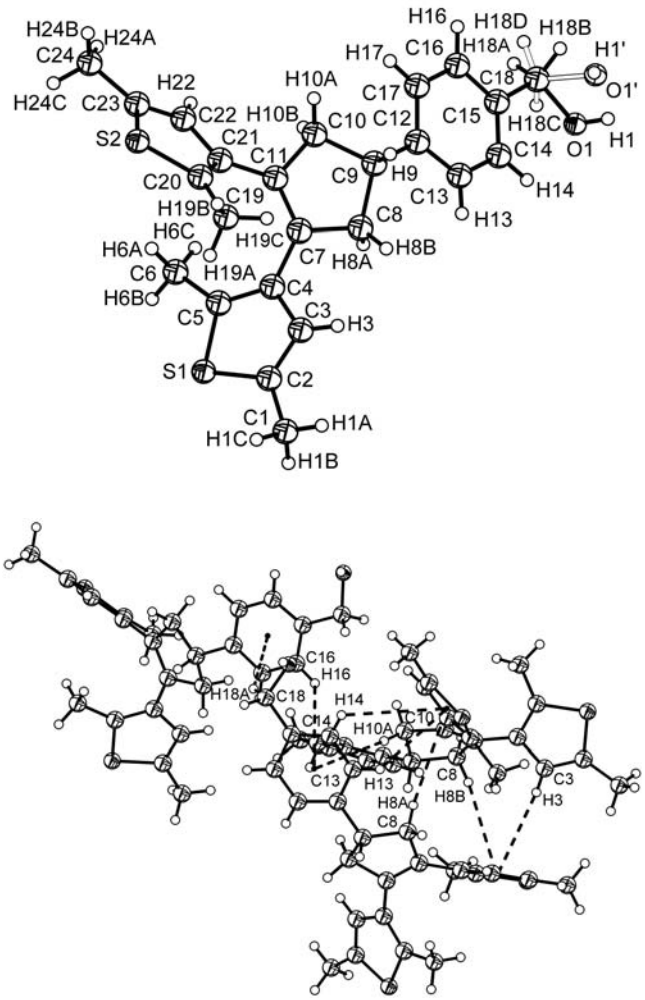
Crystal structure of (4-(3,4-bis(2,5-dimethylthiophen-3-yl)-cyclopent-3-en-1-yl)phenyl)methanol, $C_{24}H_{26}OS_2$

Xiaochuan Li[*,I], Zhengzheng Guo[I], Young-A Son[*,II], Jiange Wang[III] and Sheng Wang[IV]

[I] Henan Normal University, College of Chemistry and Environmental Science, Xinxiang 453007, Henan, P. R. China
[II] Chungnam National University, Department of Advanced Organic Materials and Textile System Engineering, Daejeon 305-764, South Korea
[III] Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China
[IV] Zhanjiang Normal University, School of Chemistry Science & Technology, Zhanjiang 524048, Guangdong, P. R. China.

Received May 6, 2010, accepted and available on-line May 18, 2010; CCDC no. 1267/3052



Abstract

$C_{24}H_{26}OS_2$, orthorhombic, *Pccn* (no. 56), a = 12.493(1) Å, b = 40.201(3) Å, c = 8.487(7) Å, V = 4262.5 Å^3, Z = 8, $R_{gt}(F)$ = 0.069, $wR_{ref}(F^2)$ = 0.208, T = 295 K.

Source of material

(4-(3,4-bis(2,5-dimethylthiophen-3-yl)cyclopent-3-en-1-yl)-phenyl)methanol was synthesized by multi-step reaction [1]. Chemicals used for the synthesis were commercially available of AR grade, and were used as received without further purification. The colorless crystals of the title compound were obtained by slow evaporation of hexane solution at room temperature.

