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Crystal structure and photochromic properties of 1-(2-methyl-5-phenyl-3-thienyl)-2-{2-methyl-5-[4-(9-fluorenone hydrazone)-phenyl]-3-thienyl} perfluorocyclopentene, $C_{41}H_{26}F_6N_2S_2$

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Abstract

$C_{41}H_{26}F_6N_2S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 11.7525(12)$ Å, $b = 12.2430(12)$ Å, $c = 13.4210(13)$ Å, $\alpha = 84.914(1)^\circ$, $\beta = 66.860(1)^\circ$, $\gamma = 82.543(1)^\circ$, $V = 1759.2(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0459$, $wR_{ref}(F^2) = 0.1268$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized by condensation reaction of a diarylethene derivative and 9-fluorenone hydrazone in 80% yield. Diarylethene derivative 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-formylphenyl)-3-thienyl] perfluorocyclopentene (0.1 g, 0.14 mmol) and 9-fluorenone hydrazone (0.027 g, 0.14 mmol) were dissolved in 20 mL absolute ethanol solution. After the solvent was removed by vacuum evaporation, an orange-yellow solid was obtained with 80% yield. *M.p* 452 K–453 K. The title compound crystallized from hexane-dichloromethane at room temperature and produced the suitable colorless crystals for X-ray analysis.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.18 × 0.160 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.22 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{max} , completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	13417, 6868, 0.018
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4799
$N(param)_{refined}$:	499
Programs:	Bruker programs [1], SHELX [2–4], OLEX2 [5]

Experimental details

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located geometrically, and their positions and thermal parameters were refined using a riding model during the structure refinement. The F atoms attached to C14 and C15 were found to be severely disordered. A suitable disordered model over two positions was constructed and the restrained refinement proceeded in a fairly satisfactory manner. The model refined against this room-temperature data set suggests that disorder of the F atoms is more extensive than the one modelled here and probably involves the whole cyclopentene ring.

Discussion

It is well known that diarylethene derivatives are typical organic photochromic compounds which have attracted significant research interest due to their excellent thermal stability [6], outstanding fatigue resistance [7] and rapid response towards light [8]. They are used in optical storage media and optical switching devices [9, 10]. In addition, introduction of certain functional moieties, diarylethenes can not only respond to light but also to some external stimuli, such as cations, anions, acids and bases [11]. Therefore, the applications of diarylethenes have been further extended to colorimetric and fluorometric sensing [12]. In recent years, Schiff bases have been extensively used in diarylethene chemosensors due to their facile syntheses, tunable electronic properties and good chelating capability [13]. Although many photochromic diarylethene compounds have been reported so far, very few crystal structures

