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Crystal structure and photochromism of 1-(2-ethyl-5-formylthiophen-3-yl)-2-(2-cyano-1,5-dimethyl-4-pyrrl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene, $C_{19}H_{14}F_6N_2OS$

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Abstract

$C_{19}H_{14}F_6N_2OS$, monoclinic, $P2_1/c$ (no. 14), $a = 16.534(2)$ Å, $b = 9.3008(12)$ Å, $c = 12.7681(16)$ Å, $\beta = 95.095(2)^\circ$, $V = 1955.7(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0466$, $wR_{ref}(F^2) = 0.1471$, $T = 296(2)$ 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.

Source of material

The title compound was prepared following previously reported literatures [4]. The title compound was crystallized from hexane at room temperature and the colorless crystals was obtained.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.26 × 0.22 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.23 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	10436, 3842, 0.024
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2672
$N(param)_{refined}$:	317
Programs:	Bruker programs [1], SHELX [2, 3]

Experimental details

The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed. The occupancies of the disordered fluorine atoms at the central cyclopentene ring are refined to a 0.639(6):0.361(6) ratio for F1 and F1', F2 and F2', F3 and F3', F4 and F4', F5 and F5', F6 and F6', respectively. 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

Photochromic compounds which exhibit different absorption and emission behaviors triggered by light, have received continuous attention [5]. They have potential application in the fields of optical memory devices [6], molecular sensors [7], and light-responsive gas separation switch [8]. Among photochromic compounds, diarylethenes are regarded as the candidates in practical application for their excellent thermal stability and high sensitivity [9–11]. The photochromic properties of diarylethenes are mainly depended on the aspects of substituents [12], the nature of the heterocyclic ring [13], and the groups at the active atoms [14]. Here, we reported a diarylethene with an ethyl chain at 2-position on the thiophene ring.

In the crystal of title compound, the distance of C8—C12, in central cyclopentene ring is 1.346(3) Å, which clearly indicates that the this distance bond is a double bond due to its length shorter than the other carbon-carbon single bonds, such as 1.504(3) Å of C8—C9. The thiophene and pyrrol moieties are linked at the C8=C12 double bond. The dihedral

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

Atom	x	y	z	<i>U</i> _{iso} ^a / <i>U</i> _{eq}
N1	0.51758(17)	0.3460(4)	0.2589(2)	0.1059(11)
N2	0.40689(10)	0.3740(2)	0.47608(15)	0.0469(5)
O1	−0.00864(14)	0.2361(3)	0.7137(2)	0.1059(9)
S1	0.07414(4)	0.32641(7)	0.51696(5)	0.0575(2)
F1 ^a	0.3078(5)	0.8874(8)	0.3844(6)	0.127(3)
F2 ^a	0.3678(3)	0.8793(6)	0.5749(5)	0.0914(15)
F3 ^a	0.1920(2)	0.9700(4)	0.4174(3)	0.0995(14)
F4 ^a	0.2459(5)	1.0575(6)	0.5634(6)	0.102(3)
F5 ^a	0.1002(2)	0.8529(4)	0.5496(6)	0.0930(15)
F6 ^a	0.1952(3)	0.8453(5)	0.6758(4)	0.0952(14)
F1 ^{rb}	0.3461(5)	0.8829(10)	0.4172(9)	0.070(3)
F2 ^{rb}	0.3794(6)	0.8795(9)	0.5144(10)	0.092(3)
F3 ^{rb}	0.2302(11)	1.0631(14)	0.5088(12)	0.135(7)
F4 ^{rb}	0.2823(4)	0.9628(10)	0.6449(6)	0.112(3)
F5 ^{rb}	0.1138(4)	0.8736(8)	0.4785(8)	0.097(3)
F6 ^{rb}	0.1426(7)	0.8555(8)	0.6442(9)	0.104(3)
C1	0.47553(16)	0.3934(3)	0.3148(2)	0.0720(8)
C2	0.42253(14)	0.4505(3)	0.38700(19)	0.0519(6)
C3	0.38041(14)	0.5768(3)	0.38358(18)	0.0499(6)
H3A	0.380791	0.647312	0.332008	0.060*
C4	0.33615(12)	0.5802(2)	0.47306(17)	0.0414(5)
C5	0.35401(13)	0.4548(2)	0.52990(17)	0.0432(5)
C6	0.32766(16)	0.4065(3)	0.6329(2)	0.0620(7)
H6A	0.291166	0.476149	0.658121	0.093*
H6B	0.300542	0.315442	0.624209	0.093*
H6C	0.374307	0.396748	0.682840	0.093*
C7	0.43742(17)	0.2321(3)	0.5043(3)	0.0753(8)
H7A	0.417730	0.203333	0.569662	0.113*
H7B	0.419084	0.164955	0.450275	0.113*
H7C	0.495701	0.233970	0.511827	0.113*
C8	0.28117(13)	0.6942(2)	0.50030(17)	0.0426(5)
C9	0.30608(17)	0.8490(3)	0.4920(2)	0.0624(7)
C10	0.2358(2)	0.9353(3)	0.5222(3)	0.0893(12)
C11	0.17726(17)	0.8324(3)	0.5635(2)	0.0650(7)
C12	0.20701(13)	0.6856(2)	0.53568(17)	0.0426(5)
C13	0.15538(12)	0.5595(2)	0.54905(16)	0.0407(5)
C14	0.13631(12)	0.4571(2)	0.47266(17)	0.0418(5)
C15	0.15750(15)	0.4524(3)	0.36133(17)	0.0518(6)
H15A	0.188948	0.537527	0.348073	0.062*
H15B	0.107632	0.456740	0.315284	0.062*
C16	0.20495(17)	0.3215(3)	0.3324(2)	0.0674(7)
H16A	0.215809	0.327516	0.259951	0.101*
H16B	0.255329	0.317334	0.375948	0.101*
H16C	0.173845	0.236381	0.343091	0.101*
C17	0.11698(13)	0.5320(3)	0.64223(18)	0.0489(6)
H17A	0.121809	0.591927	0.700764	0.059*
C18	0.07225(13)	0.4085(3)	0.6369(2)	0.0532(6)
C19	0.02688(17)	0.3477(4)	0.7188(3)	0.0753(9)
H19A	0.025513	0.400424	0.780524	0.090*

