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Crystal structure of photochromic 1-(2-methyl-5-phenyl-3-thienyl-2-[2-methyl-5-(4-ethoxylphenyl)-3-thienyl] 3,3,4,4,5,5-hexafluoro-cyclopent-1-ene, $C_{29}H_{22}F_6OS_2$

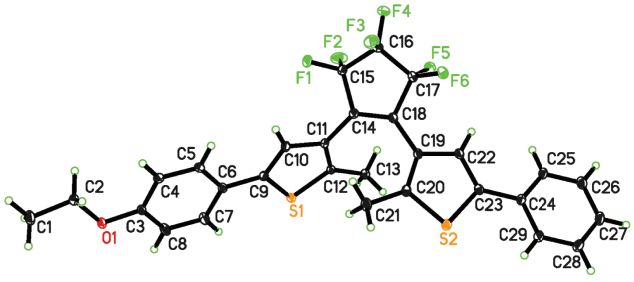

Figure: Molecular view of the title compound. Ellipsoids are drawn at 30% probability level.

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Abstract

$C_{29}H_{22}F_6OS_2$, monoclinic, $P2_1/c$, $a = 6.4504(2)$ Å, $b = 16.9752(4)$ Å, $c = 22.8762(6)$ Å, $\beta = 91.7790(10)°$, $V = 2503.66(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0377$, $wR_{ref}(F^2) = 0.1156$, $T = 100(2)$ K.

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The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared according to the literature method [1, 2] in 35.45% yield. Elemental analysis for $C_{29}H_{22}F_6OS_2$: calcd: C 61.69, H 3.93%; found: C 61.71, H 3.95%. The title compound crystallized from hexane at room temperature.

Upon irradiation with 297 nm light, the colorless single-crystals of the title structure turn blue quickly. When the blue

Table 1: Data collection and handling.

Crystal:	Colorless, block, size 0.26×0.28×0.42 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.80 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21976, 5746
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4806
$N(param)_{refined}$:	346
Programs:	SHELX [16]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	1.6534	0.6156	0.8291	0.053
H(1B)	4e	1.8022	0.6837	0.8107	0.053
H(1C)	4e	1.8097	0.6019	0.7789	0.053
H(2A)	4e	1.4777	0.7100	0.7688	0.029
H(2B)	4e	1.6262	0.6880	0.7180	0.029
H(4)	4e	1.3122	0.7311	0.6799	0.024
H(5)	4e	1.0231	0.7456	0.6194	0.024
H(7)	4e	0.8637	0.5213	0.6486	0.027
H(8)	4e	1.1506	0.5065	0.7102	0.027
H(10)	4e	0.7488	0.7602	0.5593	0.024
H(13A)	4e	0.1031	0.6437	0.4942	0.031
H(13B)	4e	0.1429	0.5619	0.5244	0.031
H(13C)	4e	0.2291	0.5784	0.4623	0.031
H(21A)	4e	0.7537	0.6964	0.4256	0.038
H(21B)	4e	0.8107	0.6250	0.3858	0.038
H(21C)	4e	0.6874	0.6109	0.4428	0.038
H(22)	4e	0.0708	0.7317	0.3362	0.022
H(25)	4e	−0.1483	0.6842	0.2633	0.026
H(26)	4e	−0.3442	0.6486	0.1809	0.031
H(27)	4e	−0.2082	0.5630	0.1131	0.035
H(28)	4e	0.1229	0.5142	0.1275	0.035
H(29)	4e	0.3203	0.5497	0.2094	0.029

