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Structure and photochromism of 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]3,3,4,4,5,5-hexafluorocyclopent-1-ene, C₂₇H₁₆ClF₆S₂

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Abstract

C₂₇H₁₆ClF₆S₂, monoclinic, *P*₂/c (no. 14), *a* = 24.1193(5) Å, *b* = 9.2419(2) Å, *c* = 10.8343(2) Å, β = 96.1260(10)°, *V* = 2401.26(8) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0292, *wR*_{ref}(*F*²) = 0.0878, *T* = 100(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.

Source of material

The title compound was prepared according to the literature method [3] in 47% yield. The title compound crystallized from *n*-hexane at room temperature and produced the suitable colorless crystals for X-ray analysis.

Experimental details

The hydrogen atoms were located by geometrically calculations, and their positions and isotropic displacement parameters were fixed during the structure refinement. The Cl1, C1 and C25 atom at the end of aromatic ring are disorder.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.18 × 0.14 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.40 mm ⁻¹
Diffractometer, scan mode:	CCD area detector, φ and ω
θ _{max} , completeness:	25.0°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	29699, 4217, 0.024
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 3900
<i>N</i> (<i>param</i>) _{refined} :	331
Programs:	Bruker [1], SHELX [2]

The occupancies of the disorder components refined to a 0.9412(11):0.0588(11) ratio for Cl1A:Cl1B and a 0.5:0.5 ratio was set for C1A:C1B and C25A:C25B. All H atoms attached to C were fixed geometrically and treated as riding with 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).

Comment

Photochromic compounds have attracted considerable interest in the fields of optical storage, fluorescence switch and sensors. Their molecular structures can change by appropriate light irradiation and their skeleton can be derivated by the other functional group [4–8]. Among various types of photochromic compounds, diarylethene derivatives are the most promising compounds for application because of their excellent fatigue resistance and thermal stability in both isomeric forms [4]. In addition, the photochromic properties of diarylethene can be predictably improved by structure variation to meet a special functional requirement. An important improvement of the photochromic properties of diarylethene is attributed to the terminal aryl moieties. There are a number of reports on the effect of different substituents at the terminal groups in the aryl moieties [9–11].

Among the substituents, the properties of chlorine substituents have aroused great interest, because the some unique natures differing from the other electron-donating and electron-withdrawing substituents, for their resonance effect and inductive effect acting on the terminal benzene ring. The chlorine substituent has an electron-donating character in resonance effect, but is working as an electron-withdrawing character in the inductive effect.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
S1	0.37308(2)	0.71339(5)	0.25566(4)	0.02337(12)
S2	0.12011(2)	0.68287(5)	0.13666(4)	0.02242(12)
F1	0.32629(5)	0.17687(11)	0.36073(10)	0.0313(3)
F2	0.34570(4)	0.18805(12)	0.16997(11)	0.0333(3)
F3	0.23206(4)	0.05698(12)	0.30340(10)	0.0310(3)
F4	0.27113(5)	−0.01149(11)	0.14093(11)	0.0329(3)
F5	0.16042(4)	0.16134(11)	0.13688(10)	0.0258(2)
F6	0.22032(4)	0.18347(11)	0.00180(9)	0.0254(2)
C1A ^a	0.52048(8)	0.7049(2)	0.66298(17)	0.0294(4)
H1A ^b	0.550787	0.725778	0.723759	0.035*
C1B ^a	0.52048(8)	0.7049(2)	0.66298(17)	0.0294(4)
Cl1B ^c	0.5597(3)	0.7097(9)	0.7815(7)	0.02855(14)
C2	0.49086(7)	0.5782(2)	0.66926(16)	0.0259(4)
H2A	0.501101	0.511430	0.734433	0.031*
C3	0.44647(7)	0.54685(19)	0.58206(15)	0.0215(4)
H3A	0.426437	0.459073	0.588019	0.026*
C4	0.43069(7)	0.64346(18)	0.48472(15)	0.0191(3)
C5	0.46112(8)	0.7715(2)	0.47953(17)	0.0275(4)
H5A	0.451205	0.839163	0.414953	0.033*
C6	0.50591(9)	0.8008(2)	0.56820(18)	0.0318(4)
H6A	0.526513	0.887810	0.563078	0.038*
C7	0.38576(7)	0.60683(18)	0.38729(15)	0.0184(3)
C8	0.35210(7)	0.48766(18)	0.37712(15)	0.0181(3)
H8A	0.352720	0.415231	0.439473	0.022*
C9	0.31584(7)	0.48211(18)	0.26385(15)	0.0181(3)
C10	0.32261(7)	0.59844(19)	0.18772(15)	0.0207(4)
C11	0.29521(8)	0.6321(2)	0.06037(16)	0.0276(4)
H11A	0.320641	0.689517	0.015309	0.041*
H11B	0.260917	0.687105	0.066981	0.041*
H11C	0.286133	0.541633	0.015487	0.041*
C12	0.27970(7)	0.35784(18)	0.22747(14)	0.0170(3)
C13	0.30385(7)	0.20797(19)	0.24387(16)	0.0214(4)
C14	0.25558(7)	0.10461(18)	0.20313(16)	0.0215(4)
C15	0.21355(7)	0.20163(18)	0.12480(15)	0.0189(3)
C16	0.22780(7)	0.35367(17)	0.16719(14)	0.0167(3)
C17	0.18632(6)	0.46728(17)	0.13401(15)	0.0171(3)
C18	0.17557(7)	0.58444(18)	0.20637(15)	0.0198(3)
C19	0.20263(8)	0.6322(2)	0.33027(16)	0.0250(4)
H19A	0.175043	0.681121	0.375786	0.038*
H19B	0.233174	0.699079	0.318695	0.038*
H19C	0.217397	0.547664	0.377528	0.038*
C20	0.14904(6)	0.45925(17)	0.02259(15)	0.0174(3)
H20A	0.150827	0.384775	−0.037293	0.021*
C21	0.11062(7)	0.56814(18)	0.00982(15)	0.0191(3)
C22	0.06448(7)	0.58663(18)	−0.08859(15)	0.0188(3)
C23	0.06762(7)	0.52516(19)	−0.20523(16)	0.0225(4)
H23A	0.100767	0.476694	−0.221803	0.027*
C24	0.02325(7)	0.53359(19)	−0.29729(16)	0.0237(4)
H24A	0.025849	0.491380	−0.376420	0.028*
C25A ^a	−0.02487(7)	0.60417(19)	−0.27259(16)	0.0228(4)
Cl1A ^b	−0.08077(2)	0.61294(6)	−0.38711(4)	0.02855(14)
C25B ^a	−0.02487(7)	0.60417(19)	−0.27259(16)	0.0228(4)
H25B ^c	−0.055508	0.609410	−0.335264	0.027*
C26	−0.02922(7)	0.66724(19)	−0.15845(17)	0.0238(4)
H26A	−0.062463	0.715819	−0.142785	0.029*
C27	0.01537(7)	0.65887(19)	−0.06725(16)	0.0224(4)
H27A	0.012636	0.702835	0.011126	0.027*

