Crystal structure of 1-(2-ethyl-3-benzothienyl)-2-[2-*n*-pentyl-5-(2,2-dicyanovinyl)-3-thienyl]perfluorocyclopentene, $C_{28}H_{22}F_6N_2S_2$

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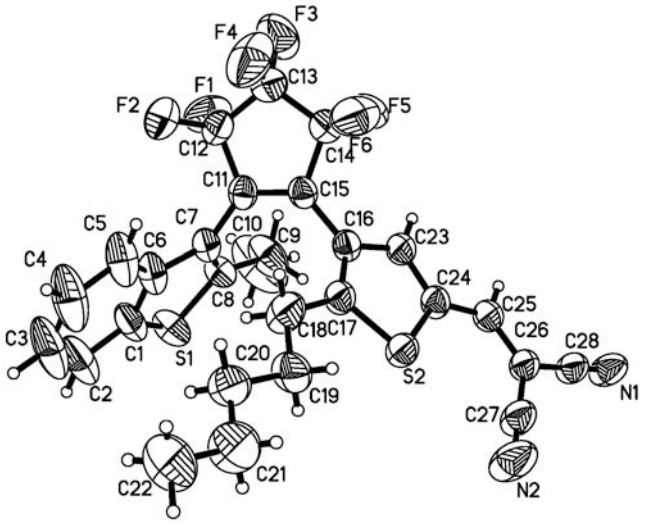

Abstract

$C_{28}H_{22}F_6N_2S_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.930(5) Å, b = 11.525(6) Å, c = 13.715(6) Å, α = 65.218(6)°, β = 67.338(6)°, γ = 64.912(6)°, V = 1374.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.074, $wR_{ref}(F^2)$ = 0.248, T = 291 K.

Source of material

The title compound was synthesized in 75.02 % yield by the method [1,2] originally derived from 5-*n*-pentyl-thiophen-2-carbaldehyde and benzothiophene. Crystals suitable for X-ray analysis were grown from a solution (diethyl ether/hexane, 1:2) by slow evaporation at room temperature (m.p. 408.2 - 408.7 K). Chemical analysis — found: C, 59.60 %; H, 3.89 %; N, 4.98 %; calculated for $C_{28}H_{22}F_6N_2S_2$: C, 59.56 %; H, 3.93 %; N, 4.96 %. ^{1}H NMR, ^{13}C NMR and IR data are available in the CIF.

Experimental details

All H atoms attached to C were fixed geometrically and treated as riding with d(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).

Discussion

Among various organic photochromic materials, diarylethene derivatives are the best candidates for optical recording and photo switches because of their good thermal stability, fatigue character and rapid response [3-5]. Generally, the backbone of all photochromic perfluorocyclopentene systems are composed of five-membered heterocyclic rings or the combination of a five-membered aryl ring and a vinyl group [1,2,6-8]. In order to investigate the substituent group effect at the backbone of the diarylethene on the photochemical properties. The title compound which contains a benzothiophene and a thiophene rings at backbone was investigated.

