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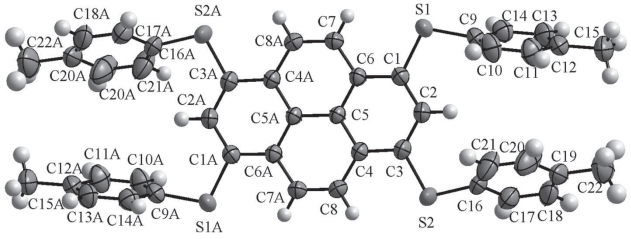
Crystal structure of 1,3,6,8-tetrakis(*p*-tolylthio) pyrene, $C_{44}H_{34}S_4$



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Abstract

$C_{44}H_{34}S_2$, triclinic, $P\bar{1}$ (no.2), $a = 9.638(5)$ Å, $b = 9.851(5)$ Å, $c = 11.615(6)$ Å, $\alpha = 69.149(7)°$, $\beta = 67.313(6)°$, $\gamma = 61.805(6)°$, $V = 876.0(8)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0529$, $wR_{ref}(F^2) = 0.1467$, $T = 296(2)$ K.

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The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was obtained by the reaction of 1,3,6,8-tetrakisbromopyrene with 4-methylphenylthiol in the solution of N,N-dimethylformamide (DMF) by a modified method according to the literature [3]. 1,3,6,8-tetrakisbromopyrene and 4-methylphenylthiol was purchased from commercial source. 1,3,6,8-tetrakisbromopyrene (2.0 mmol), 4-methylphenylthiol (9.0 mmol), NaH (purity 60%, 9.3 mmol) and DMF (20 ml) were added into a 50 ml flask. Then, the reaction was carried out at 120 °C for 12 h under a dry atmosphere of nitrogen gas. Finally, the reaction mixture was cooled slowly at room temperature for about one day. Small yellow crystals suitable for single crystal X-ray diffaction analysis were collected (Yield: 85.2%). Elemental analysis–calculated for $C_{44}H_{34}S_4$: C, 76.48%; H, 4.96%; S, 18.56%; found: C,76.14%, H, 4.82%; S, 18.28%.

Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.06×0.08×0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.03 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD area-detector, φ and ω scans
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5015, 3047
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2084
$N(param)_{refined}$:	219
Programs:	SHELX [1], PLATON [2]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	2*i*	0.8939	0.2529	0.6994	0.062
H(7)	2*i*	0.8654	0.3328	0.2890	0.054
H(8)	2*i*	0.3340	0.5465	0.8117	0.055
H(10)	2*i*	1.1572	0.3683	0.5384	0.081
H(11)	2*i*	1.3337	0.2812	0.6602	0.082
H(13)	2*i*	1.4217	−0.1613	0.6816	0.074
H(14)	2*i*	1.2371	−0.0756	0.5660	0.066
H(15A)	2*i*	1.5665	−0.1180	0.7795	0.132
H(15B)	2*i*	1.4655	0.0350	0.8351	0.132
H(15C)	2*i*	1.6047	0.0336	0.7075	0.132
H(17)	2*i*	0.7523	0.1395	1.0641	0.080
H(18)	2*i*	0.9723	0.0741	1.1350	0.093
H(20)	2*i*	1.0731	0.4234	0.8741	0.120
H(21)	2*i*	0.8497	0.4975	0.8050	0.104
H(22A)	2*i*	1.1619	0.1834	1.1480	0.186
H(22B)	2*i*	1.2441	0.2664	1.0147	0.186
H(22C)	2*i*	1.2729	0.0891	1.0391	0.186

Experimental details

All H atoms bond to C atoms were introduced using the HFIX commond in the SHELX program [1], with the value of 0.93 Å for C–H bonds distances. All H atoms were allowed for to ride

