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Synthesis, crystal structure and optical property of 1,6-bis(*p*-tolylthio)pyrene, C₃₀H₂₂S₂

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Abstract

C₃₀H₂₂S₂, triclinic, *P* $\bar{1}$ (no. 2), $a = 7.5621(2)$ Å, $b = 8.6787(3)$ Å, $c = 9.8951(3)$ Å, $\alpha = 110.4180(10)^\circ$, $\beta = 97.6810(10)^\circ$, $\gamma = 108.8430(10)^\circ$, $V = 553.33(3)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0413$, $wR_{\text{ref}}(F^2) = 0.1160$, $T = 200(2)$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list

Table 1: Data collection and handling.

Crystal:	Yellow needle
Size:	0.18 × 0.08 × 0.06 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.26 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX II, φ and ω
θ_{max} , completeness:	27.5°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23062, 2535, 0.092
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2191
$N(\text{param})_{\text{refined}}$:	147
Programs:	Bruker [1], SHELX [2], PLATON [3]

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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 compound was prepared by two steps using pyrene as the starting materials. The intermediate 1,6-dibromopyrene was prepared through the bromination of pyrene according to the literature [4]. The title compound was synthesized according to the similar method in the literature [5] and the detailed procedures were displayed as following: Firstly, 3.38 g (24 mmol) of *p*-methylthiophenol, 3.60 g (10 mmol) of 1,6-dibromopyrene and 80 mL of dimethylformamide (DMF) were added to a 150 mL round bottom flask. The resulting mixture was stirred for 20 min in an ice bath under the protection of nitrogen atmosphere. Secondly, 0.96 g (24 mmol) of NaH (60%) was slowly added to the above flask in batches and the mixture was stirred for 10 min. Then, the mixture was refluxed for 10 h. After the mixture was cooled, light yellow needle-like crystals were obtained directly. Yield: 3.80 g, 86%. The selected suitable single crystal was structurally determined by X-ray diffraction analysis. **Melting point:** 248–250 °C. **¹H NMR** (400 MHz, CDCl₃) δ (TMS, ppm): 8.74 (s, 2H, $J = 8.74$ Hz), 8.14–8.03 (m, 6H, $J = 8.07$ Hz), 7.22–7.20 (m, 4H), 7.12–7.09 (m, 4H), 2.33 (s, 6H). **¹³C NMR** (400 MHz, CDCl₃) δ (TMS, ppm): 136.72, 136.65, 133.13, 133.04, 131.63, 131.40, 131.26, 131.24, 131.15, 130.90, 130.61, 130.46, 130.23, 130.13, 130.07, 128.16, 127.62, 125.56, 125.47, 125.19, 125.04, 21.06. **MALDI-TOF MS** (m/z): calcd. for C₃₀H₂₂S₂ 446.1, found 446.1. **Elemental analysis** – calculated for C₃₀H₂₂S₂: C, 80.68%; H, 4.96%; S, 14.36%; found: C, 80.44%, H, 4.88%; S, 14.22%.

Experimental details

All H atoms bound to C atoms were introduced using the HFIX command in the SHELXL-2014 program [2], with the value of 0.93 Å or 0.96 Å for C–H bond distances. All H atoms were allowed for as riding atoms with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ or $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for hydrogen