Experimental details

The hydrogen atoms were placed geometrically and refined using a riding model with d(C—H) = 0.93 Å (aromatic), 0.96 Å (–CH_3), 0.97 Å (–CH_2–) or 0.98 Å (–CH–), U_{iso}(H) = 1.2 - 1.5 U_{eq}(C) and d(O—H) = 0.82 Å (hydroxyl), U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

The title crystal structure is built up from $C_{24}H_{26}OS_2$ molecule (figure, top), with all the bond lengths being within normal ranges. The crystal structure displays intra- and intermolecular C–H···π interactions with no hydrogen bonds and π···π interactions being established. The title molecule has photoactive antiparallel conformations. The distances between reactive carbon atoms are short enough for photocyclization reaction: 3.565(6) Å (C5 to C20^i, symmetry code i: x, y, z), which is essential to the photochromic reactivity in the crystalline phase [2,3]. Upon irradiation with ultraviolet light, the colorless crystal turns yellow. The colors are due to the photogenerated closed-ring isomer. The colored crystal can sustain several days in the dark, which demonstrate its stability. Upon irradiation with visible light, the colored crystal is completely bleached and return to the initial colorless one. The antiparallel conformation is stabilized by eight of eleven intramolecular C–H···π interactions. Four C–H···π interactions are formed between methyl hydrogen atoms and two thiophene rings. In two of the bonds (C19–H19A···π^i, C2/C3/C4/C5/S1; C6–H6A···π^i, C20/C21/C22/C23/S2), the hydrogen atom is directly above the thiophene ring and the C–H bond points towards a ring carbon. This arrangement corresponds to a type-III interaction [4]. The methylene hydrogen atoms of the five membered ring also interacted with the phenyl ring and two thiophene rings formed seven type-VI C–H···π interactions. Totally eight type-III and type-V intermolecular C–H···π interactions are found in the crystal structure (figure, bottom). Typical type-V C–H···π interaction is C10–H10A···π^{ii} (C12/C13/C14/C15/C16/C17, symmetry code ii: x,1.5–y,0.5+z), in which the hydrogen atom interacts with a carbon at the edge of the acceptor ring. The H···centroid distances range from 2.985 to 3.995 Å in both intramolecular and intermolecular C–H···π interactions, which is well inside the interval classified by Malone to 2.65 to 4.00 Å, basing on a survey of Cambridge Structural Database combined with semi-empirical and *ab initio* molecular orbital calculations [4]. The molecules are packed together only by intermolecular C–H···π interactions which are further stabilizing the molecular conformation.

* Correspondence author (e-mail: lixiaochuan@henannu.edu.cn; yason@cnu.ac.kr)

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.11 × 0.13 × 0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.61 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	29093, 3966
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2655
$N(param)_{refined}$:	255
Programs:	SHELXS-97, SHELXL-97, SHELXTL [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	8*e*	0.510	–0.2182	0.2530	1.0641	0.201
H(18A)	8*e*	0.510	–0.0273	0.2770	1.0802	0.163
H(18B)	8*e*	0.510	–0.0959	0.2726	0.9269	0.163
H(1')	8*e*	0.490	–0.1614	0.2502	0.8483	0.201
H(18C)	8*e*	0.490	–0.0869	0.2602	1.1325	0.163
H(18D)	8*e*	0.490	–0.0321	0.2820	1.0014	0.163
H(1A)	8*e*		0.2067	–0.0184	0.9918	0.171
H(1B)	8*e*		0.2423	–0.0239	1.1670	0.171
H(1C)	8*e*		0.3191	–0.0339	1.0287	0.171
H(3)	8*e*		0.2164	0.0443	0.9325	0.075
H(6A)	8*e*		0.5738	0.0894	1.0951	0.113
H(6B)	8*e*		0.5430	0.0806	1.2693	0.113
H(6C)	8*e*		0.4876	0.1106	1.1840	0.113
H(8A)	8*e*		0.1880	0.1246	1.0648	0.068
H(8B)	8*e*		0.1550	0.1034	0.9161	0.068
H(9)	8*e*		0.1929	0.1436	0.7470	0.076
H(10A)	8*e*		0.3521	0.1698	0.7538	0.069
H(10B)	8*e*		0.3481	0.1754	0.9381	0.069
H(13)	8*e*		0.0217	0.1530	1.0013	0.074
H(14)	8*e*		–0.0905	0.1961	1.0595	0.087
H(16)	8*e*		0.1065	0.2575	0.8437	0.167
H(17)	8*e*		0.2224	0.2144	0.7917	0.145
H(19A)	8*e*		0.4874	0.0467	0.7720	0.108
H(19B)	8*e*		0.5042	0.0565	0.5950	0.108
H(19C)	8*e*		0.4018	0.0686	0.6851	0.108
H(22)	8*e*		0.5672	0.1663	0.8961	0.074
H(24A)	8*e*		0.7640	0.1792	0.8302	0.150
H(24B)	8*e*		0.7967	0.1629	0.6695	0.150
H(24C)	8*e*		0.8310	0.1462	0.8287	0.150