The molecular structure shows a anti-parallel conformation. The benzothiophene and thiophene rings are condensed *via* the double bond C11=C15 (1.340(3) Å) , while the other contacts in the rings are clearly single bonds. The ethyl and *n*-pentyl groups are located on different sides of the double bond. The *trans* configuration is crucial for the compound to exhibit photochromic and photoinduced properties [9]. The dihedral angles between the least-square cyclopentene plane and those of the adjacent benzothiophene and thiophene rings are 70.6(5)° and 60.0(5)°, respectively. The intramolecular distance between the two reactive C atoms (C8···C17) is 3.979(3) Å. This distance indicates that the crystal may be expected to undergo photochromic transition, because photochromic reactivity usually appears when distance between the reactive C atoms is less than 4.2 Å [10,11]. However, upon irradiation with 365 nm light, the colorless single-crystal of the title compound did not turned colour even irradiation time last five hours. The reason may be ascribed to the backbone benzothiophene group depressing the total molecular flexibility, so that upon irradiation, the two reacitve C atoms could not form a new single bond. When the colorless crystal was dissolved in hexane, the solution is colorless. By irradiation with 365 nm light, the solution turned green with an absorption maximum at 668 nm, consistent with the presence of the closed-ring isomer. Upon irradiation with visible light with wavelength greater than 500 nm, the green solution can return to its initial colorless state, and the absorption spectrum of the hexane solution is the same as that of solution of the title compound, with the absorption maximum at 358 nm.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.22 × 0.32 × 0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.54 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10335, 5081
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2801
$N(param)_{refined}$:	345
Programs:	SHELXS-97 [12], SHELXL-97 [13], SHELXTL [14]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.8166	0.2487	0.2410	0.163
H(3)	2*i*	0.6117	0.3105	0.1946	0.194
H(4)	2*i*	0.4985	0.5311	0.1128	0.190
H(5)	2*i*	0.5897	0.6997	0.0707	0.136
H(9A)	2*i*	1.0459	0.7319	0.1031	0.143
H(9B)	2*i*	1.0165	0.6666	0.2314	0.143
H(10A)	2*i*	1.1945	0.4859	0.2059	0.322
H(10B)	2*i*	1.2340	0.6178	0.1633	0.322
H(10C)	2*i*	1.2272	0.5637	0.0786	0.322
H(18A)	2*i*	0.4773	0.8363	0.2638	0.135
H(18B)	2*i*	0.5830	0.6916	0.2914	0.135
H(19A)	2*i*	0.3604	0.7997	0.4474	0.118
H(19B)	2*i*	0.4674	0.6550	0.4761	0.118
H(20A)	2*i*	0.2885	0.7359	0.3404	0.127
H(20B)	2*i*	0.3905	0.5901	0.3761	0.127
H(21A)	2*i*	0.1621	0.7098	0.5215	0.183
H(21B)	2*i*	0.2630	0.5631	0.5555	0.183
H(22A)	2*i*	0.0716	0.6533	0.4320	0.238
H(22B)	2*i*	0.0731	0.5426	0.5479	0.238
H(22C)	2*i*	0.1874	0.5126	0.4417	0.238
H(23)	2*i*	0.8528	0.9660	0.2419	0.084
H(25)	2*i*	0.8779	0.9609	0.4177	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)	2*i*	0.9793(2)	0.4212(1)	0.2065(2)	0.112(1)	0.0681(8)	0.135(1)	–0.0312(8)	–0.034(1)	–0.0189(8)
S(2)	2*i*	0.6189(1)	0.8174(1)	0.4573(1)	0.0899(9)	0.105(1)	0.0693(8)	–0.0581(7)	–0.0103(6)	–0.0275(7)
F(1)	2*i*	0.9421(4)	0.8438(4)	–0.1014(3)	0.115(2)	0.132(3)	0.082(2)	–0.008(2)	0.002(2)	–0.034(2)
F(2)	2*i*	0.7485(5)	0.8411(4)	–0.0947(3)	0.220(4)	0.148(3)	0.114(3)	–0.086(3)	–0.076(3)	–0.031(2)
