Crystal structure of 1-[5-(3,4-difluorophenyl)-2-methylthiophen-3-yl]-2-(2-cyano-1,5-dimethyl-1*H*-pyrrol-4-yl) -3,3,4,4,5,5-hexafluoro-cyclopent-1-ene, $C_{23}H_{14}F_8N_2S$

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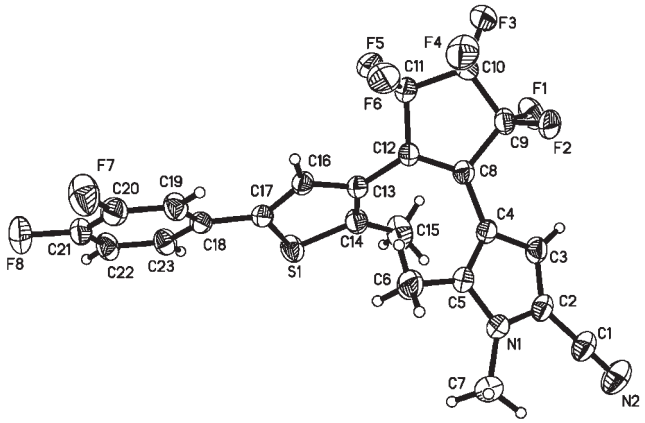

Abstract

$C_{23}H_{14}F_8N_2S$, triclinic, $P\bar{1}$ (no. 2), a = 8.701(2) Å, b = 11.881(2) Å, c = 12.342(3) Å, α = 64.932(3)°, β = 71.913(3)°, γ = 86.599(3)°, V = 1094.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0425, $wR_{ref}(F^2)$ = 0.1244, T = 294 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.14×0.20×0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.30 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5587, 3830
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2684
$N(param)_{refined}$:	364
Programs:	SHELX [15]

Source of material

To a tetrahydrofuran solution of 1-bromo-3,4-difluorobenzene (1.93 g, 10.0 mmol) was added 3-bromo-2-methyl-5-thienylboronic acid (2.50 g, 11.3 mmol) [13] in the presence of $Pd(PPh_3)_4$ (0.3 g) and Na_2CO_3 (6.4 g, 60 mmol) in 20 ml H_2O. After refluxing for 15 h, the product, 3-bromo-2-methyl-5-(3,4-difluorophenyl)thiophene (1.94 g, 6.73 mmol), was collected and dried (yield 67.3%). This compound (0.67 g, 2.3 mmol) was reacted with 1-(2-cyano-1,5-dimethyl-4-pyrrol-1-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene (0.66 g, 2.30 mmol) [14] and with *n*-butyl lithium 2.5 M in hexane (0.92 ml, 2.30 mmol) at 195K under a nitrogen atmosphere. After an hour, the reaction was quenched by addition of water. The solid product was purified by column chromatography on silica with petroleum ether as the eluent to give the title compound (0.55 g, 1.10 mmol) in 47.8% yield. **Elemental Analysis** calcd. for $C_{23}H_{14}F_8N_2S$: C, 54.98; H, 2.81%; found: C 55.02, H 2.95%.

Experimental details

All H atoms were placed in calculated positions with C–H = 0.93 Å for aromatic and 0.96 Å for CH_3 groups. They were included in the refinement in the riding model approximation with isotropic displacement parameters set equal to 1.2U_{eq}(C) and 1.5U_{eq}(C) of the carrier atom for the aromatic and methyl H atoms, respectively. The F atoms attached to the C atoms in cyclopentene ring are disordered over two positions. The occupancy factor 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 0.5/0.5. The C–F distances were restrained using SADI (SHELXL-97 [15]) instructions and similar U_{ij} restraints as well as rigid bond restraints were used in the final refinement cycles.

Discussion

Photochromism of organic compounds is defined as a reversible transformation induced by different light between two isomeric states with different molecular absorption bands [1-3]. The first published observation of what is known today as photochromism dates back to 1867, when Fritzsche found that an orange-coloured solution of tetracene tends to bleach in the day light, regenerating its color in the dark [4]. During the past decades, researching into photochromism has received a powerful impulse, more and more achievements on synthesis and studying its properties in the new families of organic photochromic molecules have been published [5-7], because of their widespread potential application in photonic devices [8,9]. Among the photochromic compounds, diarylethene derivatives are the most promising candidates for potential application to optical memory media and optical switches for their thermal stability and fatigue resistance. Hence, the synthesis of diarylethene derivatives and investigation of their structural features are of interest. The title compound, $C_{23}H_{14}F_8N_2S$, is a new asymmetrical hybrid photochromic diarylethene derivative. The molecule adopts a photo-active antiparallel conformation. The molecular structure exhibited in the solid state is shown in the figure. In the cyclopentene ring, the thiophene and pyrryl rings are linked by the C8=C12 double bond 1.347(3) Å, which is shorter than the other single bond (such as C8–C9, 1.500(4) Å and C12–C13, 1.469(4) Å. The two methyl groups are located on different sides of the central cyclopentene ring and this configuration is crucial to allow the compound to exhibit photochromic and photoinduced properties [10]. This geometry allows the breaking of the central hexafluorocyclopentene C=C double bond to form a new C–C single bond to