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	8*e*	0.510(6)	–0.1635(6)	0.2516(2)	1.117(1)	0.094(3)	0.120(4)	0.187(5)	0.040(3)	0.016(4)	–0.001(4)
C(18)	8*e*	0.510	–0.0708(7)	0.2614(2)	1.021(1)	0.099(4)	0.105(4)	0.203(5)	0.027(3)	0.020(4)	–0.008(4)
O(1')	8*e*	0.490	–0.1703(6)	0.2610(2)	0.929(1)	0.094(3)	0.120(4)	0.187(5)	0.040(3)	0.016(4)	–0.001(4)
C(18')	8*e*	0.490	–0.0706(7)	0.2615(2)	1.021(1)	0.099(4)	0.105(4)	0.203(5)	0.027(3)	0.020(4)	–0.008(4)
S(1)	8*e*		0.4301(1)	0.02472(3)	1.1689(2)	0.0819(8)	0.0681(7)	0.0773(8)	0.0224(6)	0.0044(6)	0.0143(6)
S(2)	8*e*		0.66645(9)	0.10019(3)	0.6901(2)	0.0570(7)	0.0734(8)	0.0948(9)	0.0147(5)	0.0137(6)	0.0009(6)
C(1)	8*e*		0.2664(6)	–0.0181(1)	1.0631(8)	0.159(6)	0.055(3)	0.127(5)	–0.009(3)	0.000(5)	0.015(3)
C(2)	8*e*		0.3147(4)	0.0161(1)	1.0660(6)	0.092(3)	0.055(3)	0.078(3)	0.007(2)	0.014(3)	–0.001(2)
C(3)	8*e*		0.2786(3)	0.0438(1)	0.9927(5)	0.066(3)	0.055(2)	0.067(3)	0.003(2)	0.000(2)	0.000(2)
C(4)	8*e*		0.3444(3)	0.07230(9)	1.0161(5)	0.052(2)	0.053(2)	0.054(2)	0.009(2)	0.004(2)	–0.000(2)
C(5)	8*e*		0.4305(3)	0.0659(1)	1.1116(5)	0.056(2)	0.061(2)	0.056(2)	0.012(2)	0.001(2)	0.004(2)
C(6)	8*e*		0.5164(3)	0.0887(1)	1.1703(6)	0.058(3)	0.095(3)	0.073(3)	0.006(2)	–0.009(2)	0.005(3)
C(7)	8*e*		0.3189(3)	0.10513(9)	0.9479(4)	0.053(2)	0.054(2)	0.052(2)	0.006(2)	–0.003(2)	–0.001(2)
C(8)	8*e*		0.2068(3)	0.11911(9)	0.9570(5)	0.052(2)	0.054(2)	0.063(2)	0.007(2)	0.001(2)	0.000(2)
C(9)	8*e*		0.2110(3)	0.1504(1)	0.8545(5)	0.054(2)	0.064(3)	0.071(3)	0.008(2)	0.000(2)	0.007(2)
C(10)	8*e*		0.3315(3)	0.1600(1)	0.8537(5)	0.054(2)	0.052(2)	0.065(2)	0.008(2)	0.005(2)	0.000(2)
C(11)	8*e*		0.3864(3)	0.12678(9)	0.8790(5)	0.049(2)	0.049(2)	0.061(2)	0.008(2)	–0.003(2)	–0.003(2)
C(12)	8*e*		0.1366(3)	0.1790(1)	0.8963(5)	0.052(2)	0.056(2)	0.073(3)	0.010(2)	0.001(2)	0.010(2)
C(13)	8*e*		0.0416(3)	0.1745(1)	0.9726(5)	0.053(2)	0.055(2)	0.077(3)	0.005(2)	0.000(2)	0.004(2)
C(14)	8*e*		–0.0261(3)	0.2005(1)	1.0088(6)	0.053(2)	0.066(3)	0.099(4)	0.009(2)	0.002(2)	0.000(3)
