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Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.056
 wR factor = 0.126
 Data-to-parameter ratio = 16.2

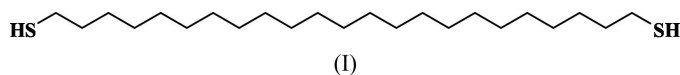
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tricosane-1,23-dithiol

In the title compound, $\text{C}_{23}\text{H}_{48}\text{S}_2$, the molecular skeleton, including both terminal S atoms, has an all-*trans* conformation. The molecules form layers in the crystal. The long axis of the molecule is inclined to the layer plane, similar to the smectic C phase of liquid crystals.

Comment

Normal long-chain compounds have been studied as basic models of polymers, since they have a very simple chemical structure with the molecular skeleton being a straight hydrocarbon chain. In addition, these compounds have a layer structure similar to that of smectic liquid crystals, and can therefore be regarded as model compounds for liquid crystals.



Compounds containing a mercapto group form self-assembled monolayers on a metal substrate (Ulman, 1996) and self-assembly phenomena have therefore been investigated using a variety of compounds with a mercapto group. Alkane- α,ω -dithiols have mercapto groups at both ends of the hydrocarbon skeleton. The melting-point alternation in alkane- α,ω -dithiols containing two to ten C atoms has been discussed on the basis of their crystal structures (Thalladi *et al.*, 2000). Recently, we reported homologues of alkane- α,ω -dithiols containing more than 11 C atoms, namely dodecane-1,12-dithiol (Nakamura *et al.*, 2001b), nonadecane-1,19-dithiol (Nakamura *et al.*, 2004), icosane-1,20-dithiol (Nakamura *et al.*, 2001a) and heneicosane-1,21-dithiol (Nakamura *et al.*, 2005). The crystal structure of tricosane-1,23-dithiol, (I), is reported in this paper as the longest member of the homologous series studied to date.

The molecular structure of (I) is shown in Fig. 1. All torsion angles involving the non-H atoms of (I) are close to $\pm 180^\circ$, so that the molecular skeleton, including both terminal S atoms, has an all-*trans* conformation. The two terminal S1–H1S and S2–H2S bonds have a *gauche* conformation with respect to the skeleton [the C2–C1–S1–H1S and C22–C23–S2–H2S torsion angles are both $-90(2)^\circ$].

Fig. 2 shows the projection of the crystal structure of (I) along the *b* axis. The molecules form layers with a thickness of $c/2$. The interlayer distances between adjacent S atoms are 3.5360 (16) Å for S1 \cdots S1ⁱ and 3.5908 (16) Å for S2 \cdots S2ⁱⁱ [symmetry codes: (i) $2-x, 5-y, 2-z$, (ii) $-x, -4-y, 1-z$]. These values are slightly less than the van der Waals contact distance of 3.63 Å. However, the mercapto groups do not form hydrogen bonds, due to the acute S1–H1S \cdots S1ⁱ [$95(2)^\circ$] and S2–H2S \cdots S2ⁱⁱ [$76.9(18)^\circ$] angles.

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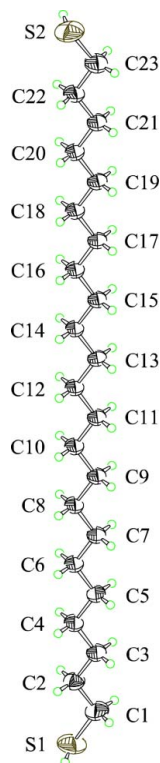


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The space group of the higher odd members of this series is $P\bar{1}$, which is different from the space group of $P2/c$ found for the lower odd members containing five to nine C atoms. The molecular arrangement of (I) is similar to those of other higher odd members, namely nonadecane-1,19-dithiol and heneicosane-1,21-dithiol, which have previously been reported. However, the features of these arrangements are not observed in the lower odd members with five to nine C atoms. In the even members of the series, the space group of dodecane-1,12-dithiol and icosane-1,20-dithiol is $P\bar{1}$, the same as for the lower even members containing four to ten C atoms. Therefore, the even members of the alkane- α,ω -dithiol series containing 14–18 C atoms probably crystallize in the same space group, $P\bar{1}$.

Alkane- α,ω -dithiols show an alternation in their calculated densities, with the odd members systematically exhibiting lower densities than the even ones. Although the U_{eq} values of the C atoms in (I) are comparable with those of icosane-1,20-dithiol, the U_{eq} values of the terminal S atoms in (I) are larger than those of icosane-1,20-dithiol. This may be caused by the larger void space around the S atoms of (I).

Experimental

The title compound was synthesized from tricosane-1,23-dioic acid (Tokyo Kasei Co.) according to the procedure of Urquhart *et al.* (1955). The single crystal of (I) used in the X-ray analysis was grown by slow evaporation of a solution in a mixture of 1,2-dichloroethane and propan-2-ol (2:1).

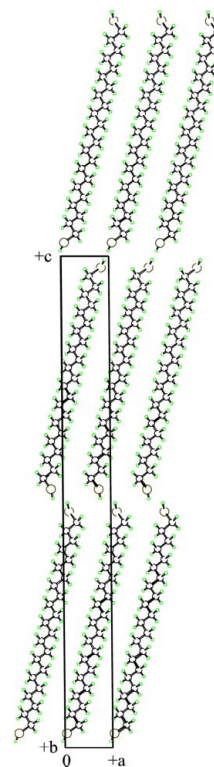


Figure 2
The projection of the crystal structure of (I) along the *b* axis.

Crystal data

$C_{23}H_{48}S_2$
 $M_r = 388.75$
Triclinic, $P\bar{1}$
 $a = 4.7477$ (5) Å
 $b = 5.5644$ (8) Å
 $c = 47.983$ (3) Å
 $\alpha = 90.205$ (9)°
 $\beta = 90.523$ (7)°
 $\gamma = 102.288$ (10)°
 $V = 1238.5$ (2) Å³

$Z = 2$
 $D_x = 1.043$ Mg m⁻³
Cu $K\alpha$ radiation
Cell parameters from 23 reflections
 $\theta = 9.8$ – 18.0 °
 $\mu = 1.94$ mm⁻¹
 $T = 296$ (1) K
Plate, colourless
 $0.58 \times 0.20 \times 0.03$ mm

Data collection

Rigaku AFC-5R diffractometer
 ω scans
Absorption correction: ψ scan
(North *et al.*, 1968)
 $T_{\text{min}} = 0.710$, $T_{\text{max}} = 0.945$
6047 measured reflections
4513 independent reflections
1976 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 70.1$ °
 $h = -5 \rightarrow 5$
 $k = -1 \rightarrow 6$
 $l = -58 \rightarrow 58$
3 standard reflections
every 150 reflections
intensity decay: 18.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.126$
 $S = 1.00$
4513 reflections
279 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = (4F_o^2)/[0.0001F_o^2 + 2.7\sigma^2(F_o) + 0.27]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.60$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.64$ e Å⁻³
Extinction correction: Larson (1970)
Extinction coefficient: 13.4 (1)

The molecule of (I) is non-centrosymmetric, so a longer data collection time was needed. Therefore, the intensity decay became somewhat high. Methylene H atoms were placed in idealized positions (C–H = 0.95 Å) and allowed to ride on their parent C atoms.

The terminal mercapto H atoms were located in a difference synthesis and their positional parameters were allowed to refine freely. $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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