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.59330 (6)	0.46231 (5)	0.78017 (5)	0.04470 (18)
C1	0.3410 (2)	0.3660 (2)	0.68812 (16)	0.0317 (3)
C2	0.2338 (2)	0.4693 (2)	0.68480 (17)	0.0351 (3)
H2	0.2964	0.5963	0.7341	0.042*
C3	0.0375 (2)	0.3889 (2)	0.61058 (17)	0.0344 (3)
H3	−0.0335	0.4617	0.6117	0.041*
C4	−0.0583 (2)	0.20304 (19)	0.53402 (15)	0.0298 (3)
C5	0.04792 (19)	0.09514 (18)	0.53799 (14)	0.0277 (3)
C6	0.2490 (2)	0.17722 (18)	0.61739 (15)	0.0288 (3)
C7	−0.2596 (2)	0.1167 (2)	0.45174 (17)	0.0338 (3)
H7	−0.3311	0.1879	0.4478	0.041*
C8	−0.3502 (2)	−0.0632 (2)	0.37955 (16)	0.0327 (3)
H8	−0.4838	−0.1159	0.3255	0.039*
C9	0.6586 (2)	0.6951 (2)	0.83391 (17)	0.0349 (3)
C10	0.7003 (2)	0.7690 (2)	0.73245 (17)	0.0400 (4)
H10	0.6856	0.6940	0.6316	0.048*
C11	0.7635 (2)	0.9525 (2)	0.77856 (18)	0.0395 (4)
H11	0.7895	1.0019	0.7079	0.047*
C12	0.7896 (2)	1.0660 (2)	0.92575 (17)	0.0353 (3)
C13	0.7460 (3)	0.9895 (2)	1.02546 (18)	0.0433 (4)
H13	0.7610	1.0646	1.1264	0.052*
C14	0.6811 (2)	0.8063 (2)	0.98101 (18)	0.0416 (4)
H14	0.6519	0.7566	1.0510	0.050*
C15	0.8636 (3)	1.2651 (2)	0.9741 (2)	0.0498 (4)
H15A	0.9370	1.2979	0.9069	0.075*
H15B	0.9486	1.3263	1.0771	0.075*
H15C	0.7534	1.3010	0.9699	0.075*

atoms bonded to pyrene ring and methyl group, respectively. The structure was checked using PLATON [3].

Comment

Organic functional molecules with tunable optical, biological and bifunctional as well as multifunctional properties have gained great deal of attention due to their

potential applications in sensors, live-cell imaging, organic solar cells (OSCs), organic light-emitting diodes (OLEDs) and so on [5–11]. As one of the most well-known functional molecules, pyrene and its derivatives have been widely investigated by many researchers because of their effectively fluorescent emission, facile synthesis and easy functionalization. Up to date, a great number of pyrene-based derivatives using pyrene as the starting material or as the functional precursor have been reported [12–18]. However, there are relatively few reports about pyrene-based thioether compounds. Organic functional molecules containing sulfur atoms have also attracted extensive research interest because their special electronic structures may result into special properties, which could develop more novel functional material precursors. Very recently, the crystal structures of pyrene-based thioether compounds such as 1,3,6,8-tetrakis(*p*-tolylthio)pyrene, 1,8-bis(*p*-tolylthio)pyrene, 1,6-bis(methylthio)pyrene and so on, have been reported by our group using pyrene as the starting material [5, 19–21], especially, some of them exhibit relatively excellent fluorescent properties and sensor function for peroxides such as *m*-chloroperoxybenzoic acid. As a continuation of this work, herein, we report the crystal structure of a new pyrene-based thioether compound which was synthesized in high yield. In addition, the optical property of the title compound was studied preliminarily.

The single X-ray diffraction analysis shows that the crystal structure agrees well with the expected structure of the title compound 1,6-bis(*p*-tolylthio)pyrene, owing inversion symmetry (see the structure drawing). The pyrene core as the main body together with the two side sulfur atoms are almost in a strict plane, whereby the largest deviation for the S1 atom from the main plane is 0.047(3) Å. The thioether bond distances are 1.7725(15) Å for C1–S1 and 1.7729(16) Å for C9–S1, respectively, which are typical $C_{\text{aryl}}\text{--S}$ bond distances. The C1–S1–C9 bond angle is 103.71°. The bond distances and angles around the sulfur atom in the molecule are comparable to

Figure 1: The supramolecular structure of the title compound linked by C–H... π interactions.

those of its derivatives 1,8-bis(*p*-tolylthio)pyrene and 1,3,6,8-tetrakis(*p*-tolylthio)pyrene [5, 19]. The dihedral angle between the pyrene and benzene ring is 81.77(3)°. There exist relatively strong C–H··· π interactions between the adjacent pyrenyl unit and the benzene segment, which link the title units into a one-dimensional supramolecular structure (Figure 1).

The optical property of the title compound was investigated preliminarily. The title compound 1,6-bis(*p*-tolylthio)pyrene was dissolved in dichloromethane, the absorption is in the range of 325 to 425 nm and a blue emission with peak around 425 nm for the above solution was observed, which are very similar to those of its derivative of 1,8-bis(*p*-tolylthio)pyrene [5]. The crystal state of the title compound emits green fluorescence with the main peak at 490 nm. Because of its extremely poor solubility, the further sensor property for peroxides has not been carried out.

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