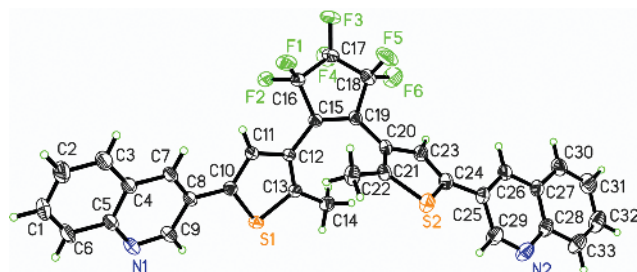


Junfei Lv, Hui Li* and Shouzhi Pu

Structure and photochromism of 1,2-bis[2-methyl-5-(3-quinoly)-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene, C₃₃H₂₀F₆N₂S₂



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Abstract

C₃₃H₂₀F₆N₂S₂, monoclinic, *P*₂₁/*c* (no. 14), *a* = 13.418(4) Å, *b* = 13.876(4) Å, *c* = 15.182(4) Å, β = 98.211(3)°, *V* = 2797.6(14) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0500, *wR*_{ref}(*F*²) = 0.1456, *T* = 296(2) K.

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The crystal structure is shown in the figure. Ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. 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 a known synthetic protocol. 2.4 M *n*-BuLi in hexane solution (4.17 mL, 10.0 mmol) was slowly added to anhydrous THF (50 mL) of 3-bromo-2-methyl-5-(3-quinoly)thiophene [1] (3.04 g, 10.0 mmol) with stirring at 195 K under an argon atmosphere. After 30 min at 195 K, C₅F₈ (0.68 mL, 5.0 mmol) was slowly

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.30 × 0.28 × 0.22 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.26 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ _{max} , completeness:	27.7°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	22123, 6188, 0.034
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4311
<i>N</i> (<i>param</i>) _{refined} :	388
Programs:	SHELX [21, 23, 25], Bruker [24]

added to the reaction mixture, and the mixture was stirred for 2 h at this low temperature. The reaction was quenched by water. The product was extracted with ethyl acetate, and washed with saturated aqueous NaCl and water. The crude product was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (v/v = 6/1) as the eluent to afford 1.43 g of the title compound as a blue solid in 46% yield. M.p. 447–448 K. The title compound crystallized from hexane at room temperature and produced colorless crystals.

Experimental details

The hydrogen atoms were located by geometrical calculations, and their positions and thermal parameters were fixed during the structure refinement. 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

Molecular switches can be triggered by light which is nature's most abundant and powerful energy source. Organic photochromic compounds is a widely studied class of molecular switch, which are capable of undergoing efficient and reversible transformations between two states with distinctive physical and chemical properties upon photoirradiation [2–5]. Among organic photochromic compounds, diarylethenes have been extensively studied for their two isomers that are both thermodynamically stable and their