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be allowed and the molecule thus can undergo a phototransition and exhibit photochromic and photoinduced properties. The dihedral angles between the least-squares planes of the cyclopentene and the adjacent thienyl ring, pyrryl ring are 53.4(5)° and 43.6(5)°, respectively. The dihedral angle between the least-squares planes of the thienyl ring and its linked phenyl ring is 17.7(6)°. The intramolecular distance between the two reactive C atoms (C5–C14) is 3.644(5) 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 [11,12]. The title compound can exhibit photochromism in solid state or dissolved in hexane. Upon irradiation with 365 nm light, the colourless hexane solution turns blue rapidly. The blue compound displays an absorption maximum at 592 nm. Upon irradiation with visible light with wavelength longer than 510 nm, the blue hexane solution reverts to its initial colourless state. A colourless hexane solution of the title compound has two absorption maximum at 253 nm and 294 nm. In a polymethylmethacrylate amorphous film, the title diarylethene also exhibits photochromism similar to that in hexane.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	2*i*	0.3932	0.5488	0.2783	0.060
H(6A)	2*i*	0.8650	0.2857	0.3338	0.098
H(6B)	2*i*	0.7042	0.2005	0.4223	0.098
H(6C)	2*i*	0.7925	0.2688	0.4734	0.098
H(7A)	2*i*	0.8373	0.4641	0.4758	0.108
H(7B)	2*i*	0.8359	0.6057	0.3890	0.108
H(7C)	2*i*	0.9417	0.5198	0.3330	0.108
H(15A)	2*i*	0.6173	0.4448	0.0223	0.119
H(15B)	2*i*	0.7975	0.4899	–0.0637	0.119
H(15C)	2*i*	0.7360	0.4958	0.0672	0.119
H(16)	2*i*	0.7307	0.0319	0.2765	0.052
H(19)	2*i*	0.9535	–0.0927	0.3028	0.063
H(22)	2*i*	1.3796	–0.0053	–0.0655	0.067
H(23)	2*i*	1.1924	0.1372	–0.0558	0.060