C(15)	8*e*		–0.0016(4)	0.2318(1)	0.9730(9)	0.060(3)	0.056(3)	0.227(8)	0.011(2)	0.018(4)	0.014(4)
C(16)	8*e*		0.0909(5)	0.2364(1)	0.882(1)	0.101(4)	0.065(3)	0.252(7)	0.015(3)	0.043(4)	0.038(4)
C(17)	8*e*		0.1599(4)	0.2104(1)	0.8480(9)	0.075(3)	0.070(3)	0.217(6)	0.018(3)	0.044(4)	0.034(4)
C(19)	8*e*		0.4768(4)	0.0639(1)	0.6947(6)	0.078(3)	0.061(3)	0.077(3)	0.012(2)	0.005(2)	–0.010(2)
C(20)	8*e*		0.5344(3)	0.0946(1)	0.7447(5)	0.055(2)	0.056(2)	0.068(3)	0.010(2)	0.001(2)	0.003(2)
C(21)	8*e*		0.4981(3)	0.12169(9)	0.8260(5)	0.050(2)	0.053(2)	0.059(2)	0.008(2)	–0.002(2)	0.002(2)
C(22)	8*e*		0.5789(3)	0.1463(1)	0.8433(5)	0.056(2)	0.059(2)	0.070(3)	0.005(2)	–0.005(2)	–0.003(2)
C(23)	8*e*		0.6740(3)	0.1386(1)	0.7770(6)	0.048(2)	0.069(3)	0.085(3)	0.004(2)	–0.001(2)	0.005(2)
C(24)	8*e*		0.7756(4)	0.1585(1)	0.7763(8)	0.055(3)	0.104(4)	0.141(5)	–0.010(3)	0.006(3)	0.000(4)

Acknowledgments. This work was supported by the National Natural Science Foundation of China for the Youth (nos. 20702011 and 20802065), the Startup Fund of Henan Normal University (no. 051004), the Science Foundation for the Youth of Henan Normal University (no. 2006033), and the Natural Science foundation of Henan Provincial Education Office (no. 2007150022).

References

1. Li, X.; Tian, H.: High-content pendant photochromic copolymer with dithienylethene/fluorene 2:1 mole ratio. Macromol. Chem. Phys. **206** (2005) 1769-1777.
2. Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M.: Single-crystalline photochromism of diarylethenes: reactivity — structure relationship. Chem. Commun. **23** (2002) 2804-2805.

3. Li, X.; Ma, Y.; Wang, B.; Li, G.: "Lock and Key control" of Photochromic Reactivity by Controlling the Oxidation/Reduction State. Org. Lett. **10** (2008) 3639-3642.
4. Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty, R.; Lavery, A. J.: X–H···π (phenyl) interactions theoretical and crystallographic observations. J. Chem. Soc. Faraday Trans. **93** (1997) 3429-3436.
5. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
6. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.