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}
C1	0.8257(2)	1.4518(2)	0.0286(2)	0.0672(8)
H1B	0.803577	1.511061	0.004650	0.081*
C2	0.8835(3)	1.4481(2)	0.1125(2)	0.0682(8)
H2B	0.898666	1.504558	0.144648	0.082*
C3	0.9177(2)	1.3620(2)	0.1475(2)	0.0572(7)
H3A	0.956754	1.360254	0.203300	0.069*
C4	0.89493(18)	1.27581(18)	0.10078(16)	0.0423(6)
C5	0.83498(18)	1.27935(18)	0.01671(16)	0.0444(6)
C6	0.8015(2)	1.3701(2)	−0.0184(2)	0.0577(7)
H6A	0.762548	1.373655	−0.074136	0.069*
C7	0.93032(17)	1.18466(18)	0.13317(15)	0.0408(5)
H7A	0.969437	1.179883	0.188735	0.049*
C8	0.90744(16)	1.10379(17)	0.08343(15)	0.0370(5)
C9	0.84477(19)	1.11633(19)	0.00025(16)	0.0464(6)
H9A	0.827615	1.061386	−0.033625	0.056*
C10	0.94495(16)	1.00813(17)	0.11188(14)	0.0368(5)
C11	1.01844(16)	0.98376(16)	0.17998(14)	0.0366(5)
H11A	1.055087	1.029059	0.216401	0.044*
C12	1.03381(16)	0.88258(16)	0.19007(14)	0.0343(5)
C13	0.97212(17)	0.83021(17)	0.12775(15)	0.0369(5)
C14	0.9649(2)	0.72408(18)	0.11277(17)	0.0499(6)
H14A	0.913695	0.710733	0.063368	0.075*
H14B	1.028422	0.700047	0.100117	0.075*
H14C	0.947903	0.693133	0.165199	0.075*
C15	1.11248(16)	0.84064(15)	0.25627(14)	0.0349(5)
C16	1.21254(18)	0.89093(18)	0.27607(16)	0.0420(5)
C17	1.28391(18)	0.8153(2)	0.32182(17)	0.0491(6)
C18	1.2147(2)	0.74233(19)	0.35749(18)	0.0512(6)
C19	1.11151(17)	0.76119(16)	0.30741(15)	0.0368(5)
C20	1.02755(17)	0.70042(16)	0.32513(15)	0.0385(5)
C21	0.93598(18)	0.73606(17)	0.34088(16)	0.0420(6)
C22	0.9010(2)	0.83792(18)	0.3440(2)	0.0549(7)
H22A	0.832856	0.838959	0.356530	0.082*
H22B	0.943533	0.872093	0.389805	0.082*
H22C	0.904005	0.868236	0.287579	0.082*
C23	1.03231(18)	0.59813(17)	0.33298(17)	0.0438(6)
H23A	1.089232	0.562721	0.325119	0.053*
C24	0.94671(19)	0.55691(18)	0.35288(16)	0.0448(6)
C25	0.92384(19)	0.45447(17)	0.36248(17)	0.0454(6)
C26	0.9960(2)	0.38782(18)	0.38927(16)	0.0479(6)
H26A	1.062175	0.407287	0.406981	0.058*
C27	0.9708(2)	0.28895(18)	0.39028(16)	0.0468(6)
C28	0.8692(2)	0.26373(18)	0.36444(19)	0.0523(7)
C29	0.8236(2)	0.4206(2)	0.3385(2)	0.0608(8)
H29A	0.773801	0.466199	0.321511	0.073*
C30	1.0420(2)	0.2160(2)	0.4144(2)	0.0624(8)
H30A	1.109289	0.232108	0.431283	0.075*
C31	1.0132(3)	0.1219(2)	0.4133(2)	0.0733(9)
H31A	1.060871	0.073983	0.428909	0.088*
C32	0.9118(3)	0.0972(2)	0.3887(2)	0.0751(10)
H32A	0.892670	0.032839	0.389107	0.090*
C33	0.8419(3)	0.1651(2)	0.3647(2)	0.0702(9)
H33A	0.775096	0.147200	0.348012	0.084*
F1	1.20590(12)	0.96585(11)	0.33317(11)	0.0641(5)
F2	1.24704(11)	0.92995(12)	0.20530(10)	0.0615(4)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
F3	1.35332(13)	0.85147(13)	0.38502(12)	0.0760(5)
F4	1.33382(13)	0.77348(13)	0.26126(12)	0.0740(5)
F5	1.21721(14)	0.75595(17)	0.44626(12)	0.0917(7)
F6	1.24768(13)	0.65216(12)	0.34869(17)	0.0922(7)
N1	0.80931(16)	1.19873(17)	−0.03249(14)	0.0519(5)
N2	0.79606(17)	0.33001(17)	0.3386(2)	0.0662(7)
S1	0.89640(4)	0.90533(5)	0.05810(4)	0.04218(18)
S2	0.85755(5)	0.64476(5)	0.36332(5)	0.0518(2)

