Crystal structure of [1-(2,5-dimethyl-3-thienyl)-2-(2-ethyl-5-formyl-3-thienyl)]- 3,3,4,4,5,5-hexafluorocyclopentene, $C_{18}H_{14}F_6OS_2$

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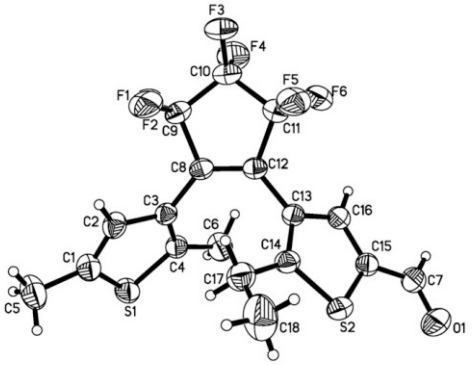
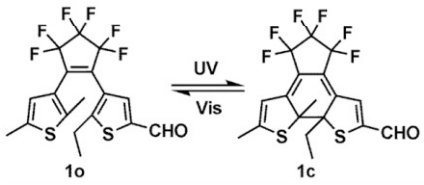
Received November 24, 2011, accepted April 17, 2012, available online July 05, 2012, CCDC no. 1267/3760





Abstract

$C_{18}H_{14}F_6OS_2$, monoclinic, $P2_1/c$ (no. 14), a = 12.720(2) Å, b = 9.029(2) Å, c = 16.794(3) Å, β = 99.914(2)°, V = 1900.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0478, $wR_{ref}(F^2)$ = 0.1418, T = 291 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.34×0.36×0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.41 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13997, 3534
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2519
$N(param)_{refined}$:	275
Programs:	SHELXS-97 [16]

Experimental details

All H atoms attached to C were fixed geometrically and treated by a riding model with C–H = 0.96 Å (methyl) or 0.93 Å (aromatic) with U_{iso}(H) = 1.2 U_{eq}(aromatic) or U_{iso}(H) = 1.5 U_{eq}(methyl). The F atoms attached to the C atoms in cyclopentene ring are disordered over two crystallographic sites. The occupancy factors of the two positions were refined using an overall isotropic thermal parameter and by restraining the sum of the occupancy to remain equal to 1.0. The ratio between the two occupancies was found to be 0.89/0.11. The C-F distances were restrained using SADI (SHELXL-97) instructions and similar U_{ij} restraints as well as rigid bond restraints were used in the final refinement cycles.

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Source of material

The (2,5-dimethyl-3-thienyl)perfluorocyclopentene (1.52 g, 5.0 mmol) was reacted with 4-bromo-5-ethyl-2-(1,3-dioxolane) -thiophene (1.32 g, 5.0 mmol) in the presence of *n*-butyllithium (2.5 M in hexane, 2.0 ml, 5.0 mmol) at 195 K under a nitrogen atmosphere. After an hour, the reaction was quenched by the addition of water. The solid product was purified by column chromatography on silica using petroleum ether as the eluant to give the compound {1-(2,5-dimethyl-3-thienyl)-2-[2-ethyl-5-(1,3-dioxolane)-3-thienyl]}-3,3,4,4,5,5-hexafluorocyclopentene (1.17 g, 2.50 mmol, yield 50%). This compound (1.17 g, 2.50 mmol) and p-toluenesulfonic acid (0.4 g) were dissolved in mixture of water (30 mL) and acetone (90 mL); 2 mL pyridine was added into the mixture and reaction mixture was refluxed for 24 h. After stopping the reaction, the mixture was washed sequentially by aqueous $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using ethyl acetate and petroleum ether mixture (v/v=1/6) as the eluent to give 0.90 g of the title compound (figure, top) in 85% yield.
Analysis calculated for $C_{18}H_{14}F_6O_1S_2$: C 50.94%, H 3.32%; found: C 50.92%, H 3.37%.

Discussion

Photochromism is a light-initiated, nondestructive process resulting in reversible transformation between two isomeric forms that have remarkable differences not only in their absorption spectra, but also in various physical and chemical properties, such as fluorescence [1,2], refractive index [3,4], chiral [5], magnetic [6], oxidation-reduction potential [7-9], and geometric structure [10]. Among the photochromic compounds, diarylethene derivatives are the most promising candidates for potential application to optical memory media and optical switches because of their thermal stability and fatigue resistance. Hence, the synthesis of diarylethene derivatives and investigation of their structural features are of both scientific and practical interest. The molecular structure (1o) is shown. In the cyclopentene ring, it is clear that the C8–C12 bond is a double bond, while the others in the ring are single bonds. The two thiophene rings are linked by the C8=C12 bond. The methyl and ethyl rings are located on opposite sides of the double bond and are directed trans relative to the thiophene planes, as reflected in the torsion angles 127.69° for C11–C12–C13–C14 and 135.23° for C4–C3–C8–C7. The dihedral angle between the main central cyclopentene ring and adjacent thiophene ring are 54.0° for S1/C1–C4 and 53.5° for S2/C13–16. The conformation leads to a C4–C14 separation of 3.664 Å. This distance is short enough, theoretically, for a ring-closure reaction

