Crystal structure of 1-[2-*n*-butyl-5-formyl-3-thienyl]-2-[2-cyano-1,5-dimethyl-4-pyrryl]-3,3,4,4,5,5-hexafluoro-cyclopent-1-ene, $C_{21}H_{18}F_6N_2OS$

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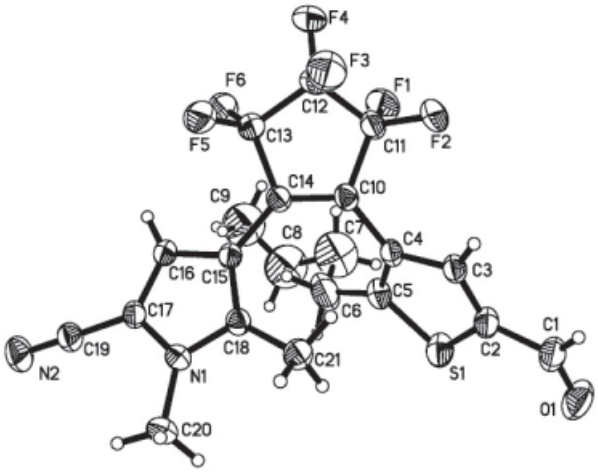

Abstract

$C_{21}H_{18}F_6N_2OS$, monoclinic, $P2_1/c$ (no. 14), a = 9.331(1) Å, b = 20.492(2) Å, c = 11.998(1) Å, β = 108.748(1)°, V = 2172.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.0710, $wR_{ref}(F^2)$ = 0.2198, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.35×0.44×0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.15 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16495, 4050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3108
$N(param)_{refined}$:	283
Programs:	SHELX [11]

Source of material

To a stirred solution of compound 4-bromo-5-*n*-butyl-2-(1,3-dioxolane)thiophene [10] (1.30 g, 4.69 mmol) in THF, *n*-BuLi (1.6 M in hexane) (2.93 mL, 4.69 mmol) was added at 195 K under nitrogen atmosphere. Stirring was continued for 40 min, perfluorocyclopentene (0.64 mL, 4.69 mmol) was slowly added to the reaction mixture, and the mixture was stirred for 3.0 h at this low temperature. The reaction was stopped by the addition of water. After extracting with ether, the organic layer was washed sequentially by concentrated sodium chloride solution and water. The organic layer was dried over anhydrous $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using chloroform and petroleum ether mixture (*v*/*v*:1/1) as the eluent to give 1.14 g of compound 1-(2-*n*-butyl-5-dioxolanylthiophene-3-yl)-2,3,3,4,4,5,5-heptafluorocyclopent-1-ene in 42% yield. This compound (3.61 g, 8.20 mmol) was reacted with 4-bromo-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile (1.58 g, 8.20 mmol) in the presence of *n*-butyllithium at 195 K under a nitrogen atmosphere. After an hour, the reaction was quenched by the addition of water. The product was purified by column chromatography on silica using petroleum ether as the eluant to give the title compound with a yield of 53.73%. The title compound crystallized from hexane at room temperature yielded crystals suitable for X-ray analysis. **^{1}H-NMR** (400 MHz, $CDCl_3$, TMS): δ 0.84 (t, 3H, J = 7.5 Hz, $-CH_3$), 1.21 (t, 1H, $-CH_2$), 1.38 (m, 1H, $-CH_2$), 1.74 (s, 3H, $-CH_3$), 2.29 (m, 1H, $-CH_2$), 3.61 (s, 3H, $-CH_3$), 6.81 (s, 1H, thienyl–H), 7.72 (s, 1H, pyrrolyl–H), 9.87(s, 1H, –CHO). **^{13}C-NMR** ($CDCl_3$, 100 MHz, TMS): δ 11.53, 15.71, 23.11, 35.33, 40.58, 42.37, 102.65, 108.83, 110.70, 114.90, 123.22, 133.85, 135.95, 137.11, 139.67, 143.96, 185.15.

Experimental details

All hydrogen atoms attached to carbon were fixed geometrically and treated as riding with C–H = 0.96 Å (methyl and butyl) with $U_{iso}(H) = 1.5U_{eq}$ (methyl and butyl). The C8–C9 distance was restrained to 1.40(1) Å.

