)	0.76401(7)	0.53506(7)	0.0628(3)
C8	0.1935(4)	0.7602(3)	0.9962(3)	0.0697(9)
F1[a]	0.0598(8)	0.8465(5)	0.9990(9)	0.155(3)
F2[a]	0.2725(12)	0.7392(9)	1.0888(3)	0.138(3)
F1′[b]	0.0493(12)	0.8362(12)	0.9577(14)	0.069(3)
F2′[b]	0.2053(15)	0.7993(13)	1.0812(9)	0.073(4)
C9	0.1548(3)	0.6354(3)	1.0059(2)	0.0549(7)
F3[c]	−0.0003(8)	0.6230(9)	1.0358(12)	0.082(3)
F4[c]	0.2421(19)	0.5580(8)	1.0901(6)	0.083(3)
F3′[d]	−0.0035(9)	0.6623(14)	0.9817(16)	0.101(3)
F4′[d]	0.159(2)	0.5446(6)	1.1010(5)	0.082(3)
C10	0.2385(4)	0.6033(3)	0.9044(3)	0.0638(8)
F5[a]	0.1430(11)[a]	0.5787(10)	0.8424(4)	0.146(3)
F6[a]	0.3485(9)[a]	0.4952(4)	0.9419(6)	0.118(2)
F5′[b]	0.0987(12)	0.6305(11)	0.8500(12)	0.062(3)
F6′[b]	0.2983(16)	0.4852(6)	0.9105(12)	0.065(3)
C1	0.3505(6)	1.2412(3)	0.8404(4)	0.0916(13)
H1A	0.2334	1.2604	0.8543	0.137*
H1B	0.3835	1.2914	0.7678	0.137*
H1C	0.4020	1.2584	0.8945	0.137*
C2	0.4014(5)	1.1053(3)	0.8474(3)	0.0637(9)
C3	0.3037(4)	1.0192(3)	0.8737(3)	0.0574(8)
H3A	0.1909	1.0368	0.8907	0.069*
C4	0.3906(3)	0.8987(2)	0.8729(2)	0.0448(6)
C5	0.5545(4)	0.8953(3)	0.8479(2)	0.0501(7)
C6	0.6879(5)	0.7887(4)	0.8421(4)	0.0688(10)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C7	0.3121(3)	0.7897(2)	0.8973(2)	0.0447(6)
C11	0.3319(3)	0.7049(2)	0.8430(2)	0.0437(6)
C12	0.4210(3)	0.7031(2)	0.7362(2)	0.0439(6)
C13	0.4194(4)	0.8045(3)	0.6440(2)	0.0516(7)
C14	0.3326(6)	0.9357(3)	0.6273(4)	0.0684(10)
C15	0.5164(3)	0.5933(2)	0.7155(2)	0.0471(7)
H15A	0.5287	0.5161	0.7694	0.056*
C16	0.5876(4)	0.6102(3)	0.6116(2)	0.0495(7)
C17	0.6920(4)	0.5195(3)	0.5613(2)	0.0500(7)
C18	0.7212(5)	0.3940(3)	0.6188(3)	0.0723(10)
H18A	0.6752	0.3672	0.6912	0.087*
C19	0.8158(5)	0.3083(3)	0.5719(3)	0.0736(10)
H19A	0.8319	0.2245	0.6128	0.088*
C20	0.8877(4)	0.3432(3)	0.4659(3)	0.0563(8)
C21	0.8621(5)	0.4678(3)	0.4091(3)	0.0723(10)
H21A	0.9101	0.4943	0.3372	0.087*
C22	0.7673(5)	0.5545(3)	0.4559(3)	0.0685(9)
H22A	0.7538	0.6386	0.4155	0.082*
C23	0.9867(4)	0.2543(3)	0.4124(3)	0.0663(9)
H23A	1.0450	0.2844	0.3447	0.080*
H14A	0.232(5)	0.937(3)	0.671(3)	0.077(12)*
H14B	0.309(4)	0.971(3)	0.556(3)	0.082(12)*
H14C	0.401(5)	0.982(4)	0.646(3)	0.085(12)*
H6A	0.665(4)	0.712(4)	0.893(3)	0.083(12)*
H6C	0.787(6)	0.802(4)	0.850(4)	0.125(17)*
H6B	0.702(6)	0.776(4)	0.767(4)	0.123(17)*