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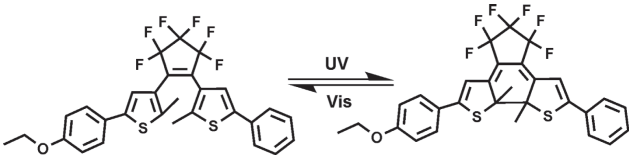
Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4e	1.7209(3)	0.6397(1)	0.7968(1)	0.030(1)	0.029(1)	0.045(1)	−0.0018(9)	−0.0200(9)	0.0005(9)
C(2)	4e	1.5597(3)	0.6680(1)	0.75242(8)	0.0218(9)	0.0212(9)	0.0278(9)	0.0013(7)	−0.0082(7)	−0.0043(7)
C(3)	4e	1.2625(3)	0.6171(1)	0.70114(7)	0.0143(8)	0.0209(8)	0.0147(8)	0.0032(6)	−0.0004(6)	−0.0012(6)
C(4)	4e	1.2223(3)	0.6889(1)	0.67380(8)	0.0210(9)	0.0155(8)	0.0243(9)	−0.0007(7)	−0.0029(7)	−0.0023(7)
C(5)	4e	1.0483(3)	0.6973(1)	0.63743(8)	0.0234(9)	0.0149(8)	0.0205(8)	0.0021(7)	−0.0027(7)	0.0012(6)
C(6)	4e	0.9098(3)	0.6356(1)	0.62697(7)	0.0171(8)	0.0186(8)	0.0145(8)	0.0018(7)	0.0005(6)	0.0007(6)
C(7)	4e	0.9529(3)	0.5637(1)	0.65490(8)	0.0197(9)	0.0207(9)	0.0277(9)	−0.0042(7)	−0.0050(7)	0.0070(7)
C(8)	4e	1.1258(3)	0.5546(1)	0.69172(8)	0.0201(9)	0.0208(9)	0.0271(9)	−0.0006(7)	−0.0032(7)	0.0088(7)
C(9)	4e	0.7273(3)	0.6473(1)	0.58768(7)	0.0185(8)	0.0170(8)	0.0156(8)	−0.0006(7)	−0.0007(6)	−0.0006(6)
C(10)	4e	0.6724(3)	0.7138(1)	0.55731(7)	0.0238(9)	0.0178(8)	0.0176(8)	−0.0019(7)	−0.0049(7)	0.0005(6)
C(11)	4e	0.4860(3)	0.7053(1)	0.52219(7)	0.0221(9)	0.0174(8)	0.0147(8)	0.0022(7)	−0.0044(6)	−0.0018(6)
C(12)	4e	0.3972(3)	0.6323(1)	0.52718(7)	0.0175(8)	0.0182(8)	0.0143(8)	0.0036(6)	−0.0010(6)	−0.0016(6)
C(13)	4e	0.2004(3)	0.6013(1)	0.49955(8)	0.0189(9)	0.0219(9)	0.0205(9)	0.0005(7)	−0.0019(7)	−0.0011(7)
C(14)	4e	0.3992(3)	0.7692(1)	0.48575(8)	0.0241(9)	0.0158(8)	0.0201(8)	−0.0002(7)	−0.0054(7)	−0.0010(7)
C(15)	4e	0.3562(4)	0.8480(1)	0.51352(8)	0.045(1)	0.0185(9)	0.0205(9)	0.0039(8)	−0.0116(8)	−0.0023(7)
C(16)	4e	0.3013(3)	0.9027(1)	0.46203(8)	0.036(1)	0.0169(9)	0.025(1)	0.0044(8)	−0.0066(8)	−0.0003(7)
C(17)	4e	0.2230(3)	0.8453(1)	0.41457(8)	0.028(1)	0.0216(9)	0.0194(9)	0.0050(8)	−0.0061(7)	0.0008(7)
C(18)	4e	0.3323(3)	0.7685(1)	0.42914(8)	0.0201(8)	0.0166(8)	0.0197(8)	−0.0002(7)	−0.0047(7)	0.0012(7)
C(19)	4e	0.3463(3)	0.7082(1)	0.38379(7)	0.0201(8)	0.0158(8)	0.0161(8)	−0.0020(7)	−0.0032(6)	0.0018(6)
C(20)	4e	0.5082(3)	0.6564(1)	0.37674(7)	0.0178(8)	0.0209(9)	0.0152(8)	−0.0030(7)	−0.0001(6)	0.0015(6)
C(21)	4e	0.7078(3)	0.6463(1)	0.41078(8)	0.0175(9)	0.037(1)	0.0221(9)	0.0026(8)	−0.0015(7)	−0.0012(8)
C(22)	4e	0.1895(3)	0.7006(1)	0.33824(7)	0.0183(8)	0.0185(8)	0.0185(8)	0.0007(7)	−0.0032(7)	0.0012(6)
C(23)	4e	0.2302(3)	0.6435(1)	0.29816(7)	0.0172(8)	0.0165(8)	0.0165(8)	−0.0022(6)	−0.0004(6)	0.0040(6)
C(24)	4e	0.1068(3)	0.6209(1)	0.24539(7)	0.0238(9)	0.0148(8)	0.0150(8)	−0.0057(7)	−0.0017(6)	0.0024(6)
C(25)	4e	−0.0929(3)	0.6500(1)	0.23613(8)	0.0230(9)	0.0217(9)	0.0196(8)	−0.0029(7)	−0.0021(7)	−0.0006(7)
C(26)	4e	−0.2108(3)	0.6286(1)	0.18672(8)	0.026(1)	0.025(1)	0.025(1)	−0.0030(8)	−0.0078(8)	0.0027(7)
C(27)	4e	−0.1294(3)	0.5776(1)	0.14615(8)	0.042(1)	0.023(1)	0.0201(9)	−0.0070(9)	−0.0115(8)	0.0007(7)
C(28)	4e	0.0683(3)	0.5484(1)	0.15478(8)	0.042(1)	0.024(1)	0.0200(9)	−0.0004(9)	−0.0036(8)	−0.0055(7)
C(29)	4e	0.1868(3)	0.5697(1)	0.20398(8)	0.028(1)	0.0209(9)	0.0227(9)	0.0001(8)	−0.0020(7)	−0.0017(7)
F(1)	4e	0.5140(3)	0.87658(8)	0.54642(7)	0.087(1)	0.0205(6)	0.0556(9)	0.0058(7)	−0.0519(8)	−0.0095(6)
F(2)	4e	0.1909(3)	0.84331(8)	0.54884(6)	0.085(1)	0.0314(7)	0.0271(7)	0.0181(7)	0.0163(7)	0.0015(5)
F(3)	4e	0.4734(2)	0.93884(7)	0.44376(6)	0.0466(8)	0.0244(6)	0.0406(7)	−0.0071(6)	−0.0054(6)	−0.0008(5)
F(4)	4e	0.1643(2)	0.95866(7)	0.47495(5)	0.0546(8)	0.0234(6)	0.0281(6)	0.0155(6)	−0.0060(5)	−0.0036(5)
F(5)	4e	0.0124(2)	0.83709(7)	0.41781(5)	0.0269(6)	0.0312(6)	0.0341(6)	0.0089(5)	−0.0091(5)	−0.0060(5)
F(6)	4e	0.2567(2)	0.87300(7)	0.36040(5)	0.0511(8)	0.0240(6)	0.0208(6)	0.0062(5)	−0.0045(5)	0.0055(4)
O(1)	4e	1.4302(2)	0.60236(7)	0.73724(5)	0.0176(6)	0.0200(6)	0.0232(6)	0.0009(5)	−0.0061(5)	−0.0002(5)
S(1)	4e	0.54413(7)	0.57411(2)	0.57437(2)	0.0179(2)	0.0155(2)	0.0176(2)	0.0007(2)	−0.0014(2)	0.0012(2)
S(2)	4e	0.46363(7)	0.59855(3)	0.31584(2)	0.0181(2)	0.0236(2)	0.0174(2)	0.0014(2)	0.0007(2)	−0.0017(2)



