Crystal structure and optical properties of 1,6-bis(methylthio)pyrene, C$_{18}$H$_{14}$S$_{2}$

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, $\beta = 103.965(14)^\circ$, $V = 1388.3(7)$ Å$^3$, $Z = 4$, $R_p(F) = 0.0480$, $wR_{int}(F^2) = 0.1207$, $T = 200(2)$ 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. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (TMS, p.p.m.): 8.64 (s, 2H, $J = 8.63$ Hz), 8.16—8.12 (m, 2H), 8.10—7.96 (m, 4H, 2H), 7.23 (s, 6H).

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 $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(C)$ for aromatic and methyl hydrogen atoms, 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...
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 dimers such as 1,3,6,8-tetrakis(p-tolylthio)pyrene and 1,8-bis(p-tolylthio)pyrene [16, 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 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 alkylaryl sulfide is difficult compared to diarylsulfide.

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References
16. Xu, L. H.; Ni, Z. H.: Crystal structure of 1,3,6,8-tetrakis(p-tolylthio) pyrene, C_{44}H_{34}S_{4}. Z. Kristallogr. NCS 231 (2016) 255–257.