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
F1	0.9484(2)	0.29439(16)	−0.16731(13)	0.1306(8)
F2	1.02429(13)	0.40426(17)	−0.10231(15)	0.1168(7)
F3 ^a	0.7760(5)	0.4123(7)	−0.1723(4)	0.115(2)
F4 ^b	0.8799(4)	0.5430(6)	−0.1723(5)	0.104(2)
F5 ^b	0.6282(4)	0.4263(6)	−0.0431(4)	0.0973(18)
F6 ^b	0.6586(6)	0.5610(4)	0.0334(3)	0.095(2)
F3 ^b	0.8251(9)	0.4863(8)	−0.1983(4)	0.118(3)
F4 ^a	0.8844(4)	0.5595(3)	−0.0929(8)	0.135(3)
F5 ^a	0.6167(3)	0.5053(6)	−0.0049(4)	0.093(2)
F6 ^a	0.7533(6)	0.5797(3)	0.0279(3)	0.0941(16)
N1	−0.13525(15)	0.31597(16)	0.51902(15)	0.0617(5)
N2	−0.26247(15)	0.32805(16)	0.58410(15)	0.0610(5)
S1	0.92116(7)	0.03001(6)	0.14938(6)	0.0770(2)
S2	0.55771(5)	0.35659(5)	0.39021(4)	0.06134(18)
C1	1.3808(4)	−0.0203(6)	0.1504(4)	0.1439(19)
H1B	1.453541	−0.047180	0.160255	0.173*
C2	1.3692(4)	0.0834(5)	0.1084(4)	0.1464(17)
H2B	1.434077	0.127343	0.089218	0.176*
C3	1.2605(3)	0.1242(3)	0.0938(3)	0.1119(12)
H3A	1.253870	0.195076	0.063841	0.134*
C4	1.1625(3)	0.0612(3)	0.1230(2)	0.0797(8)
C5	1.1767(3)	−0.0451(3)	0.1652(3)	0.1111(11)
H5A	1.112300	−0.089580	0.184762	0.133*
C6	1.2858(5)	−0.0855(4)	0.1784(3)	0.1398(17)
H6A	1.294433	−0.156911	0.206333	0.168*
C7	1.0478(2)	0.1047(2)	0.10652(19)	0.0663(6)
C8	1.02234(19)	0.2030(2)	0.06018(18)	0.0606(6)
H8A	1.079945	0.254253	0.030068	0.073*
C9	0.89940(18)	0.22050(18)	0.06197(16)	0.0531(5)
C10	0.8331(2)	0.13182(19)	0.10734(18)	0.0604(6)
C11	0.7037(2)	0.1155(2)	0.1207(2)	0.0756(7)
H11A	0.646199	0.138901	0.190855	0.113*
H11B	0.698772	0.038952	0.114504	0.113*
H11C	0.683204	0.158345	0.065486	0.113*
C12	0.84844(17)	0.32167(18)	0.02092(15)	0.0498(5)
C13	0.9167(2)	0.3678(2)	−0.09137(18)	0.0647(6)
C14	0.8304(2)	0.4643(2)	−0.1088(2)	0.0776(8)
C15	0.7206(2)	0.4738(3)	−0.00520(19)	0.0772(8)
C16	0.74114(17)	0.38448(18)	0.07047(16)	0.0502(5)
C17	0.65238(17)	0.37506(17)	0.18390(15)	0.0495(5)
C18	0.68617(17)	0.36555(19)	0.27139(16)	0.0534(5)
C19	0.81168(19)	0.3652(2)	0.27591(19)	0.0704(7)
H19A	0.847515	0.290461	0.278735	0.106*
H19B	0.803106	0.401357	0.339444	0.106*
H19C	0.864771	0.403401	0.212437	0.106*
C20	0.52138(17)	0.37666(17)	0.21478(16)	0.0521(5)
H20A	0.483462	0.384304	0.165042	0.062*
C21	0.45702(17)	0.36594(17)	0.32385(16)	0.0509(5)
C22	0.32271(17)	0.36236(17)	0.38465(15)	0.0488(5)
C23	0.25063(19)	0.3255(2)	0.33636(17)	0.0595(6)
H23A	0.288213	0.302510	0.265448	0.071*
C24	0.12437(19)	0.32235(19)	0.39153(17)	0.0577(5)
H24A	0.077719	0.297651	0.357504	0.069*
C25	0.06615(17)	0.35592(16)	0.49792(16)	0.0502(5)
C26	0.13806(19)	0.39093(19)	0.54677(17)	0.0590(6)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H26A	0.100717	0.412656	0.618114	0.071*
C27	0.26482(19)	0.39416(19)	0.49116(17)	0.0577(5)
H27A	0.311654	0.417883	0.525530	0.069*
C28	−0.06851(18)	0.35538(18)	0.55759(18)	0.0567(5)
H28A	−0.105480	0.385020	0.625844	0.068*
C29	−0.31922(18)	0.24389(18)	0.58810(16)	0.0522(5)
C30	−0.27560(19)	0.13312(18)	0.54287(17)	0.0549(5)
C31	−0.1575(2)	0.0834(2)	0.48302(19)	0.0693(6)
H31A	−0.088128	0.122228	0.462057	0.083*
C32	−0.1452(3)	−0.0249(2)	0.4553(2)	0.0832(8)
H32A	−0.066976	−0.059058	0.414707	0.100*
C33	−0.2478(3)	−0.0828(2)	0.4873(3)	0.0892(9)
H33A	−0.237589	−0.155593	0.468097	0.107*
C34	−0.3656(3)	−0.0345(2)	0.5475(2)	0.0784(7)
H34A	−0.434231	−0.074277	0.569020	0.094*
C35	−0.3794(2)	0.07322(18)	0.57472(18)	0.0585(5)
C36	−0.45522(18)	0.24630(18)	0.64832(16)	0.0526(5)
C37	−0.5412(2)	0.3291(2)	0.7046(2)	0.0676(6)
H37A	−0.516800	0.396733	0.710500	0.081*
C38	−0.6652(2)	0.3093(2)	0.7525(2)	0.0794(8)
H38A	−0.724669	0.364441	0.790828	0.095*
C39	−0.7013(2)	0.2101(2)	0.7440(2)	0.0800(8)
H39A	−0.785033	0.198858	0.776692	0.096*
C40	−0.6158(2)	0.1259(2)	0.6877(2)	0.0717(7)
H40A	−0.641114	0.058546	0.682389	0.086*
C41	−0.49143(19)	0.14445(18)	0.63951(17)	0.0558(5)

Occupancies: ^a = 0.518(7), ^b = 0.482(7).

of diarylethene derivatives having an ion-recognizing group have been reported.

To date, many diarylethene-derived Schiff base derivatives have been reported [14, 15]. However, few publications report the molecular structural conformation and photochromical behavior in the crystalline phase. It was found that photochromic reactivity in the single crystalline phase depended on both anti-parallel mode and the distance between active carbon atoms, which should be less than 4.2 Å [16, 17]. Here, we report a new diarylethene derivative with 9-fluorenone hydrazone unit and investigated its photochromical properties. A novel diarylethene compound 1-(2-methyl-5-phenyl-3-thienyl)-2-{2-methyl-5-[4-(9-fluorenonehydrazone)-phenyl]-3-thienyl}perfluorocyclopentene (C₄₁H₂₆F₆N₂S₂) was synthesized and its crystal structure was analyzed in detail.

The molecular structure of the title compound is shown in the figure. It is interesting that the molecule is packed in an anti-parallel conformation, and the intramolecular distance between the two reactive carbon atoms (C11...C19) is 3.591 Å. The colorless crystal turned purple upon irradiation with 297 nm light, and the colored crystals reverted to a colorless state upon irradiation with visible light (>510 nm). The photochromism was highly reproducible in the crystalline

phase even after 100 repeat cycles, indicating that it could potentially find application in certain optoelectronic devices [18–21]. In the perfluorocyclopentene ring, both thiophene rings are linked by the C12=C16 double bond 1.353(4) Å [22], which is shorter than the formal single bond (such as C9–C12, 1.462(4) Å and C16–C17, 1.463(4) Å). The molecule includes four kinds of planar rings. The dihedral angles between the perfluorocyclopentene ring and the two adjacent thiophene rings are 51.8° for S1/C7–C10 and 49.3° for S2/C17,18–C20,21. The dihedral angle between the thiophene ring (S1) and its adjacent phenyl ring is 4.3°. Finally, the dihedral angle between the thiophene ring (S2) and its attached phenyl ring is 25.8°.

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