to take place in the crystalline phase to generate an isomeric compound (figure, bottom). It is known that photochromic activity in similar compounds is usually present when this distance is less than 4.2Å [11,12]. We have been able to verify this experimentally. Upon irradiation with 297 nm light, the colorless single crystals of the title compound turned blue quickly to form the ring closure isomer (figure, bottom). When the blue crystal was dissolved in dichloromethane, the solution also showed a blue color, with an absorption maximum at 582 nm, consistent with the closed-ring isomer 1c. Upon irradiation with visible light with wavelength greater than 510 nm, the blue crystal can return to its initial colorless state, and the absorption spectrum of the dichloromethane solution containing the colorless crystal is the same as that of solution of the open-ring form 1o, with the absorption maximum at 252 nm. In a poly(methyl methacylate) amorphous film, the title diarylethene also demonstrates photochromism. Yamamoto et al. [13] have tested photocyclization of a photochromic diarylethene derivative in single crystals. The results showed a photogenerated closed-ring diarylethene whose occupancy was estimated to be roughly 9%. In order to prove that the diarylethene crystal structure is changed by UV light, we hope to design an experiment where a continually irradiated crystal can be subjected to *X*-ray crystallographic analysis to see if changes in the intensities and the unit cell can be observed and interpreted.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	4*e*	0.7018	0.4332	1.1020	0.067
H(5A)	4*e*	0.8349	0.4885	1.2343	0.136
H(5B)	4*e*	0.9400	0.5514	1.2105	0.136
H(5C)	4*e*	0.9370	0.3887	1.2426	0.136
H(6A)	4*e*	0.8279	0.1883	0.8835	0.113
H(6B)	4*e*	0.9456	0.1726	0.9292	0.113
H(6C)	4*e*	0.9099	0.3167	0.8799	0.113
H(7)	4*e*	0.8029	0.4244	0.6022	0.082
H(16)	4*e*	0.6964	0.3266	0.7174	0.062
H(17A)	4*e*	0.6669	0.6523	0.9373	0.082
H(17B)	4*e*	0.7916	0.6523	0.9605	0.082
H(18A)	4*e*	0.8002	0.8736	0.8940	0.178
H(18B)	4*e*	0.7245	0.8913	0.9578	0.178
H(18C)	4*e*	0.6761	0.8725	0.8660	0.178