F(3)	2*i*	0.8312(7)	1.0944(5)	–0.1457(4)	0.295(6)	0.146(3)	0.117(3)	–0.135(4)	0.048(3)	–0.054(3)
F(4)	2*i*	0.6309(5)	1.0781(5)	–0.0926(4)	0.195(4)	0.165(4)	0.181(4)	0.048(3)	–0.131(3)	–0.086(3)
F(5)	2*i*	0.8180(5)	1.0930(4)	0.0423(3)	0.251(4)	0.117(3)	0.135(3)	–0.119(3)	–0.099(3)	0.019(2)
F(6)	2*i*	0.6009(5)	1.1283(4)	0.0735(3)	0.170(3)	0.094(2)	0.100(2)	0.030(2)	–0.028(2)	–0.033(2)
N(1)	2*i*	0.9268(6)	0.9525(6)	0.6455(4)	0.149(4)	0.159(5)	0.070(3)	–0.103(4)	–0.023(3)	–0.020(3)
N(2)	2*i*	0.6015(8)	0.7853(8)	0.7148(5)	0.183(6)	0.250(8)	0.087(4)	–0.158(6)	0.006(4)	–0.044(4)
C(1)	2*i*	0.8311(6)	0.4401(5)	0.1809(5)	0.102(4)	0.072(3)	0.117(4)	–0.043(3)	0.009(3)	–0.047(3)
C(2)	2*i*	0.7728(8)	0.3384(7)	0.2067(7)	0.123(6)	0.111(5)	0.187(7)	–0.075(4)	0.034(5)	–0.085(5)
C(3)	2*i*	0.6501(9)	0.376(1)	0.1793(9)	0.110(6)	0.164(8)	0.26(1)	–0.087(6)	0.036(6)	–0.142(8)
C(4)	2*i*	0.5817(7)	0.509(1)	0.1297(9)	0.086(4)	0.176(8)	0.28(1)	–0.053(5)	–0.003(5)	–0.153(8)
C(5)	2*i*	0.6354(6)	0.6106(7)	0.1049(6)	0.077(3)	0.119(5)	0.181(6)	–0.028(3)	–0.019(4)	–0.094(5)
C(6)	2*i*	0.7591(5)	0.5768(5)	0.1320(5)	0.065(3)	0.090(4)	0.113(4)	–0.032(3)	0.001(3)	–0.062(3)
C(7)	2*i*	0.8311(5)	0.6638(4)	0.1210(4)	0.067(3)	0.066(3)	0.078(3)	–0.024(2)	–0.011(2)	–0.032(2)
C(8)	2*i*	0.9483(5)	0.5943(5)	0.1589(4)	0.082(3)	0.063(3)	0.088(3)	–0.028(2)	–0.023(3)	–0.017(2)
C(9)	2*i*	1.0503(6)	0.6467(6)	0.1618(7)	0.099(4)	0.090(4)	0.188(7)	–0.034(3)	–0.071(4)	–0.025(4)
C(10)	2*i*	1.1863(9)	0.573(1)	0.152(1)	0.117(5)	0.149(7)	0.38(1)	–0.040(5)	–0.090(8)	–0.057(8)
C(11)	2*i*	0.7865(4)	0.8112(5)	0.0749(4)	0.061(2)	0.077(3)	0.076(3)	–0.028(2)	–0.016(2)	–0.031(2)
C(12)	2*i*	0.8065(6)	0.8779(5)	–0.0482(4)	0.089(3)	0.093(3)	0.073(3)	–0.030(2)	–0.024(2)	–0.031(2)
C(13)	2*i*	0.7531(6)	1.0277(6)	–0.0641(5)	0.105(3)	0.090(3)	0.079(3)	–0.032(3)	–0.021(3)	–0.023(2)
C(14)	2*i*	0.7255(6)	1.0416(5)	0.0472(4)	0.098(3)	0.073(3)	0.080(3)	–0.027(2)	–0.029(3)	–0.021(2)
C(15)	2*i*	0.7427(4)	0.9019(4)	0.1279(4)	0.061(2)	0.065(3)	0.070(3)	–0.026(2)	–0.011(2)	–0.024(2)
C(16)	2*i*	0.7183(4)	0.8803(4)	0.2463(3)	0.063(2)	0.062(2)	0.066(3)	–0.023(2)	–0.013(2)	–0.024(2)
C(17)	2*i*	0.6226(5)	0.8224(5)	0.3290(4)	0.077(3)	0.083(3)	0.073(3)	–0.041(2)	–0.016(2)	–0.026(2)
C(18)	2*i*	0.5259(7)	0.7676(8)	0.3195(5)	0.124(5)	0.179(6)	0.084(4)	–0.107(5)	–0.010(3)	–0.040(4)
C(19)	2*i*	0.4205(6)	0.7239(6)	0.4195(5)	0.096(4)	0.109(4)	0.112(4)	–0.058(3)	–0.030(3)	–0.025(3)
C(20)	2*i*	0.3306(6)	0.6687(7)	0.4003(5)	0.110(4)	0.137(5)	0.097(4)	–0.075(4)	–0.029(3)	–0.021(4)
C(21)	2*i*	0.2205(8)	0.632(1)	0.4963(7)	0.139(6)	0.216(9)	0.144(6)	–0.118(6)	–0.012(5)	–0.050(6)
C(22)	2*i*	0.1302(8)	0.5806(9)	0.4779(7)	0.131(6)	0.199(8)	0.189(8)	–0.110(6)	–0.025(5)	–0.054(7)
C(23)	2*i*	0.7867(5)	0.9221(4)	0.2875(4)	0.079(3)	0.075(3)	0.068(3)	–0.039(2)	–0.013(2)	–0.022(2)
C(24)	2*i*	0.7477(4)	0.8927(5)	0.4011(4)	0.070(3)	0.077(3)	0.073(3)	–0.035(2)	–0.012(2)	–0.029(2)
C(25)	2*i*	0.8098(5)	0.9190(5)	0.4614(4)	0.083(3)	0.081(3)	0.076(3)	–0.044(2)	–0.016(2)	–0.023(2)
C(26)	2*i*	0.7849(5)	0.8924(5)	0.5710(4)	0.084(3)	0.083(3)	0.068(3)	–0.041(2)	–0.017(2)	–0.024(2)
C(27)	2*i*	0.6843(6)	0.8316(7)	0.6515(5)	0.115(4)	0.142(5)	0.073(3)	–0.079(4)	–0.011(3)	–0.035(3)
C(28)	2*i*	0.8635(6)	0.9258(5)	0.6132(4)	0.101(4)	0.106(4)	0.065(3)	–0.060(3)	–0.019(3)	–0.021(3)

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