Crystal structure of 3,3′-(4-(4-bromophenyl)cyclopent-1-ene-1,2-diyl)-bis(2,5-dimethylthiophene), $C_{23}H_{23}BrS_2$

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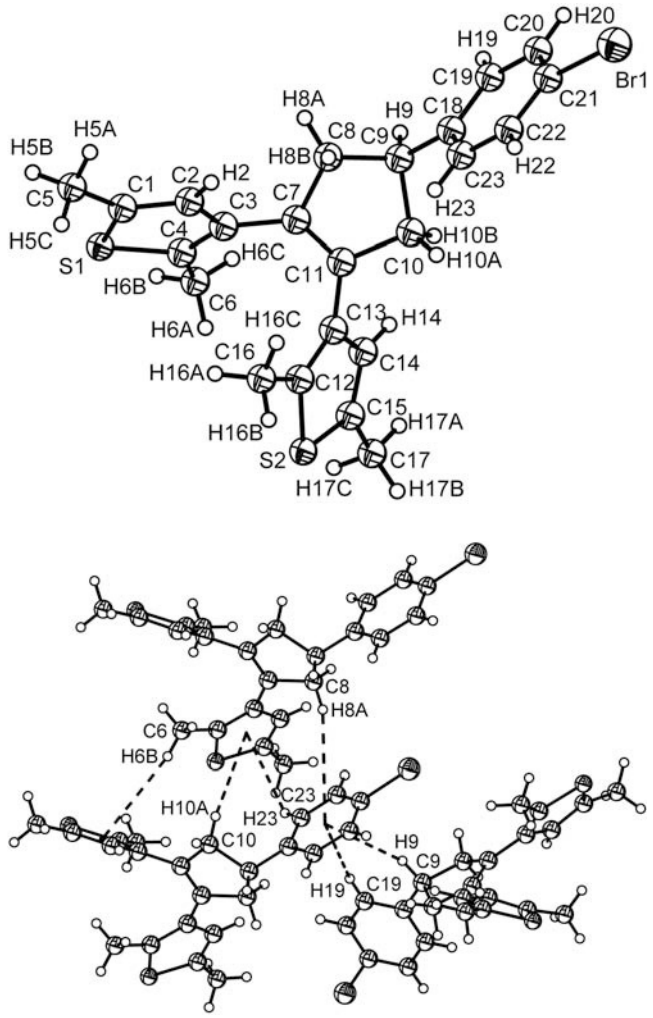

Abstract

$C_{23}H_{23}BrS_2$, monoclinic, $P12_1/c1$ (no. 14), a = 7.341(2) Å, b = 8.949(2) Å, c = 32.747(9) Å, β = 94.825(3)°, V = 2143.7 Å^3, Z = 4, $R(F)$ = 0.076, $wR_{ref}(F^2)$ = 0.178, T = 291 K.

Source of material

3,3′-(4-(4-bromophenyl)cyclopent-1-ene-1,2-diyl)bis(2,5-dimethylthiophene) was synthesized by multi-step reaction according to our early published method [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 U_{eq}(C) for CH and CH_2 groups or U_{iso}(H) = 1.5 U_{eq}(C) for CH_3 groups. The larger residual values are caused mainly by the disordered two thiophene rings, for which the photosensitive molecule are easy to generate a closed form (hexatriene structure).

