Crystal structure of 1,3,5,7-tetrapropyl-2,4,6,8,9,10-hexathiaadamantane, $C_{44}H_{40}S_6$

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Abstract

$C_{44}H_{40}S_6$, tetragonal, $I4_1/acd$ (No. 142), $a = 10.290(2)$ Å, $c = 37.72(2)$ Å, $V = 3994.2$ Å³, $Z = 8$, $R_{gt}(F) = 0.025$, $wR_{all}(F^2) = 0.069$, $T = 148$ K.

Source of material

Tetrapropylhexathiaadamantane was synthesized by stirring a mixture of butanedithioic acid with boron trifluoride metherate in hexane at 298 K. The obtained solid was crystallised from acetone. Single crystals of TPHTA were grown by evaporating an acetone solution. Temperature of measurements was fixed at 148 K because an apparent instability of the crystal.

Discussion

Hexathiaadamantane systems are known [1] but only few structural data have been reported [2, 3, 4]. These compounds have focused attention as complexing agent with metallic salts [5, 6]. Following our work on dithioacids polycondensation reaction we

described recently [7] the structure of the product isolated by treatment of propanedithioic acid by $BF_3 \cdot Me_2O$.

We expose in the present work our results concerning butanedithioic acid. When it is treated in the same way, this dithioacid turns into H_2S and tetrapropylhexathiaadamantane (TPHTA). The last is the unique solid phase isolated from this reaction.

In the structure, the C1—C2 (1.549 Å) contact between the carbon of adamantane cage and the carbon that bound immediately to him is slightly longer than all other C—C distances of the aliphatic chain (1.529 Å for C2—C3). The S—C distances range between 1.822 Å and 1.827 Å whereas those of C—C vary in the range 1.528 Å to 1.547 Å. These values agree with those reported for hexathiaadamantane $C_4S_6(H)_4$ [2] and tetraethylhexathiaadamantane $C_4S_6(CH_2CH_3)_4$ [7]. The C—H distances vary in the range between 0.94 Å and 0.99 Å and are very close to those found for tetramethylhexathiaadamantane [8].

Table 1. Data collection and handling.

Crystal:	colourless prism, size $0.15 \times 0.2 \times 0.4$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	6.80 cm^{-1}
Diffractometer, scan mode:	Syntex P21, ω
$2\theta_{\text{max}}$:	57.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4892, 1316
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1189
$N(\text{param})_{\text{refined}}$:	79
Program:	SHELXTL-Plus [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2A)	32g	0.711(1)	0.082(2)	0.1899(4)	0.025(4)
H(2B)	32g	0.698(2)	−0.022(2)	0.1588(4)	0.029(4)
H(3A)	32g	0.503(2)	−0.093(2)	0.1854(4)	0.043(5)
H(3B)	32g	0.518(2)	0.007(2)	0.2159(5)	0.038(5)
H(4A)	32g	0.603(2)	−0.191(2)	0.2368(5)	0.038(5)
H(4B)	32g	0.717(2)	−0.098(2)	0.2326(5)	0.041(5)
H(4C)	32g	0.697(2)	−0.203(2)	0.2047(6)	0.068(7)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	16d	1/2	1/4	0.182126(9)	0.0165(2)	U ₁₁	0.0113(2)	0.0029(1)	0	0
S(2)	32g	0.46148(2)	0.04544(2)	0.124626(6)	0.0153(2)	0.0130(1)	0.0144(1)	-0.00056(8)	-0.00054(8)	0.00059(8)
C(1)	32g	0.57683(9)	0.13537(9)	0.15184(3)	0.0141(4)	0.0138(4)	0.0130(4)	0.0010(4)	0.0002(3)	-0.0001(3)
C(2)	32g	0.6492(1)	0.0342(1)	0.17489(3)	0.0164(5)	0.0164(5)	0.0158(4)	0.0035(4)	-0.0006(4)	0.0027(4)
C(3)	32g	0.5659(1)	-0.0499(1)	0.19937(3)	0.0216(5)	0.0253(6)	0.0231(5)	0.0019(5)	0.0005(4)	0.0102(4)
C(4)	32g	0.6520(1)	-0.1446(1)	0.21991(3)	0.0329(6)	0.0228(5)	0.0234(6)	0.0064(5)	0.0000(5)	0.0076(4)

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