Crystal structure of 2,3-bis(3'-methylthiophene-5'-carbaldehyde-2-yl) thiophene, $C_{16}H_{12}O_2S_3$

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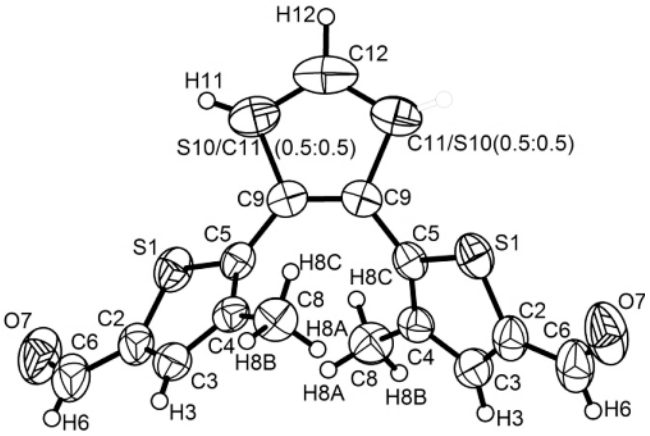

Abstract

$C_{16}H_{12}O_2S_3$, orthorhombic, *Pbcn* (no. 60), a = 10.8457(4) Å, b = 8.1000(3) Å, c = 17.6048(6) Å, V = 1546.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0401, $wR_{ref}(F^2)$ = 0.0953, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.15×0.23×0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.79 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ and ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6441, 1920
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 980
$N(param)_{refined}$:	99
Programs:	SHELX [10], DIAMOND [11]

Source of material

2,3-Bis(3'-methylthiophene-5'-carbaldehyde-2-yl)thiophene was synthesized by two step reactions. Firstly, 2,3-dibromothiophene coupled with (3-methylthiophen-2-yl)magnesium bromide by a conventional Kumada coupling reaction generated 2,3-bis-(3'-methylthiophene-2-yl)thiophene [1-5]. Secondly, 2,3-bis(3'-methylthiophene-2-yl)thiophene was formylated under standard Vilsmeier-Haack conditions and yielded the target compound, 2,3-bis(3'-methylthiophene-5'-carbaldehyde-2-yl)thiophene [6-8]. Colourless crystals suitable for X-ray diffraction were obtained by slow evaporation of the petroleum ether solution at room temperature.

Experimental details

Hydrogen atoms were placed geometrically and refined using a riding model with d(C–H) = 0.93 Å (aromatic), 0.96 Å (–CH_3). U_{iso}(H) = 1.2 U_{eq}(C) for CH groups or U_{iso}(H) = 1.5 U_{eq}(C) for –CH_3 groups. The central thiophene ring was disordered over opposite direction and overlapped each other with site occupation factors of 0.5 and 0.5.

Discussion

2,3-Bis(3'-methylthiophene-5'-carbaldehyde-2-yl)thiophene shows photochromic activity with the tow side thiophene rings configuring anti-parallel conformation. The distance between the reactive carbon atoms (C4^{i1} and C4^{i2}, i1: 0.5+x, 0.5–y, 1–z, i2: 1.5–x, 0.5–y, 0.5+z) is estimated to be 3.69 Å. It is shorter than the distance (4.2 Å) defined by Irie and co-authors, which is an experience rule for determining the solid photochromic activity of diarylethene derivatives [9]. Upon irradiation of the crystal with UV light (254 nm), the colour of crystal turns to yellow gradually. Photo-induced conrotatory cyclization reaction occurr between the two anti-paralleled thiophene rings. The ring closed isomer shows an expanded π conjugated system with respect to the ring-opened isomer, and thus lead to enhanced absorbance in the visible region. The yellow colour can be bleached by irradiation of visible light (>400 nm). The cycles between colour and colourless in crystal state can be repeated by alternated irradiation of UV (254 nm) and Visible light (>400 nm) without observable degradation. The photochromic property in crystalline state is similar to that in solution. It should be noted that the photo-induced conrotatory cyclization reaction in solid state is more effective than that in solution due to the uniformly anti-parellel configured molecule array promoted by inter-molecular weak interaction.

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

Atom	Site	x	y	z	U_{iso}
H(3)	8*d*	0.5414	–0.2530	0.4239	0.067
H(6)	8*d*	0.3555	–0.2701	0.5249	0.094
H(8A)	8*d*	0.6565	–0.1444	0.2661	0.089
H(8B)	8*d*	0.7241	–0.1389	0.3448	0.089
H(8C)	8*d*	0.7051	0.0240	0.2981	0.089
H(11)	8*d*	0.4540	0.4473	0.3716	0.084
H(12)	4*c*	$\frac{1}{2}$	0.637(6)	$\frac{1}{4}$	0.14(2)

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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}
S(1)	8*d*	0.34524(5)	0.07626(8)	0.39793(3)	0.0497(4)	0.0717(4)	0.0547(3)	–0.0024(3)	0.0083(3)	–0.0114(3)
C(2)	8*d*	0.3941(2)	–0.1028(3)	0.4397(1)	0.061(2)	0.067(2)	0.043(1)	–0.021(1)	–0.003(1)	–0.005(1)
C(3)	8*d*	0.5020(2)	–0.1568(3)	0.4085(1)	0.066(2)	0.052(2)	0.048(1)	–0.009(1)	–0.016(1)	–0.002(1)
C(4)	8*d*	0.5484(2)	–0.0531(3)	0.3504(1)	0.043(1)	0.044(1)	0.045(1)	–0.001(1)	–0.010(1)	–0.006(1)
C(5)	8*d*	0.4717(2)	0.0803(3)	0.3388(1)	0.039(1)	0.050(1)	0.042(1)	–0.002(1)	–0.0007(9)	–0.008(1)
C(6)	8*d*	0.3265(3)	–0.1727(4)	0.5034(2)	0.095(2)	0.090(2)	0.050(2)	–0.042(2)	–0.003(2)	–0.009(2)
O(7)	8*d*	0.2342(2)	–0.1107(3)	0.5302(1)	0.106(2)	0.126(2)	0.072(1)	–0.054(1)	0.032(1)	–0.023(1)
C(8)	8*d*	0.6694(2)	–0.0806(3)	0.3113(1)	0.047(1)	0.064(2)	0.068(1)	0.011(1)	–0.005(1)	0.001(1)
C(9)	8*d*	0.4858(2)	0.2223(3)	0.2883(1)	0.036(1)	0.046(1)	0.057(1)	0.001(1)	–0.003(1)	–0.004(1)
S(10)	8*d*	0.4725(1)	0.4104(1)	0.32289(7)	0.0617(7)	0.0558(7)	0.0918(8)	0.0069(5)	–0.0037(6)	–0.0085(6)
C(11)	8*d*	0.4725(1)	0.4104(1)	0.32289(7)	0.0617(7)	0.0558(7)	0.0918(8)	0.0069(5)	–0.0037(6)	–0.0085(6)
C(12)	4*c*	$\frac{1}{2}$	0.5050(5)	$\frac{1}{4}$	0.063(2)	0.050(2)	0.143(4)	0	–0.029(3)	0

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