Discussion

Photochromic materials have been applied in optical memory media, optical switches and full color display areas of the modern opto-electronic industry due to their responsive behvior to external light stimulus [1, 2]. Among current technical applications for the light responsive complexes, their great potential for use as crystal-based optical switches has been recognized [3,4]. This has enlightened us to apply this kind of photochromic diarylethene compounds to perform as photochromical molecular switches. In our previous crystallographic studies of photochromic diarylethene, we have reported the structures of two related compounds [5, 6]. Most the backbone of photochromic perfluorocyclopent- ene systems are composed of five-membered thienyl or six-membered benzyl rings. In order to investigate the effect of the pyrryl group on the photochemical properties, we have determined the title structure. The title compound, $C_{21}H_{18}F_6N_2OS$, 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 Fig.1. In the cyclopentene ring, the thiophene and indolyl rings are linked by the C10=C14 double bond (1.345(5)) Å. The methyl and *n*-butyl groups are located on different sides of the C10=C14 double bond and this configuration is crucial to allow the compound to exhibit photochromic and photoinduced properties [7]. This geometry allows the breaking of the central hexafluorocyclopentene C=C double bond to form a new C–C single bond to be allowed and the molecule thus can undergo a phototransition and exhibit photochromic and photoinduced properties. The dihedral angles between the least-squre planes of the cyclopentene and the adjacent

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thienyl ring, pyrryl ring are 44.2(5)° and 51.4(6)°, respectively. The dihedral angle between the least-square planes of the thienyl ring and pyrryl ring is 61.9(6)°. The intramolecular distance between the two reactive C atoms (C5–C18) is 3.634(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 [8, 9]. Crystals of the title compound show photochromism in accordance with the expected ring closure. Upon irradiation with 313 nm light, the colourless crystals of the title compound turn blue-green quickly. When the blue-green crystals were dissolved in hexane, the solution also showed a blue-green colour with an absorption maximum at 630 nm. Upon alternate irradiation with visible light (wavelength λ = 510 nm), the blue-green crystals return to their initial colourless state, such colourless crystals the same as that of the open-ring form with an absorption maximum at 250 nm in hexane.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	4*e*	0.0586	0.5990	0.4243	0.057
H(1)	4*e*	–0.1274	0.6743	0.2618	0.083
H(6A)	4*e*	0.1756	0.7511	0.7898	0.120
H(6B)	4*e*	0.2509	0.6823	0.8195	0.120
H(16)	4*e*	0.3043	0.5558	1.0026	0.054
H(21A)	4*e*	–0.2082	0.5591	0.6801	0.086
H(21B)	4*e*	–0.0795	0.5645	0.6229	0.086
H(21C)	4*e*	–0.1465	0.6278	0.6603	0.086
H(8A)	4*e*	0.5127	0.8208	0.9098	0.190
H(8B)	4*e*	0.3687	0.7976	0.9409	0.190
H(7A)	4*e*	0.3765	0.7801	0.7229	0.186
H(7B)	4*e*	0.4544	0.7145	0.7775	0.186
H(9A)	4*e*	0.4700	0.7014	0.9927	0.237
H(9B)	4*e*	0.5858	0.7546	1.0612	0.237
H(9C)	4*e*	0.6085	0.7197	0.9518	0.237
H(20A)	4*e*	–0.2318	0.6386	0.8625	0.089
H(20B)	4*e*	–0.1886	0.6035	0.9850	0.089
H(20C)	4*e*	–0.2589	0.5634	0.8689	0.089

