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Crystal structure and optical properties of 1,6-bis(methylthio)pyrene, $C_{18}H_{14}S_2$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.12 × 0.10 × 0.08 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.37 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	29.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12544, 3858, 0.094
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2747
$N(\text{param})_{\text{refined}}$:	183
Programs:	Bruker [1], SHELX [2], PLATON [3]

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Abstract

$C_{18}H_{14}S_2$, monoclinic, $P2_1/c$ (no. 14), $a = 10.196(3)$ Å, $b = 14.756(4)$ Å, $c = 9.508(3)$ Å, $\beta = 103.965(14)^\circ$, $V = 1388.3(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0480$, $wR_{\text{ref}}(F^2) = 0.1207$, $T = 200(2)$ K.

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The molecular 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

All chemicals were purchased from commercial sources and used as received without further purification. The title

complex was prepared in two steps using pyrene as the starting material. The intermediate 1,6-dibromopyrene was prepared through the bromination of pyrene according to the literature [4]. The final product was synthesized as following: 1.69 g (12 mmol) sodium thiomethoxide (50%) and 1.80 g (5 mmol) 1,6-dibromopyrene were added subsequently to a 50 mL two-neck round bottom flask. Then, 40 mL DMF was added into the above flask. The mixture was stirred at 160 °C overnight under the protection of nitrogen. After the reaction was completed, a yellow solid precipitate was observed, which was separated by filtration and washed with ethanol several times, and then recrystallized with toluene to obtain yellow block crystals. Yield: 85%. **Melting point**, 200–202 °C. **¹H NMR** (400 MHz, $CDCl_3$) δ (TMS, p.p.m.): 8.64 (s, 2H, $J = 8.63$ Hz), 8.16–8.12 (m, 2H), 8.10–7.96 (m, 4H), 2.73 (s, 6H). **MALDI-TOF MS** (m/z): calculated for $C_{18}H_{14}S_2$ 294.42, found 294.32. **Elemental analysis**—calculated for $C_{18}H_{14}S_2$: C, 73.42%; H, 4.79%; S, 21.78%; found: C, 73.34%; H, 4.78%; S, 21.67%.

Experimental details

All H atoms bond to C atoms were introduced using the appropriate HFIX command in the *SHELXL2014* program [2], with the value of 0.93 Å or 0.96 Å for C–H bonds distances. All H atoms were set as riding, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ or $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for aromatic and methyl hydrogens, respectively. The structure was checked using *PLATON* [3].

Comment

It is well known that organic functional materials with interesting optical, electronic, magnetic, biological and multifunctional properties have attracted considerable attention, and have for instance been used as organic

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
S1	0.00589(5)	0.33725(4)	0.21136(5)	0.03660(15)
S2	0.78548(5)	0.45468(4)	0.91573(5)	0.04127(16)
C1	−0.0261(2)	0.24411(17)	0.0884(3)	0.0548(6)
H1A	0.0340	0.2471	0.0249	0.082 [*]
H1B	−0.1179	0.2468	0.0322	0.082 [*]
H1C	−0.0118	0.1883	0.1419	0.082 [*]
C2	0.17725(18)	0.32077(13)	0.30699(19)	0.0296(4)
C3	0.2541(2)	0.24787(14)	0.2787(2)	0.0368(5)
H3	0.2162	0.2068	0.2061	0.044 [*]
C4	0.3861(2)	0.23588(14)	0.3575(2)	0.0361(4)
H4	0.4353	0.1867	0.3369	0.043 [*]
C5	0.44687(18)	0.29607(13)	0.46726(18)	0.0289(4)
C6	0.58327(19)	0.28427(13)	0.5508(2)	0.0335(4)
H6	0.6337	0.2357	0.5304	0.040 [*]
C7	0.63992(19)	0.34228(13)	0.65835(19)	0.0314(4)
H7	0.7283	0.3325	0.7108	0.038 [*]
C8	0.56661(18)	0.41880(12)	0.69357(18)	0.0267(4)
C9	0.62123(18)	0.47889(13)	0.80919(18)	0.0299(4)
C10	0.5450(2)	0.55189(14)	0.83734(19)	0.0342(4)
H10	0.5818	0.5914	0.9127	0.041 [*]
C11	0.4148(2)	0.56641(13)	0.7544(2)	0.0336(4)
H11	0.3663	0.6163	0.7740	0.040 [*]
C12	0.35513(18)	0.50757(12)	0.64194(18)	0.0276(4)
C13	0.21914(19)	0.51930(13)	0.55777(19)	0.0314(4)
H13	0.1690	0.5683	0.5774	0.038 [*]
C14	0.16201(18)	0.46113(13)	0.45084(19)	0.0297(4)
H14	0.0737	0.4711	0.3983	0.036 [*]
C15	0.23474(18)	0.38416(12)	0.41665(18)	0.0265(4)
C16	0.37095(17)	0.37133(12)	0.49730(17)	0.0254(4)
C17	0.43139(17)	0.43322(12)	0.61025(17)	0.0249(4)
C18	0.8190(2)	0.54611(16)	1.0436(2)	0.0440(5)
H18A	0.8119	0.6027	0.9926	0.066 [*]
H18B	0.9086	0.5398	1.1043	0.066 [*]
H18C	0.7546	0.5447	1.1023	0.066 [*]