Discussion

The title crystal structure is built up from $C_{23}H_{23}BrS_2$ molecules (figure, top), with all the bond lengths being within normal ranges. The crystal structure displays only one kind of hydrogen bonds (figure bottom). The characteristic hydrogen bonding parameters (H···acceptor distance, donor···acceptor distance, donor–H···acceptor angle) of C5–H5C···S2^{i} (symmetry code i: –x,½+y,½–z) are 2.972(2) Å, 3.89(1) Å, and 161.0(6)°. The molecules form dimers through hydrogen bonding. There are six intermolecular C–H···π interactions, involving six hydrogen atoms and the π electron system of three carbon rings (figure bottom). The H···centroid distance range from 3.070 to 3.710 Å, which is well inside the interval classified to 2.65 to 4.0 Å, based on a survey of Cambridge Structural Database, combined with semi-empirical and ab initio molecular orbital calculations [2]. Two typical intermolecular C–H···π interactions are observed in the crystals: C6–H6B···π^{ii} (C12/C13/C14/C15/S2, symmetry code ii: x,y,z) and C6–H9···π^{ii} (C18/C19/C20/C21/C22/C23). The classical T-shape geometry is almost accomplished, but a slight deviation of the H atom from the centre of the ring makes it more of the type II [2]. Configuration of C23–H23···π^{ii} (C1/C2/C3/C4/S1) corresponds to type III with the hydrogen atom being directly above the centre of ring and the C—H bond pointing towards to a ring carbon. In the other C–H···π interactions (C10–H10A···π^{ii}, C1/C2/C3/C4/S1; C8–H8A···π^{ii}, C18/C19/C20/C21/C22/C23; C19–H19···π^{ii}, C18/C19/C20/C21/C22/C23), the hydrogen atom interacts with a carbon at the edge of the acceptor ring (type V). Molecules in a typical antiparallel conformation are packed in the crystals. The crystals can be turned to yellow irradiated with ultraviolet light (254 nm) and can be bleached upon irradiation with visible light ($\lambda \geq$ 405 nm). Therefore, the photochromic activity was maintained with the

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distance of reactivity carbon atoms (3.523 Å) shorter than 4.2 Å [3,4]. There are ten kinds of intramolecular C–H···π interactions involved four configuration types (type III, IV, V, and VI). Except for type III C–H···π interactions, the hydrogen atoms are deviated from the top of carbon rings while the hydrogen atoms approach to the edge of carbon rings or to a carbon.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.36 × 0.38 × 0.47 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.16 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12809, 3908
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2915
$N(param)_{refined}$:	239
Programs:	SHELXS-97, SHELXL-97, SHELXTL [5], DIAMOND [6]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.0802	0.6315	0.1346	0.062
H(5A)	4*e*	–0.1826	0.8325	0.1227	0.135
H(5B)	4*e*	–0.3688	0.7738	0.1017	0.135
H(5C)	4*e*	–0.2109	0.8189	0.0748	0.135
H(6A)	4*e*	–0.0989	0.1506	0.0637	0.079
H(6B)	4*e*	–0.2826	0.1592	0.0848	0.079
H(6C)	4*e*	–0.1002	0.1188	0.1108	0.079
H(8A)	4*e*	0.1693	0.4155	0.1981	0.075
H(8B)	4*e*	0.3241	0.4988	0.1763	0.075
H(9)	4*e*	0.3436	0.2170	0.2143	0.065
H(10A)	4*e*	0.5655	0.2293	0.1484	0.062
H(10B)	4*e*	0.4581	0.0901	0.1637	0.062
H(14)	4*e*	0.3067	–0.0708	0.1081	0.056
H(16A)	4*e*	0.1189	0.3972	0.0298	0.083
H(16B)	4*e*	0.3122	0.3888	0.0129	0.083
H(16C)	4*e*	0.2944	0.4341	0.0587	0.083
H(17A)	4*e*	0.2925	–0.2907	0.0573	0.114
H(17B)	4*e*	0.3731	–0.2444	0.0164	0.114
H(17C)	4*e*	0.1609	–0.2519	0.0186	0.114
H(19)	4*e*	0.5363	0.2376	0.2733	0.071
H(20)	4*e*	0.7901	0.3307	0.3115	0.079
H(22)	4*e*	0.9110	0.5773	0.2153	0.069
H(23)	4*e*	0.6569	0.4822	0.1779	0.063