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.0416(2)	0.75059(5)	0.5440(1)	0.1029(9)	0.0479(6)	0.0546(6)	0.0050(5)	0.0241(6)	0.0006(4)
C(4)	4*e*	0.1572(4)	0.6367(2)	0.5924(3)	0.047(2)	0.054(2)	0.034(2)	–0.003(2)	0.015(1)	0.001(1)
C(5)	4*e*	0.1548(5)	0.6969(2)	0.6435(3)	0.068(2)	0.055(2)	0.043(2)	–0.007(2)	0.021(2)	–0.004(2)
C(2)	4*e*	–0.0033(5)	0.6932(2)	0.4338(3)	0.068(2)	0.056(2)	0.043(2)	0.002(2)	0.017(2)	0.005(2)
C(3)	4*e*	0.0678(4)	0.6355(2)	0.4722(3)	0.057(2)	0.051(2)	0.036(2)	0.001(2)	0.017(2)	–0.001(2)
C(1)	4*e*	–0.1052(6)	0.7078(2)	0.3171(4)	0.083(3)	0.072(3)	0.047(2)	0.010(2)	0.014(2)	0.008(2)
C(6)	4*e*	0.2382(8)	0.7194(3)	0.7669(5)	0.144(4)	0.097(3)	0.083(3)	0.008(3)	0.069(2)	0.007(2)
O(1)	4*e*	–0.1633(5)	0.7600(2)	0.2866(3)	0.133(3)	0.082(2)	0.069(2)	0.038(2)	0.014(2)	0.022(2)
C(14)	4*e*	0.2401(4)	0.5520(2)	0.7556(3)	0.038(2)	0.053(2)	0.038(2)	–0.002(1)	0.011(1)	–0.001(1)
C(10)	4*e*	0.2425(4)	0.5799(2)	0.6548(3)	0.042(2)	0.056(2)	0.034(2)	–0.003(2)	0.011(1)	–0.004(1)
C(13)	4*e*	0.3590(4)	0.5000(2)	0.7925(3)	0.044(2)	0.070(3)	0.048(2)	0.009(2)	0.015(2)	0.009(2)
C(11)	4*e*	0.3585(4)	0.5477(2)	0.6102(3)	0.048(2)	0.076(3)	0.040(2)	0.004(2)	0.017(2)	–0.001(2)
C(12)	4*e*	0.4011(5)	0.4852(2)	0.6820(4)	0.052(2)	0.076(3)	0.057(2)	0.015(2)	0.018(2)	–0.004(2)
C(16)	4*e*	0.2051(4)	0.5641(2)	0.9560(3)	0.043(2)	0.051(2)	0.038(2)	0.004(2)	0.011(1)	0.007(1)
C(17)	4*e*	0.0854(4)	0.5769(2)	0.9947(3)	0.054(2)	0.045(2)	0.038(2)	0.002(2)	0.018(2)	0.005(1)
C(18)	4*e*	–0.0041(4)	0.5796(2)	0.7985(3)	0.042(2)	0.045(2)	0.040(2)	–0.004(1)	0.013(1)	0.002(1)
C(15)	4*e*	0.1500(4)	0.5659(2)	0.8320(3)	0.041(2)	0.046(2)	0.035(2)	0.001(1)	0.011(1)	0.004(1)
C(21)	4*e*	–0.1198(4)	0.5831(2)	0.6800(3)	0.042(2)	0.078(3)	0.045(2)	–0.004(2)	0.005(2)	–0.001(2)
C(19)	4*e*	0.0804(5)	0.5808(2)	1.1119(3)	0.066(2)	0.056(2)	0.046(2)	0.005(2)	0.024(2)	0.002(2)
N(1)	4*e*	–0.0416(3)	0.5863(1)	0.8986(2)	0.042(2)	0.048(2)	0.046(2)	–0.000(1)	0.018(1)	0.002(1)
N(2)	4*e*	0.0771(5)	0.5832(2)	1.2054(3)	0.107(3)	0.093(3)	0.047(2)	0.012(2)	0.037(2)	–0.000(2)
F(6)	4*e*	0.4842(2)	0.5219(2)	0.8788(2)	0.046(1)	0.121(2)	0.048(1)	0.017(1)	0.006(1)	0.005(1)
F(5)	4*e*	0.3158(3)	0.4460(1)	0.8368(3)	0.091(2)	0.069(2)	0.100(2)	0.021(1)	0.051(2)	0.031(2)
F(2)	4*e*	0.3101(3)	0.5356(2)	0.4940(2)	0.094(2)	0.112(2)	0.042(1)	0.027(2)	0.027(1)	–0.008(1)
F(1)	4*e*	0.4833(3)	0.5862(2)	0.6301(3)	0.057(2)	0.106(2)	0.088(2)	–0.004(1)	0.037(1)	0.008(2)
F(4)	4*e*	0.5475(3)	0.4684(2)	0.7063(3)	0.070(2)	0.133(3)	0.084(2)	0.048(2)	0.038(1)	0.019(2)
F(3)	4*e*	0.3152(4)	0.4358(1)	0.6226(3)	0.120(2)	0.071(2)	0.085(2)	0.003(2)	0.033(2)	–0.015(2)
C(8)	4*e*	0.451(1)	0.7834(5)	0.9133(8)	0.157(2)	0.157(2)	0.155(2)	–0.006(1)	0.040(2)	–0.007(1)
C(7)	4*e*	0.384(1)	0.7481(5)	0.7841(9)	0.152(4)	0.164(4)	0.148(3)	–0.025(3)	0.047(3)	–0.016(3)
C(9)	4*e*	0.535(1)	0.7363(5)	0.9850(9)	0.158(2)	0.158(2)	0.156(2)	–0.002(1)	0.045(1)	–0.004(1)
C(20)	4*e*	–0.1933(4)	0.5991(2)	0.9042(4)	0.047(2)	0.068(3)	0.068(2)	0.004(2)	0.027(2)	0.005(2)

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