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(1)	4*e*	0.889	0.5194(2)	0.3331(3)	1.0214(2)	0.063(1)	0.139(2)	0.095(1)	–0.021(1)	0.046(1)	–0.034(2)
F(2)	4*e*	0.889	0.5939(3)	0.1221(2)	1.0109(2)	0.081(1)	0.088(2)	0.106(2)	–0.028(1)	0.001(1)	0.042(1)
F(3)	4*e*	0.889	0.3841(1)	0.2403(3)	0.9022(1)	0.0391(9)	0.149(2)	0.099(1)	–0.021(1)	0.0155(9)	0.011(2)
F(4)	4*e*	0.889	0.4958(2)	0.0783(2)	0.8715(1)	0.111(2)	0.070(1)	0.103(2)	–0.027(1)	0.013(1)	–0.003(1)
F(5)	4*e*	0.889	0.4541(1)	0.4417(2)	0.8187(1)	0.046(1)	0.093(1)	0.108(2)	0.0090(9)	0.004(1)	0.024(1)
F(6)	4*e*	0.889	0.5129(2)	0.2569(3)	0.7583(1)	0.071(1)	0.118(2)	0.065(1)	–0.032(1)	0.0051(9)	–0.016(1)
C(9)	4*e*	0.889	0.5664(2)	0.2479(3)	0.9708(2)	0.048(1)	0.061(2)	0.065(2)	–0.005(1)	0.021(1)	0.006(1)
C(10)	4*e*	0.889	0.4861(2)	0.2193(4)	0.8934(2)	0.047(1)	0.069(2)	0.077(2)	–0.013(1)	0.014(1)	–0.001(2)
C(11)	4*e*	0.889	0.5212(2)	0.3240(3)	0.8309(2)	0.047(1)	0.064(2)	0.062(2)	–0.004(1)	0.005(1)	–0.001(1)
F(1')	4*e*	0.111	0.519(2)	0.374(3)	1.026(2)	0.063(1)	0.139(2)	0.095(1)	–0.021(1)	0.046(1)	–0.034(2)
F(2')	4*e*	0.111	0.597(2)	0.163(2)	1.027(2)	0.081(1)	0.088(2)	0.106(2)	–0.028(1)	0.001(1)	0.042(1)
F(3')	4*e*	0.111	0.406(1)	0.337(2)	0.916(1)	0.0391(9)	0.149(2)	0.099(1)	–0.021(1)	0.0155(9)	0.011(2)
F(4')	4*e*	0.111	0.439(2)	0.113(2)	0.885(1)	0.111(2)	0.070(1)	0.103(2)	–0.027(1)	0.013(1)	–0.003(1)
F(5')	4*e*	0.111	0.477(1)	0.400(2)	0.785(1)	0.046(1)	0.093(1)	0.108(2)	0.0090(9)	0.004(1)	0.024(1)
F(6')	4*e*	0.111	0.557(1)	0.192(2)	0.779(1)	0.071(1)	0.118(2)	0.065(1)	–0.032(1)	0.0051(9)	–0.016(1)
C(9')	4*e*	0.111	0.5621(9)	0.279(2)	0.9799(8)	0.048(1)	0.061(2)	0.065(2)	–0.005(1)	0.021(1)	0.006(1)
C(10')	4*e*	0.111	0.484(1)	0.245(2)	0.9031(9)	0.047(1)	0.069(2)	0.077(2)	–0.013(1)	0.014(1)	–0.001(2)
C(11')	4*e*	0.111	0.5307(8)	0.293(2)	0.8298(8)	0.047(1)	0.064(2)	0.062(2)	–0.004(1)	0.005(1)	–0.001(1)
S(1)	4*e*		0.95299(5)	0.34387(9)	1.06998(4)	0.0427(3)	0.0963(5)	0.0608(4)	0.0005(3)	0.0065(3)	–0.0030(4)
S(2)	4*e*		0.80936(5)	0.66557(8)	0.77306(4)	0.0584(4)	0.0674(4)	0.0603(4)	–0.0168(3)	0.0160(3)	0.0016(3)
O(1)	4*e*		0.8757(2)	0.6002(3)	0.6117(1)	0.094(2)	0.142(2)	0.077(1)	–0.040(2)	0.037(1)	0.003(1)
C(1)	4*e*		0.8619(2)	0.4104(3)	1.1262(2)	0.062(2)	0.068(2)	0.054(2)	0.004(1)	0.009(1)	–0.003(1)
C(2)	4*e*		0.7622(2)	0.4037(3)	1.0820(1)	0.051(1)	0.067(2)	0.052(1)	0.009(1)	0.017(1)	0.002(1)
C(3)	4*e*		0.7582(2)	0.3475(2)	1.0022(1)	0.040(1)	0.053(1)	0.048(1)	0.0019(9)	0.0110(9)	0.004(1)
C(4)	4*e*		0.8567(2)	0.3087(3)	0.9868(1)	0.041(1)	0.068(2)	0.049(1)	0.002(1)	0.010(1)	0.004(1)
C(5)	4*e*		0.8966(3)	0.4647(4)	1.2110(2)	0.092(2)	0.117(3)	0.060(2)	0.006(2)	0.005(2)	–0.018(2)
C(6)	4*e*		0.8878(2)	0.2405(4)	0.9133(2)	0.054(2)	0.110(2)	0.065(2)	0.015(2)	0.019(1)	–0.010(2)
C(7)	4*e*		0.8212(2)	0.5067(4)	0.6349(2)	0.060(2)	0.094(2)	0.054(2)	–0.011(2)	0.016(1)	–0.001(2)
C(8)	4*e*		0.6585(2)	0.3280(3)	0.9445(1)	0.037(1)	0.053(1)	0.054(1)	0.0010(9)	0.014(1)	–0.000(1)
C(12)	4*e*		0.6336(2)	0.3690(2)	0.8671(1)	0.041(1)	0.050(1)	0.054(1)	–0.0013(9)	0.011(1)	–0.002(1)
C(13)	4*e*		0.6974(2)	0.4581(3)	0.8191(1)	0.039(1)	0.055(1)	0.047(1)	0.000(1)	0.0066(9)	0.004(1)
C(14)	4*e*		0.7399(2)	0.5940(3)	0.8432(1)	0.044(1)	0.056(1)	0.056(1)	–0.005(1)	0.012(1)	–0.000(1)
C(15)	4*e*		0.7821(2)	0.5145(3)	0.7114(1)	0.041(1)	0.069(2)	0.049(1)	–0.002(1)	0.007(1)	0.004(1)
C(16)	4*e*		0.7207(2)	0.4145(3)	0.7431(1)	0.048(1)	0.058(1)	0.048(1)	–0.003(1)	0.006(1)	–0.002(1)
C(17)	4*e*		0.7323(2)	0.6801(3)	0.9187(2)	0.077(2)	0.069(2)	0.064(2)	–0.009(1)	0.023(1)	–0.009(1)
C(18)	4*e*		0.7334(4)	0.8440(4)	0.9082(2)	0.198(5)	0.073(2)	0.083(3)	0.011(2)	0.018(3)	–0.017(2)

Acknowledgments. This work was supported by the Natural Science Foundation of Jiangxi (2010GZH0040, 2010GQH0038).

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