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Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	2*i*	1.0524(1)	0.2167(1)	0.43861(8)	0.0333(4)	0.1027(8)	0.0517(6)	−0.0029(4)	−0.0130(4)	−0.0329(5)
S(2)	2*i*	0.5959(1)	0.3796(2)	0.88883(9)	0.0455(5)	0.174(1)	0.0458(6)	−0.0165(6)	−0.0153(4)	−0.0467(6)
C(1)	2*i*	0.8501(3)	0.3067(4)	0.5292(3)	0.033(2)	0.053(2)	0.045(2)	−0.011(1)	−0.011(1)	−0.017(1)
C(2)	2*i*	0.8116(3)	0.3055(4)	0.6575(3)	0.039(2)	0.069(2)	0.044(2)	−0.011(2)	−0.018(1)	−0.015(2)
C(3)	2*i*	0.6530(4)	0.3812(4)	0.7242(3)	0.042(2)	0.071(2)	0.043(2)	−0.015(2)	−0.016(1)	−0.019(2)
C(4)	2*i*	0.5255(3)	0.4621(3)	0.6627(3)	0.038(2)	0.048(2)	0.035(2)	−0.016(1)	−0.011(1)	−0.012(1)
C(5)	2*i*	0.5637(3)	0.4599(3)	0.5325(3)	0.034(1)	0.041(2)	0.037(2)	−0.014(1)	−0.011(1)	−0.012(1)
C(6)	2*i*	0.7267(3)	0.3822(3)	0.4648(3)	0.034(1)	0.041(2)	0.039(2)	−0.013(1)	−0.011(1)	−0.013(1)
C(7)	2*i*	0.7588(3)	0.3837(4)	0.3339(3)	0.036(2)	0.056(2)	0.041(2)	−0.010(1)	−0.009(1)	−0.020(1)
C(8)	2*i*	0.3600(3)	0.5436(4)	0.7265(3)	0.040(2)	0.060(2)	0.036(2)	−0.014(1)	−0.009(1)	−0.018(1)
C(9)	2*i*	1.1771(3)	0.1553(4)	0.5408(3)	0.032(2)	0.059(2)	0.049(2)	−0.013(1)	−0.010(1)	−0.015(2)
C(10)	2*i*	1.2088(4)	0.2607(4)	0.5685(4)	0.063(2)	0.047(2)	0.092(3)	−0.014(2)	−0.036(2)	−0.007(2)
C(11)	2*i*	1.3161(4)	0.2081(5)	0.6402(4)	0.061(2)	0.070(3)	0.089(3)	−0.029(2)	−0.029(2)	−0.019(2)
C(12)	2*i*	1.3984(4)	0.0498(5)	0.6832(3)	0.038(2)	0.078(3)	0.047(2)	−0.016(2)	−0.012(2)	−0.014(2)
C(13)	2*i*	1.3673(4)	−0.0536(4)	0.6539(3)	0.059(2)	0.053(2)	0.060(2)	−0.008(2)	−0.025(2)	−0.007(2)
C(14)	2*i*	1.2570(4)	−0.0026(4)	0.5838(3)	0.054(2)	0.052(2)	0.055(2)	−0.018(2)	−0.016(2)	−0.011(2)
C(15)	2*i*	1.5198(5)	−0.0049(6)	0.7581(4)	0.054(2)	0.134(4)	0.069(3)	−0.021(2)	−0.028(2)	−0.025(3)
C(16)	2*i*	0.7782(4)	0.3247(5)	0.9267(3)	0.046(2)	0.085(3)	0.040(2)	−0.013(2)	−0.017(2)	−0.023(2)
C(17)	2*i*	0.8164(4)	0.1989(5)	1.0250(3)	0.070(2)	0.086(3)	0.048(2)	−0.032(2)	−0.020(2)	−0.011(2)
C(18)	2*i*	0.9495(5)	0.1590(5)	1.0668(4)	0.078(3)	0.079(3)	0.064(2)	−0.002(2)	−0.042(2)	−0.018(2)
C(19)	2*i*	1.0477(5)	0.2402(6)	1.0112(4)	0.049(2)	0.137(4)	0.062(3)	−0.018(2)	−0.018(2)	−0.050(3)
C(20)	2*i*	1.0077(6)	0.3655(7)	0.9137(4)	0.105(4)	0.170(5)	0.067(3)	−0.092(4)	−0.023(3)	−0.016(3)
C(21)	2*i*	0.8743(6)	0.4100(6)	0.8711(4)	0.112(4)	0.105(3)	0.058(2)	−0.057(3)	−0.043(3)	0.010(2)
C(22)	2*i*	1.1951(5)	0.1902(7)	1.0575(5)	0.074(3)	0.194(5)	0.119(4)	−0.022(3)	−0.045(3)	−0.071(3)

on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The structure was checked using PLATON [2].

Discussion

As one of the most known polycyclic aromatic hydrocarbons, pyrene and its derivatives have been paid everlasting attention in the past century because they are widely used as fluorescent probes and organic photoelectric materials [4, 5]. On the other hand, the design and synthesis of organic sulfur-containing compounds have also raised much attention in the field of chemistry, physics, materials and biochemistry and life science [6]. Therefore, pyrene-based sulfur-containing compounds may exhibit interesting photoelectric properties. However, up to date, there are only a few crystal structures of pyrene-based sulfur-containing compounds [7, 8]. Recently, Gingras group has reported the synthesis and photoelectric properties of some polysulfurated pyrene-cored dendrimers including the title compound [3].

The molecular structure of the title compound looks like a person who stretches his limbs and is centrosymmetric. The pryenyl core as the main body together with the four sulfur atoms are plane with the largest deviation from the main plane is 0.049(3) Å. The dihedral angle between the pyrene and two benzene rings are 71.8(3)° and 65.9(3)°, respectively. The dihedral angle between the two benzene rings is 42.4(3)°. The C-S bond distances in the title compound are very similar and distribute in a very narrow range of 1.761(3)-1.771(3) Å. The C-S-C bond angles are 105.30(14)° for C1-S1-C9 and 105.67(15)° for C3-S2-C16. The C-S bond distances and C-S-C bond angles are all normal for diaryl sulfide compounds. There exists significant S—S interaction with the distance of 3.499(3) Å, which links the units of the title compound to form a one-dimensional supramolecular structure. Then these one-dimensional chains are further linked together by C-H-π interactions between the pyrene and benzene rings, giving a two-dimensional layer-like supramolecular structure.

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