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Crystal structure and photochromic properties of a novel photochromic perfluordiarylethene containing a triazole bridged pyridine group moiety, $C_{24}H_{18}F_6N_4S_2$

<https://doi.org/10.1515/ncrs-2019-0159>

Received March 3, 2019; accepted April 23, 2019; available online June 21, 2019

Abstract

$C_{24}H_{18}F_6N_4S_2$, monoclinic, $P2_1/c$ (no. 14), $a = 19.0525(18)$ Å, $b = 8.5569(9)$ Å, $c = 15.3792(15)$ Å, $\beta = 97.241(2)^\circ$, $V = 2487.3(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0513$, $wR_{ref}(F^2) = 0.1425$, $T = 296(2)$ K.

CCDC no.: 1911676

The molecular 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 2-ethynylpyridine in 45% yield. Diarylethene derivative (0.1 g, 0.23 mmol) was dissolved in 20 mL solution THF : H₂O (v:v = 4:1), 2-ethynylpyridine (0.024 g, 0.23 mmol) was added. Then add the catalyst, stir for 1 h in an ice bath, then stir at room temperature for 6 h. And no more educt was detected by TLC silica gel plate. After the solvent was removed by vacuum evaporation, a yellow solid was obtained with 45% yield.

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Table 1: Data collection and handling.

Crystal:	Colorless, block
Size:	0.28 × 0.22 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.28 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{max} , completeness:	27.7°, >97% (up to 25.3, >99%)
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	14666, 5652, 0.052
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2432
$N(param)_{refined}$:	373
Programs:	Bruker programs [1], SHELX [2, 3]

M.p. 451 K–453 K. The title compound crystallized from hexane-dichloromethane cosolvent at room temperature and produced the suitable colorless crystal.

Experimental details

The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. The occupancies of the disorder fluorine atoms at the central cyclopentene ring are refined. All H atoms attached to C were fixed geometrically and treated as riding with C–CH = 0.96 Å (methyl) or 0.93 Å (ethyl and thienyl) with $U_{iso}(H) = 1.2U_{eq}$ (ethyl and thienyl) or $U_{iso}(H) = 1.5U_{eq}$ (methyl).

Discussion

Among the organic photochromic compounds, diarylethene derivatives have attracted remarkable research interests due to their wide applications in optical memory media and photo-optical switching devices [4–6]. In recent years, various diarylethene chemosensors have been developed to identify various chemical species, such as metal ions, anions, and amino acids [7, 8]. The sensing mechanism of these diarylethene derivatives can be determined by analytical methods such as nuclearmagnetic resonance, mass spectrometry, and infrared, but few of them are analyzed from their own structural characteristics. Therefore, in order to understand the binding mechanism, the structure of the sensor is necessary to be confirmed by single-crystal X-ray diffraction analysis. Although many photochromic diarylethene compounds have been reported so far,