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4*e*	1.0897(1)	0.5349(2)	0.29661(3)	0.0790(6)	0.157(1)	0.0891(7)	–0.0346(7)	–0.0217(5)	–0.0264(7)
S(1)	4*e*	–0.2882(2)	0.4692(2)	0.08090(5)	0.0481(9)	0.064(1)	0.055(1)	0.0071(8)	–0.0071(8)	0.0026(9)
S(2)	4*e*	0.2523(2)	0.0738(2)	0.01136(5)	0.065(1)	0.053(1)	0.047(1)	–0.0014(9)	0.0089(8)	–0.0123(8)
C(1)	4*e*	–0.1666(9)	0.6171(8)	0.1029(2)	0.053(4)	0.051(4)	0.060(4)	0.005(3)	0.003(3)	0.004(3)
C(2)	4*e*	–0.0052(9)	0.5678(7)	0.1212(2)	0.047(3)	0.048(3)	0.058(4)	0.000(3)	–0.001(3)	–0.007(3)
C(3)	4*e*	0.0232(8)	0.4117(7)	0.1183(2)	0.039(3)	0.047(3)	0.046(3)	0.003(2)	0.006(2)	–0.009(3)
C(4)	4*e*	–0.1198(8)	0.3409(7)	0.0972(2)	0.036(3)	0.051(3)	0.043(3)	–0.002(3)	0.008(2)	–0.007(3)
C(5)	4*e*	–0.239(1)	0.7749(9)	0.1003(3)	0.108(7)	0.063(5)	0.095(7)	0.024(5)	–0.017(5)	0.008(5)
C(6)	4*e*	–0.1534(9)	0.1775(7)	0.0883(2)	0.048(4)	0.056(4)	0.053(4)	–0.006(3)	0.003(3)	–0.012(3)
C(7)	4*e*	0.1887(8)	0.3402(7)	0.1386(2)	0.040(3)	0.051(3)	0.049(3)	0.003(3)	0.001(3)	–0.012(3)
C(8)	4*e*	0.2654(9)	0.4031(9)	0.1798(2)	0.050(3)	0.074(4)	0.061(4)	0.019(3)	–0.008(3)	–0.027(3)
C(9)	4*e*	0.4054(9)	0.2850(8)	0.1965(2)	0.045(3)	0.067(4)	0.050(3)	0.004(3)	–0.003(3)	–0.010(3)
C(10)	4*e*	0.4504(9)	0.1963(8)	0.1579(2)	0.046(3)	0.053(4)	0.054(4)	0.009(3)	–0.006(3)	–0.008(3)
C(11)	4*e*	0.2925(8)	0.2296(7)	0.1260(2)	0.041(3)	0.042(3)	0.048(3)	0.002(2)	0.003(2)	–0.006(3)
C(12)	4*e*	0.2606(8)	0.2099(7)	0.0490(2)	0.044(3)	0.038(3)	0.047(3)	–0.002(3)	0.008(3)	–0.006(3)
C(13)	4*e*	0.2793(8)	0.1480(7)	0.0869(2)	0.037(3)	0.038(3)	0.049(3)	0.001(2)	0.003(2)	–0.006(3)
C(14)	4*e*	0.2902(8)	–0.0111(7)	0.0849(2)	0.050(3)	0.038(3)	0.053(3)	0.008(3)	0.007(3)	–0.002(3)
C(15)	4*e*	0.2745(9)	–0.0681(7)	0.0465(2)	0.057(4)	0.040(3)	0.062(4)	0.004(3)	0.011(3)	–0.011(3)
C(16)	4*e*	0.245(1)	0.3723(7)	0.0365(2)	0.065(4)	0.046(4)	0.055(4)	0.000(3)	0.008(3)	0.008(3)
C(17)	4*e*	0.275(1)	–0.2281(8)	0.0335(3)	0.102(6)	0.042(4)	0.083(6)	0.002(4)	–0.002(5)	–0.013(4)
C(18)	4*e*	0.5713(8)	0.3475(8)	0.2210(2)	0.046(3)	0.057(3)	0.040(3)	0.007(3)	0.000(3)	–0.003(3)
C(19)	4*e*	0.613(1)	0.3049(8)	0.2614(2)	0.064(4)	0.067(4)	0.046(3)	–0.010(3)	0.004(3)	0.006(3)
C(20)	4*e*	0.765(1)	0.3601(9)	0.2844(2)	0.071(4)	0.081(4)	0.041(4)	–0.004(4)	–0.017(3)	0.007(3)
C(21)	4*e*	0.8781(9)	0.4594(9)	0.2665(2)	0.047(3)	0.072(4)	0.047(3)	–0.001(3)	–0.001(3)	–0.010(3)
C(22)	4*e*	0.8372(9)	0.5075(8)	0.2269(2)	0.050(3)	0.068(4)	0.056(4)	–0.006(3)	0.009(3)	0.001(3)
C(23)	4*e*	0.6842(9)	0.4502(8)	0.2047(2)	0.052(3)	0.064(4)	0.040(3)	0.009(3)	0.004(3)	0.003(3)

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