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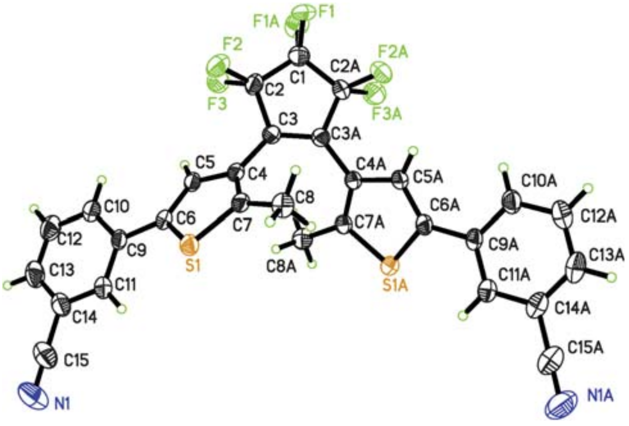
The crystal structure of 1,2-bis[2-methyl-5-(3-cyanophenyl)-3-thienyl]-3,3,4,4,5,5-hexafluoro-cyclopent-1-ene, $C_{29}H_{16}F_6N_2S_2$



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Abstract

$C_{29}H_{16}F_6N_2S_2$, monoclinic, $C2/c$, $a = 18.910(3)$ Å, $b = 8.5720(14)$ Å, $c = 16.757(3)$ Å, $\beta = 100.474(2)°$, $V = 2670.9(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0825$, $wR_{ref}(F^2) = 0.1833$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.25 \times 0.20 \times 0.16$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.6 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
$2\theta_{max}$, completeness:	56.6°, >93% (>99% up to 2θ = 50.4°)
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9927, 2961, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1902
$N(param)_{refined}$:	206
Programs:	Bruker programs [1], SHELX [2]

Source of material

The title compound was prepared according to the literature method [3] in 76.42% yield. The title compound was recrystallized from hexane at room temperature and colorless crystals were obtained.

Experimental details

Hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms. Residual electron density maps indicated the presence of disorder, particularly for the hexafluoropentene moiety, which could not be modelled satisfactorily and which ultimately resulted in deviations from normal geometry. Refinement of a disordered model was hampered by the fact that the molecule sits on a special position (2-fold rotation axis). The presence of whole-molecule disorder for this ambient-temperature dataset cannot be ruled out in this instance.

Discussion

Photochromic compounds that behave as key smart materials in various optoelectronic devices, can specifically switch the physical and chemical properties between two or more states, when stimulated with different wavelength of light [4]. In the past decades, scientists have been paying much attention to the design and fabrication of functional photochromic

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

Atom	x	y	z	$U_{iso}*/U_{eq}$
S1	0.48786(5)	0.67983(10)	0.07755(5)	0.0501(3)
N1	0.2781(3)	1.1298(5)	−0.1342(3)	0.1120(16)
C1	0.5000	0.0243(7)	0.2500	0.091(2)
C2	0.4785(2)	0.1298(4)	0.1778(2)	0.0559(9)
C3	0.48826(16)	0.2934(3)	0.20951(19)	0.0420(7)
C4	0.47489(16)	0.4263(4)	0.15310(18)	0.0417(8)
C5	0.41170(17)	0.4411(4)	0.09288(17)	0.0436(8)
H5	0.3753	0.3668	0.0849	0.052*
C6	0.40953(17)	0.5741(4)	0.04802(18)	0.0452(8)
C7	0.52227(17)	0.5476(4)	0.15188(18)	0.0432(8)
C8	0.59361(17)	0.5767(4)	0.2036(2)	0.0560(9)
H8A	0.5871	0.6247	0.2535	0.084*
H8B	0.6212	0.6446	0.1756	0.084*
H8C	0.6186	0.4795	0.2151	0.084*
C9	0.35279(17)	0.6287(4)	−0.01729(18)	0.0448(8)
C10	0.30496(19)	0.5242(4)	−0.0612(2)	0.0579(9)
H10	0.3086	0.4188	−0.0479	0.069*
C11	0.34578(19)	0.7862(4)	−0.0380(2)	0.0532(9)
H11	0.3772	0.8585	−0.0093	0.064*
C12	0.2522(2)	0.5727(5)	−0.1242(2)	0.0716(11)
H12	0.2207	0.5006	−0.1529	0.086*
C13	0.2464(2)	0.7291(6)	−0.1443(2)	0.0731(12)
H13	0.2114	0.7624	−0.1873	0.088*
C14	0.2928(2)	0.8359(5)	−0.1006(2)	0.0618(10)
C15	0.2850(2)	0.9997(6)	−0.1198(3)	0.0813(13)
F1[a]	0.5248(7)	−0.1031(9)	0.2482(7)	0.099(7)
F2[a]	0.4183(11)	0.096(2)	0.1278(9)	0.082(4)
F3[a]	0.4998(9)	0.1060(16)	0.1083(7)	0.094(4)
F1A[b]	0.5776(6)	−0.0184(16)	0.2315(4)	0.106(4)
F2A[b]	0.4050(10)	0.103(2)	0.1576(11)	0.102(5)
F3A[b]	0.5311(7)	0.0952(15)	0.1335(8)	0.084(3)

[a]Occupancy: 0.482(16); [b]Occupancy: 0.518(16).

compounds, such as photochromic diarylethene derivatives [5], spiropyran devatives [6] and azobenzene derivatives [7]. Among all these photochromic compounds, diarylethene derivatives are regarded as the best promising candidates for their notable thermal irreversible photochromic behaviour and remarkable fatigue resistance [4, 8]. In addition, the photochromic properties of diarylethene can be predictably improved by structure variation to meet a specific functional requirement. The photochromic properties of diarylethene can be strongly influenced by introducing substituents to the aryl groups, e.g. by intriducing long π conjugation or chosing appropriate electron-donating/withdrawing substituents [5, 9].

In order to investigate the effect of the cyanophenyl group on the photochemical properties, we have now determined the structure of 1,2-bis[2-methyl-5-(3-cyanophenyl)-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene. The title compound is a new symmetrical hybrid photochromic diarylethene derivative. The two thiophene rings are linked by the C3 = C3A double bond (1.349(6) Å), which is shorter than the formal single bonds [such as C2–C3, 1.499(5) Å and C3–C4, 1.473(4) Å] in the perfluorocyclopentene ring. The angle between the planes formed by the perfluorocyclopentene and thiophene rings is 48.73(18)°. The molecule adopts an antiparallel conformation [5] of C2 symmetry, which is a crucial prerequisite for photoactivity. The molecular structure of the title compound is shown in the figure. An antiparallel conformation [5] was adopted in the molecule with a 3.540(4) Å distance between the photoactive carbon atoms (C7–C7A). 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 [10, 11].

In the crystal structure, the centroid-to-centroid distance between phenyl rings of neighboring molecules related by inversions symmetry at sites 4c and 4d is 3.756(4) Å, and the molecules are involved in a π-π-type interaction. The crystal can display a notable color change upon irradiation with UV light based on the empirical rule [4, 12]. Colourless crystals turn blue when irradiated by 313 UV light, and the reversible transition can be triggered by exposure to visible light. The photochromism was highly reproducible in the crystalline phase even after 200 successive cycles, indicating that it may find application in certain optoelectronic devices [4, 13].

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