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 ^a	0.122(2)	0.881(2)	0.9431(18)	0.138(8)
F2 ^a	0.0652(8)	0.869(2)	0.8118(17)	0.105(5)
F3 ^a	0.2161(10)	1.051(2)	0.870(2)	0.131(6)
F4	0.14665(11)	1.0525(3)	0.76538(17)	0.1213(9)
F5 ^a	0.2974(13)	0.881(3)	0.790(2)	0.087(6)
F6 ^a	0.2149(9)	0.850(2)	0.6875(12)	0.095(5)
F1 ^{ra}	0.1410(19)	0.889(2)	0.9535(14)	0.144(7)
F2 ^{ra}	0.0671(10)	0.8676(18)	0.843(3)	0.134(8)
F3 ^{ra}	0.2215(6)	1.040(2)	0.8928(18)	0.106(5)
F5 ^{ra}	0.3003(15)	0.886(4)	0.814(3)	0.100(6)
F6 ^{ra}	0.2220(10)	0.870(2)	0.6941(11)	0.105(5)
N1	0.45454(12)	0.2803(3)	0.72093(16)	0.0626(7)
N2	0.43846(15)	0.1486(3)	0.6751(2)	0.0863(9)
N3	0.47471(15)	0.1516(3)	0.60742(19)	0.0827(8)
N4	0.58665(12)	0.4671(3)	0.54917(17)	0.0713(7)
S1	0.28102(4)	0.28684(9)	0.71636(5)	0.0659(3)
S2	0.10461(6)	0.30905(11)	0.97695(6)	0.0964(4)
C1	−0.0385(2)	0.3078(5)	0.9069(3)	0.1278(17)
H1A	−0.034798	0.216889	0.943729	0.192 [*]
H1B	−0.072353	0.378864	0.926100	0.192 [*]
H1C	−0.053622	0.277287	0.847376	0.192 [*]
C2	0.03233(18)	0.3866(4)	0.9121(2)	0.0792(10)
C3	0.05223(17)	0.5156(4)	0.8724(2)	0.0709(9)
H3SA	0.020912	0.575774	0.835041	0.085 [*]
C4	0.12584(15)	0.5533(3)	0.89234(18)	0.0541(7)
C5	0.16155(17)	0.4518(4)	0.94930(19)	0.0646(8)
C6	0.23656(18)	0.4527(5)	0.9881(2)	0.0997(12)
H6A	0.263116	0.383301	0.955636	0.150 [*]
H6B	0.240115	0.418834	1.047965	0.150 [*]
H6C	0.255171	0.556713	0.985794	0.150 [*]
C7	0.15880(14)	0.6873(3)	0.85387(17)	0.0517(7)
C8	0.1325(2)	0.8487(4)	0.8648(3)	0.0759(11)
C9	0.18205(19)	0.9565(4)	0.8228(3)	0.0746(10)
C10	0.23103(18)	0.8471(3)	0.7793(2)	0.0637(8)
C11	0.21366(14)	0.6858(3)	0.80750(17)	0.0494(7)
C12	0.25258(13)	0.5486(3)	0.78073(16)	0.0451(6)
C13	0.22139(14)	0.4319(3)	0.73069(18)	0.0525(7)
C14	0.14653(16)	0.4188(4)	0.6881(2)	0.0821(10)
H14A	0.122517	0.516171	0.693949	0.123 [*]
H14B	0.122909	0.337243	0.715903	0.123 [*]
H14C	0.146151	0.394734	0.627058	0.123 [*]
C15	0.32546(14)	0.5210(3)	0.80656(17)	0.0533(7)
H15A	0.354723	0.591713	0.839714	0.064 [*]
C16	0.34867(14)	0.3831(3)	0.77876(17)	0.0530(7)
C17	0.42050(15)	0.3130(4)	0.7994(2)	0.0685(9)
H17A	0.450181	0.383935	0.837082	0.082 [*]
H17B	0.416672	0.216390	0.831533	0.082 [*]
C18	0.49961(14)	0.3666(4)	0.6817(2)	0.0648(8)
H18	0.518537	0.463015	0.699980	0.078 [*]
C19	0.51219(14)	0.2852(3)	0.60984(19)	0.0564(7)
C20	0.55885(14)	0.3229(4)	0.54358(19)	0.0575(8)
C21	0.57266(16)	0.2141(4)	0.4813(2)	0.0692(9)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H21A	0.551516	0.116015	0.479184	0.083 [*]
C22	0.61857(19)	0.2548(5)	0.4223(2)	0.0850(10)
H22A	0.629064	0.184065	0.379879	0.102 [*]
C23	0.64814(18)	0.3992(5)	0.4272(2)	0.0914(12)
H23A	0.679658	0.428616	0.388644	0.110 [*]
C24	0.63076(18)	0.5008(5)	0.4899(3)	0.0875(11)
H24	0.650801	0.600071	0.491588	0.105 [*]

^aOccupancy: 0.5.

very few diarylethene derivatives having an ion-recognizing group have been reported, which undergo the photocyclization reaction in the crystalline phase. The single-crystalline photochromic reactivity depended on both anti-parallel mode and the distance between active carbon atoms which is less than 4.2 Å [9, 10].

To date, novel diarylethene derivatives with a triazole bridged group base moiety have attracted much attention because their photochromic reactivity could be effectively modulated by light, and metal ions [11]. It is well known that these diarylethenes having a symmetric thienyl group have excellent thermal stabilities [12]. Our group has reported a lot of diarylethene compounds with excellent optical properties and analyzed their crystal structures to further guide the functional molecular design [13–15]. In addition, the introduction of fluorophores with ions recognition on the diarylethene of the symmetric thienyl group has attracted a great deal of interest among researchers. In this work, a diarylethene derived triazole bridged derivative has been synthesized through condensation reaction [16, 17]. A novel crystal 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-[(2-pyridyl)-triazole-methyl]-3-thienyl]-perfluorocyclopentene was obtained.

The molecule adopts an antiparallel conformation, and the distance between the photoactive carbon atoms (C5...C13) was 3.684 Å. Based on the empirical rule, the crystal displayed a notable color change upon irradiation with UV light. The colorless crystal turned purple upon irradiation with 313 nm light, and the colored crystals reverted to a colorless state upon irradiation with visible light. 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 [18]. In the perfluorocyclopentene ring, the both thiophene rings are linked by the C7=C11 double bond 1.339(7) Å, which is shorter than the formal single bond (such as C4–C7, 1.469(7) Å and C7–C8, 1.485(8) Å). The molecule includes four kinds of planar rings and they can form three dihedral angles between every two adjacent planar rings. The dihedral angles between the

perfluorocyclopentene ring and the two adjacent thiophene rings were 58.5° for S2/C7—C11 and 61.2° for S1/C12,13—C15,16, and that between the triazole ring and pyridine ring was 8.6° .

The title compound is packed with antiparallel and crisscross neighbouring molecules each other. Intermolecular hydrogen bonds connect molecules of the title compound with each other. These molecular interactions together with hydrogen bonding may strengthen the stability of the framework structure.

The absorption spectrum of open-form the title compound exhibited an intense band centered at 248 nm in acetonitrile. Irradiation with UV light (297 nm) resulted in the emergence of a new absorption band at 555 nm with a color change from colorless to purple due to the formation of the closed-ring isomer. The purple color faded to colorless upon irradiation with visible light (>510 nm), and the absorption spectrum returned to the initial state. After 100 repeat cycles, the diarylethenes still showed good photochromism with only 13% degradation for its closed-ring isomer.

Acknowledgements: This work was supported by the Project of Jiangxi Education Office (GJJ180621). We thank the editor for providing the figure.

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