^aOccupancy: 0.5, ^bOccupancy: 0.9412(11),^cOccupancy: 0.0588(11).

In this paper, we reported a diarylethene with a chlorine atom at one terminal phenyl ring, the structure of this diarylethene named 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]3,3,4,4,5,5-hexafluorocyclopent-1-ene (*cf.* the figure) was analyzed in detail.

In the perfluorocyclopentene ring, the two thiophene rings are linked by the C12=C16 double bond 1.353(3) Å, which is shorter than the other single bond (such as C12–C13, 1.507(3) Å and C16–C17, 1.468(3) Å). The dihedral angles between the perfluorocyclopentene ring and the two thiophene rings were 138.2° for S1/C7–C10 and 140.6° for S2/C17, C18, C20, C21. The dihedral angle between the thiophene ring and its attached phenyl ring is 171.1°, and the dihedral angle between the thiophene ring and its attached chlorophenyl ring is 25.2°. The perfluorocyclopentene unit with two thiophene rings is antiparallel in the solid state with the two methyl groups on the thiophene rings in a *trans* position to each other, reflected in the torsion angles −38.53(5)° for C12–C16–C17–C18 and −43.11(3)° for C16–C12–C9–C10. This conformation is crucial to its photochromic properties [3]. The intramolecular distance between the two reactive C atoms (C10 and C18) that comprise the cyclisation termini is 3.582 Å. This distance is less than 4.2 Å and indicates that the compound can be expected to exhibit photochromism in the solid crystalline phase [12, 13].

Crystals of the title compound show photochromism in accordance with the expected ring closure. Upon irradiation with 313 nm light, the colorless single-crystals of the title compound turn blue quickly. When the blue crystals were dissolved in *n*-hexane, the solution also showed a blue color, with an absorption maximum at 577 nm, consistent with the presence of the closed-ring isomer. Upon irradiation with visible light with a wavelength greater than 510 nm, the blue crystals return to their initial colorless state, and the absorption spectrum of a hexane solution of such colorless crystals is the same as that of a solution of the open-ring form, with an absorption maximum at 289 nm. The photochromism was highly consistent in crystalline phase even after 100 repeat cycles, indicating that it is favorable for applications in a certain optoelectronic device [14]. The photoconversion ratio from the open- to closed-ring isomer was analysed by HPLC in hexane. The photoconversion ratio from open- to closed-ring isomer in the photostationary state was 61.4%.

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