Scheme: Left: ground state as found in the crystal structure, right: excited state as found in the structure.

crystals were dissolved in hexane, the colorless solution also showed a blue color, with an absorption maximum at 575 nm, accompanied with the formation of the closed-ring isomer. Upon irradiation with visible light (≥510 nm), blue crystals return to their colorless state. The absorption spectrum of a hexane solution of such colorless crystals is the same as that of the open-ring form, with an absorption maximum at 292 nm.

Experimental details

The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement.

Discussion

Photochromism is defined as the phenomenon that a compound can be switched between two distinct states with its corresponding isomers by external light-triggered reversible reaction with chemical bond rearrangement which induces electronic as well as geometrical structure changes of the molecules (see the Scheme). Photochormic compounds have been attracted interest due to their promising wide applications in photonic devices, such as optical memory media, full-color display and various photoswitching devices [3]. Among various photochromic compounds, diarylethenes

are promising candidates for such applications due to their excellent thermal stability of both isomers, fatigue-resistant property, high sensitivity, rapid response, and reactivity in solid state [4]. On one hand, the photochromic properties of diarylethene is strongly influenced by the substituents at the terminal groups at the aryl moieties [4]. Recently we have reported the photochromic diarylethene bearing different group, such as fluorine, chlorine, methoxy and methyl [5–7]. On the other hand, the application of the light responsive compounds need the solid state – especial crystal-based state – for their easily using [8]. In general, photochromic reactions rarely occur in crystals, [9, 10] because the photochromic reactions require large geometrical structural changes to form the closed-ring isomer. In our previous crystallographic studies of photochromic diarylethene, we have found that the diarylethenes can exhibite the photochromism in crystal states when they are bearing some special heterocyclic groups [11–13]. On the basis of these considerations, we have designed an assymmetrical photochromic diarylethene bearing an ethoxy group.

The title molecule adopts a photo-active antiparallel conformation (see the Figure). In the cyclopentene ring, the two thiophene rings are linked by the C14=C18 double bond 1.352(2) Å. The two methyl groups are located on different sides of the C14=C18 double bond and this configuration is crucial to allow the compound to exhibit photochromic and photoinduced properties [4]. This geometry allows the breaking of the central hexafluorocyclopentene C=C double bond to form a new C—C single bond and the molecule thus can undergo a phototransition. The dihedral angles between the least-square planes of the cyclopentene (C14, C15, C17, C18) and the adjacent phenyl thienyl ring, ethoxylphenyl thienyl ring are 32.3(5)° and 126.9(6), respectively. The dihedral angle between the least-square planes of phenyl, ethoxylphenyl and their adjacent thienyl rings are 32.3(5)° and 1.9(7)°, respectively. The angle between the thienyl rings is 118.6(4)°.

The intramolecular distance between the two reactive C atoms (C20—C12) is 3.560(2) Å. This distance indicates that the crystal can be expected to undergo photochromism 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 [14, 15].

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