Occupancy: ^a = 0.639, ^b = 0.361.

angle between the plane of the thiophene ring and the plane of the central cyclopentene ring is 51.5°. The angle between the plane of the pyrrolyl ring and the plane of the central cyclopentene ring is 42.6°. The title diarylethene is an antiparallel structure in the crystal state with the two methyl groups on the thiophene rings in a *trans* position to each other, as reflected in the torsion angles 135.3(8)° for C9—C8—C4—C5 and 129.4(4)° for C14—C13—C12—C11. This kind of conformation is crucial to its photochromic and photoinduced properties [9]. The distance between the two reactive C atoms (C5 and C14) is 3.609 Å, which is less than 4.2 Å. Thus, the compound can be expected to exhibit photochromism in the crystalline phase [8, 15]. Bond lengths and other geometric parameters are in the expected ranges [14, 16].

The title compound is packed in an unit cell with antiparallel and crisscross neighbouring molecules each other. Intermolecular weak hydrogen bonds C—CH···π 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-ring form of the title compound centered at 253 nm in acetonitrile solution. Upon irradiation with 297 nm, the absorbance at 253 nm decreased along with a new peak appearing at 665 nm, corresponding to the closed-ring form of the title compound. 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 100 times without any change.

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References

1. Bruker: APEX3, SAINT-Plus, XPREP. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Zheng, C. H.; Fan, C. B.; Pu, S. Z.: Crystal structure of the photochromic compound 1-(2-cyano-1,5-dimethyl-4-pyrrolyl)-2-(2-methyl-5-formyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene, C₁₈H₁₂F₆N₂OS. *Z. Kristallogr. NCS* **230** (2015) 19–20.
5. Zhang, J.; Zou, Q.; Tian, H.: Photochromic materials: more than meets the eye. *Adv. Mater.* **25** (2013) 378–399.
6. Uchida, K.; Saito, M.; Murakami, A.; Kobayashi, T.; Nakamura, S.; Irie, M.: Three bits eight states photochromic recording and nondestructive readout by using IR light. *Chem. Eur. J.* **11** (2005) 534–542.
7. Feng, E. T.; Fan, C. B.; Wang, N. S.; Liu, G.; Pu, S. Z.: A highly selective diarylethene chemosensor for colorimetric detection

- of CN^- , and fluorescent relay-detection of Al^{3+}/Cr^{3+} . *Dyes Pigments* **151** (2018) 22–27.
8. Fan, C. B.; Gong, L. L.; Huang, L.; Luo, F.; Krishna, R.; Yi, X.; Zheng, A.; Zhang, L.; Pu, S. Z.; Feng, X. F.; Luo, M. B.; Guo, G. C.: Significant enhancement of C_2H_2/C_2H_4 separation by a photochromic diarylethene unit: a temperature- and light-responsive separation switch. *Angew. Chem. Int. Ed.* **56** (2017) 7900–7906.
 9. Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S.: Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem. Rev.* **114** (2014) 12174–12277.
 10. Tian, H.; Yang, S. J.: Recent progresses on diarylethene based photochromic switches. *Chem. Soc. Rev.* **33** (2004) 85–97.
 11. Fihey, A.; Perrier, A.; Browne, W. R.; Jacquemin, D.: Multi-photochromic molecular systems. *Chem. Soc. Rev.* **44** (2015) 3719–3759.
 12. Yun, C.; You, J.; Kim, J.; Huh, J.; Kim, E.: Photochromic fluorescence switching from diarylethenes and its applications. *J. Photoch. Photobio.* **C10** (2009) 111–129.
 13. Zhang, J. J.; Tian, H.: The endeavor of diarylethenes: new structures, high performance, and bright future. *Adv. Opt. Mater.* **6** (2018) 1701278.
 14. He, S. H.; Fan, C. B.: Crystal structure of 1-[2-n-butyl-5-formyl-3-thienyl]-2-[2-cyano-1,5-dimethyl-4-pyrryl]-3,3,4,4,5,5-hexafluoro-cyclopent-1-ene, $C_{21}H_{18}F_6N_2OS$. *Z. Kristallogr. NCS* **228** (2013) 219–220.
 15. Ramamurthy, V.; Venkatesan, K. Photochemical reactions of organic crystals. *Chem. Rev.* **87** (1987) 433–481.
 16. Wang, J.; Liu, G.; Fan, C.; Pu, S.: Structure and photochromism of 1,2-bis[2-methyl-5-(2-chlorophenyl)-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene, $C_{27}H_{16}Cl_2F_6S_2$. *Z. Kristallogr. NCS* **232** (2017) 359–361.