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}
S(1)	2*i*		0.96590(9)	0.28174(7)	0.01842(7)	0.0445(4)	0.0534(5)	0.0544(5)	0.0023(3)	0.0001(3)	–0.0156(4)
F(1)	2*i*	0.5	0.203(1)	0.3655(7)	0.2806(6)	0.052(3)	0.064(3)	0.073(4)	0.023(2)	–0.021(3)	–0.017(3)
F(2)	2*i*	0.5	0.200(1)	0.2750(8)	0.4745(7)	0.057(3)	0.074(4)	0.065(3)	–0.001(3)	0.006(2)	–0.049(3)
F(3)	2*i*	0.5	0.0970(6)	0.1390(6)	0.3374(7)	0.046(2)	0.099(4)	0.124(5)	0.010(3)	–0.028(3)	–0.075(4)
F(4)	2*i*	0.5	0.2137(6)	0.0572(3)	0.4784(4)	0.094(3)	0.048(2)	0.071(3)	–0.004(2)	–0.003(2)	–0.012(2)
F(5)	2*i*	0.5	0.4066(6)	0.0900(7)	0.1975(7)	0.062(3)	0.094(4)	0.115(5)	–0.007(3)	–0.004(3)	–0.082(4)
F(6)	2*i*	0.5	0.4032(6)	0.0167(4)	0.3886(5)	0.076(3)	0.043(2)	0.108(4)	–0.006(2)	–0.014(3)	–0.015(2)
F(1')	2*i*	0.5	0.193(1)	0.3783(8)	0.3259(7)	0.046(3)	0.073(3)	0.122(6)	0.024(2)	–0.021(4)	–0.054(4)
F(2')	2*i*	0.5	0.227(2)	0.2313(9)	0.4891(7)	0.077(5)	0.110(7)	0.061(3)	–0.019(5)	0.012(3)	–0.047(4)
F(3')	2*i*	0.5	0.1841(6)	0.2357(5)	0.2251(5)	0.092(3)	0.116(4)	0.117(4)	0.033(3)	–0.064(3)	–0.076(3)
F(4')	2*i*	0.5	0.1156(7)	0.0963(6)	0.4136(7)	0.058(3)	0.079(4)	0.125(5)	–0.019(3)	0.012(3)	–0.051(4)
F(5')	2*i*	0.5	0.3639(7)	0.1718(7)	0.1543(5)	0.087(4)	0.147(5)	0.088(3)	–0.024(3)	–0.013(3)	–0.081(4)
F(6')	2*i*	0.5	0.4176(6)	0.0162(5)	0.3006(9)	0.062(3)	0.063(3)	0.166(6)	–0.002(2)	0.000(4)	–0.073(4)
F(7)	2*i*		1.1403(3)	–0.2694(2)	0.3210(2)	0.087(2)	0.063(1)	0.086(1)	0.019(1)	–0.015(1)	–0.007(1)
F(8)	2*i*		1.3847(2)	–0.2204(2)	0.1079(2)	0.077(1)	0.081(1)	0.098(2)	0.040(1)	–0.030(1)	–0.049(1)
N(1)	2*i*		0.7052(3)	0.4939(2)	0.3610(2)	0.047(1)	0.047(1)	0.055(1)	0.004(1)	–0.013(1)	–0.029(1)
N(2)	2*i*		0.6030(4)	0.7957(3)	0.3114(3)	0.120(3)	0.050(2)	0.089(2)	0.007(2)	–0.027(2)	–0.036(2)
C(1)	2*i*		0.5966(4)	0.6971(3)	0.3183(3)	0.077(2)	0.044(2)	0.059(2)	0.006(2)	–0.013(2)	–0.026(2)
C(2)	2*i*		0.5913(4)	0.5750(2)	0.3253(3)	0.058(2)	0.038(2)	0.049(2)	0.007(1)	–0.010(1)	–0.022(1)
C(3)	2*i*		0.4831(4)	0.5159(2)	0.3026(3)	0.052(2)	0.043(2)	0.058(2)	0.015(1)	–0.019(1)	–0.025(1)
C(4)	2*i*		0.5334(3)	0.3956(2)	0.3229(2)	0.043(2)	0.040(1)	0.047(2)	0.007(1)	–0.011(1)	–0.023(1)
C(5)	2*i*		0.6709(3)	0.3841(2)	0.3602(3)	0.046(2)	0.044(2)	0.048(2)	0.009(1)	–0.013(1)	–0.025(1)
C(6)	2*i*		0.7666(4)	0.2752(3)	0.4010(3)	0.067(2)	0.062(2)	0.087(2)	0.025(2)	–0.041(2)	–0.042(2)
C(7)	2*i*		0.8417(4)	0.5234(3)	0.3924(4)	0.062(2)	0.078(2)	0.099(3)	0.006(2)	–0.029(2)	–0.056(2)
C(8)	2*i*		0.4535(3)	0.2990(2)	0.3104(2)	0.041(1)	0.038(1)	0.042(1)	0.007(1)	–0.013(1)	–0.017(1)
C(9)	2*i*		0.2722(3)	0.2754(2)	0.3613(2)	0.043(2)	0.047(2)	0.050(2)	0.009(1)	–0.007(1)	–0.024(1)
C(10)	2*i*		0.2333(4)	0.1653(4)	0.3423(4)	0.036(2)	0.094(3)	0.118(3)	–0.002(2)	–0.005(2)	–0.076(3)
C(11)	2*i*		0.3897(4)	0.1296(3)	0.2796(3)	0.048(2)	0.060(2)	0.089(2)	–0.001(2)	–0.000(2)	–0.049(2)
C(12)	2*i*		0.5191(3)	0.2208(2)	0.2585(2)	0.039(1)	0.040(1)	0.048(2)	0.006(1)	–0.010(1)	–0.022(1)
C(13)	2*i*		0.6878(3)	0.2183(2)	0.1860(3)	0.039(1)	0.045(2)	0.048(2)	0.003(1)	–0.008(1)	–0.026(1)
C(14)	2*i*		0.7759(3)	0.3205(3)	0.0830(3)	0.047(2)	0.049(2)	0.054(2)	0.006(1)	–0.010(1)	–0.022(1)
C(15)	2*i*		0.7273(5)	0.4492(3)	0.0217(3)	0.075(2)	0.057(2)	0.070(2)	0.013(2)	–0.004(2)	–0.008(2)
C(16)	2*i*		0.7748(3)	0.1090(2)	0.2107(2)	0.044(2)	0.040(1)	0.045(2)	0.002(1)	–0.006(1)	–0.022(1)
C(17)	2*i*		0.9288(3)	0.1283(2)	0.1287(2)	0.039(1)	0.046(2)	0.046(2)	0.003(1)	–0.011(1)	–0.024(1)
C(18)	2*i*		1.0516(3)	0.0390(2)	0.1233(2)	0.036(1)	0.051(2)	0.046(2)	0.003(1)	–0.011(1)	–0.029(1)
C(19)	2*i*		1.0381(4)	–0.0744(3)	0.2283(3)	0.045(2)	0.055(2)	0.051(2)	0.005(1)	–0.005(1)	–0.023(1)
C(20)	2*i*		1.1513(4)	–0.1582(3)	0.2199(3)	0.057(2)	0.051(2)	0.063(2)	0.007(2)	–0.021(2)	–0.020(2)
C(21)	2*i*		1.2774(4)	–0.1335(3)	0.1113(3)	0.048(2)	0.061(2)	0.071(2)	0.018(2)	–0.021(2)	–0.041(2)
C(22)	2*i*		1.2936(4)	–0.0229(3)	0.0082(3)	0.045(2)	0.076(2)	0.054(2)	0.016(2)	–0.011(1)	–0.039(2)
C(23)	2*i*		1.1814(3)	0.0619(3)	0.0147(3)	0.046(2)	0.060(2)	0.044(2)	0.009(1)	–0.010(1)	–0.025(1)

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