light-emitting diodes (OLED), organic field effect transistors (OFET), organic lasers, chemosensors and as solar cell components, *etc* [5–9]. As one of the most important organic functional building precursors, pyrene and its derivatives have attracted particular attention because of their interesting optical and electronic properties [10–12]. Up to date, a large number of new pyrene-based functional materials have been characterized and their properties have been investigated [13–15]. Sulfur-containing organic compounds have also attracted interest on the basis of their special electronic structures. Compared with the reports on nitrogen-containing, pyrene-based compounds, the studies on pyrene-based thioether compounds are relatively limited. Recently, Xu and Wen *et al.* have reported the crystal structure of one diaryl sulfide 1,3,6,8-tetrakis(*p*-tolylthio)pyrene and 1,8-bis(*p*-tolylthio)pyrene using pyrene as the starting precursor [16, 17]. Herein, we report the crystal structure of a new pyrene-based arylalkyl thioether, 1,6-bis(methylthio)pyrene,

which was synthesized by the nucleophilic substitution reaction of sodium thiomethoxide with 1,6-dibromopyrene in high yield. In addition, the optical properties of the title compound were studied preliminarily.

The single X-ray diffraction analysis of the title compound shows that the crystal structure agrees well with expected structure. All the non hydrogen atoms are almost in a strict plane with the largest deviation from the main plane of 0.127(3) Å. The C–S bond distances in the title compound are distributed in a relatively narrow range of 1.7719(19)–1.793(2) Å, in which the C_{alkyl}–S bond distances are slightly larger than those of C_{aryl}–S. The two C–S–C bond angles are very similar with 103.38(10)° for C2–S1–C1 and 103.61(10)° for C9–S2–C18. The C–S bond distances and C–S–C bond angles are within the expected values for diaryl sulfide compounds and they are comparable to those found in 1,3,6,8-tetrakis(*p*-tolylthio)pyrene and 1,8-bis(*p*-tolylthio)pyrene [16, 17]. The crystal packing of the title compound can be described by the analysis of three main intermolecular interactions. Firstly, dimers of molecules related by inversion symmetry are held together by $\pi \cdots \pi$ interactions. Secondly, these dimers form zigzag one-dimensional chains held together by intermolecular C–H $\cdots \pi$ interactions. Then, these chains are linked together by S $\cdots$ S interactions.

The optical properties of the title compound were investigated preliminarily. The title compound was dissolved in dichloromethane and absorption was observed in the range of 325 to 425 nm. A main emission peak around 421 nm with an obvious shoulder emission peak at 436 nm for the above solution were also observed. The emission intensity is significantly higher than that of its precursor pyrene with a ca. 8-fold increase. The crystal state emits yellow-green fluorescence with a peak at 530 nm. Similar to 1,8-bis(*p*-tolylthio)pyrene [17], the title compound also can be oxidized by some peroxides such as *m*-chloroperoxybenzoic acid and displays “on–off” optical switching property. However, its sensitivity for *m*-chloroperoxybenzoic acid is significantly lower than that of 1,8-bis(*p*-tolylthio)pyrene, which may be due to the fact that the oxidation of alkylarylsulfide is difficult compared to diarylsulfide.

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