Occupancies: [a] = 0.748(15), [b] = 0.0.252(15), [c] = 0.54(2), [d] = 0.46(2)

petroleum ether/ethyl acetate = 4/1 as the eluant to give the title compound with a yield of 75%. The title compound crystallized from hexane at room temperature. **Mp**. 306–307 K; **^{1}H NMR** (400 MHz), CD_3CN, TMS): (ppm): 1.80 (s, 3H, -CH_3), 1.88 (s, 3H, -CH_3), 2.08 (s, 1H, -OH), 2.3280 (s, 3H, -CH_3), 6.71 (s, 1H, thiophene-H), 8.95 (d, 1H, J = 4 Hz, = CH-), 7.51 (m, 2H, phenyl-H), 8.01 (d, 2H, J = 4 Hz, phenyl-H), 8.95 (d, 1H, J = 4 Hz, = CH-); **^{13}C NMR** (100 MHz), CD_3CN, TMS): (ppm): 13.85, 13.96, 14.62, 102.80, 113.62, 114.27, 123.44, 123.89, 124.37, 125.29, 125.55, 126.95, 128.65, 129.84, 134.99, 135.13, 138.17, 139.66, 140.69, 142.10, 154.12.

Experimental details

All non-hydrogen atoms were refined anisotropically. The fluorine atoms of the central cyclopentene ring show extensive disorder. A two-site split model was used in the refinement yielding ratios of 0.748(15) : 0.252(15) for F1/F2 : F1′/F2′, 0.54(2) : 0.46(2) for F3/F4 : F3′/F4′ and 0.748(15) : 0.252(15) for F5/F6 : F5′/F6′. All H atoms attached to C were fixed geometrically and treated as riding with C—CH = 0.96 Å (methyl) with U_{iso}(H) = 1.2U_{eq} (thienyl) or U_{iso}(H) = 1.5U_{eq} (methyl, hydroxy).

Comment

Organic photochromic dyes represent a rapidly expanding area of molecular switches due to their wide applications in optical memory media [6], photo- and supramolecular chemistry [7], materials science [8], optogenetics [9], and bioimaging [10]. As representative of photochromic compounds, diarylethene derivatives can undergo reversible changes due to high thermal stability [6], rapid response [6], and fatigue resistance [11], and high reactivity in the solid state [12].

On one hand, molecular modification is one of the most important methods to improve the photochromic performance of diarylethenes. Generally, the photochromic characteristics of diarylethenes strongly depend on the functional substituents [13]. Recently we have reported a series of photochromic diarylethenes bearing different substituents, such as trifluoromethyl, fluorine, chlorine, methoxy and methyl. Aryl aldoximes are important reaction ragents that exhibit biological activity. However, photochromic diarylethenes with aldoxime substituents have not hitherto been reported.

On the other hand, most research on photochromic diarylethenes concentrate on their tautomerization between the bistable states in solution or in polymer blends and limited examples show tunable tautomerization in constraint crystal states. The application of fluorescent photo switching molecules would be facilitated in the solid state, in particular in the crystalline state for ease of use. Several photochromic diarylethenes have been reported but reports of their crystal structures remain limited [14–17]. On the basis of these considerations, we have explored a aldoxime-containing diarylethene 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(benzaldehyde)-3-thienyl]perfluorocyclopentene and investigated its photochromism both in crystalline solids and in solution. The title compound, $C_{23}H_{17}F_6NOS_2$, is a new asymmetrical hybrid photochromic diarylethene derivative.

The title molecule adopts a photo-active antiparallel conformation. In the cyclopentene ring, the two thiophene rings are linked by the C7 = C11 double bond [1.340(4) Å]. The two methyl groups are located on opposite sides of the C7 = C11 double bond and this configuration is crucial to allow the compound to exhibit photochromic and photoinduced properties [18]. Upon UV-light irradiation the open-ring isomer of the diarylethene undergoes a 6π-electrocyclization to furnish the closed-ring isomer which can be back-converted upon exposure to visible light. The distance between the two photoreactive C atoms (C5···C13) is 3.515 Å. This distance indicates that the crystal can be expected to undergo photochromic reaction to form the closed ring isomer because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 Å [19, 20]. Upon irradiation with 297 nm light, the color change of the single-crystals

from colorless to purple as the ring-closed isomer is observed. When the purple crystals were dissolved in acetonitrile, the acetonitrile solution also showed a purple color, with a band in the visible region centred at 599 nm, accompanied with the formation of the closed-ring isomer. It should be noted that the purple crystals can revert to their initial colorless state upon irradiation with visible light ($\lambda > 500$ nm), and the absorption spectrum of an acetonitrile solution prepared from the colourless crystals is the same as that of a solution of the open ring form, with an absorption maximum at 319 nm.

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