cyclization/cycloreversion reaction occurs fast on the picosecond time scale [6–8]. Owing to these excellent characteristics, diarylethene materials have potential applications in the fields of optical memory media and optical switching devices [7]. In the past decades, a significant progress on design and synthesis of diarylethene compounds by the introduction of specific functional groups has enabled diarylethenes to respond not only to UV and visible lights but also to other special external stimuli [9]. Thus, functionalized photochromic diarylethenes with multi-responsive characteristics could be extended to colorimetric and fluorometric sensing, bioimaging, construction of logic gates [10, 11], and control of biological activity [12]. Based on the development of diarylethene, Feringa et al. forecast that the photochromic diarylethene can be used in the field of photopharmacology [13]. The quinoline scaffold is well known to have diverse bioactive units through acting on organisms [14, 15]. Certain quinoline compounds with such response characteristics as pharmacophore have been developed into marketed drugs [16]. On the other hand, the nitrogen atom of quinoline is the same as that of pyridine, which can be easily protonated by external acid stimuli [17–19]. The protonation of nitrogen atom may affect the photochromism of the diarylethenes, such as their absorptions, photoisomerizations, and other physical characteristics. Thus, the photochromic diarylethene bearing a quinolone unit can be functionalized as multi-respond to UV/Vis and acid/alkali in solution, thereby providing the second dimensional control of their optical properties [1]. In this paper, we have explored a new symmetrical diarylethene with quinolone units and investigated its multi-responsive properties.

In the crystal of diarylethene title compound distances of C15–C19, C15–C16 and C19–C20 in the central cyclopentene ring are 1.349(3), 1.505(3) and 1.463(3) Å, respectively. These data clearly indicate that the C15, C19 bond is a double bond due to its length shorter than the other carbon-carbon single bonds. The two thiophene moieties are linked on the C15=C19 double bond. The angle between the planes

of the thiophene ring and the adjacent quinolyl ring are 167.6° and 29.6°, respectively. The dihedral angles between the corresponding thiophene rings and central cyclopentene ring are 45.0° and 40.6°, respectively. The perfluorocyclopentene unit is antiparallel in the crystal state with the two methyl groups on the thiophene rings in a *trans* disposition to each other, as reflected in the torsion angles $-42.8(4)^\circ$ for C19–C15–C12–C13 and $-42.0(4)^\circ$ for C15–C19–C20–C21. This kind of conformation is crucial to its photochromic and photoinduced properties [6]. The intramolecular distance between the two reactive C atoms (C13 and C21) that comprise the cyclisation termini is 3.586 Å. This distance is less than 4.2 Å and indicates that the compound can be expected to exhibit photochromism in the crystalline phase [7, 20].

The molecules of the title structure are packed with antiparallel and crisscross arrangement. Intermolecular C–F···π halogen bond, hydrogen bonds C–H···π, C–H···F, C–H···S and C–H···N connect molecules with each other. These molecular interactions together with halogen and hydrogen bonding may strengthen the stability of the framework structure.

The absorption spectrum of open-form of the title compound exhibited an intense band centered at 272 nm in acetonitrile solution. Upon irradiation with 365 nm, the absorbance at 272 nm decreased along with a new peak appearing at 602 nm, corresponding to the closed-form. And upon visible light irradiation, the absorption spectrum returned to its original state, regenerating the original ring-open conformation. And this cycle can be repeated hundreds times without any change. And this diarylethene could also exhibit photochromic behavior in crystal state.

The multi-response photoswitching characteristic of diarylethene title compound was investigated by stimulation of acid/base and light. Gradual addition of HCl in acetonitrile solution, the diarylethene can form the *N*-protonated form and it can be transformed back by neutralization with NaOH solution. Coupling with the protonated process, its intensity of fluorescence enhanced by a factor of 8, the emission peak showed a notable red-shift from 400 nm to 550 nm. The increase of emission intensity may be attributed to the formation of the *N*-protonated open-ring isomer. Furthermore, the diarylethene title compound exhibited photoisomerization by light irradiation. Upon irradiation with UV light, the colorless solution turned blue to form the formation of *N*-protonated ring-closed isomer. Its absorption maximum was redshifted from 603 to 612 nm. At the same time, the fluorescence emission intensity at 550 nm decreased as irradiation time increases, and reduced to about 2% of the starting value in photostationary state.

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