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Dodecane-1,12-dithiol

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.138
Data-to-parameter ratio = 18.9

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

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In the molecular structure of the title compound, $C_{12}H_{26}S_2$, the hydrocarbon skeleton has an all-*trans* conformation. The terminal S—H bond is in the *gauche* conformation with respect to the skeleton. In the crystal structure, the molecules are arranged along the *c* axis, the longest axis, forming layers in which the long axis of the molecule is inclined to the layer plane as in the smectic C layer structure of liquid crystals. The mercapto groups do not form hydrogen bonds. These features are similar to those of the homologues with an even number of C atoms containing more than four C atoms.

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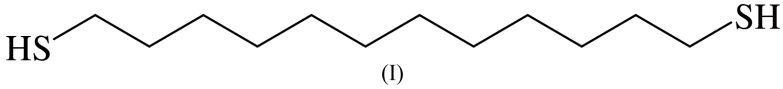
Comment

In biology, the mercapto group plays an important role in maintaining the structure of a protein or hormone, for example, making a disulfide bond. As a material, long-chain alkanethiols with a terminal mercapto group have been used as ligands which form self-assembled monolayers in soft lithography (Xia & Whitesides, 1998). On the other hand, the crystal structures of alkane-α,ω-dithiols which have the mercapto group at both ends of the hydrocarbon skeleton have attracted attention as basic models for smectic liquid crystals. The overall molecular shape can be regarded as rod-like, which is one of the typical features of liquid crystalline molecules. In the crystalline state, the molecules form layers similar to those of the smectic liquid crystals. The melting-point alternation in the alkane-α,ω-dithiols with 2–10 C atoms has been investigated (Thalladi *et al.*, 2000). In that study, the crystal structures of the alkane-α,ω-dithiols were analyzed at 130 K by X-ray diffraction using single crystals grown using a miniature zone-melting procedure. Alkane-α,ω-dithiols containing more than four C atoms have $P\bar{1}$ as space group for an even number of C atoms, and $P2/c$ for an odd number of C atoms. Recently, the crystal structure of icosane-1,20-dithiol, (I), was analyzed at 296 K using a single-crystal which was grown by a slow evaporation method (Nakamura *et al.*, 2001*a*). In this paper, the crystal structure of dodecane-1,12-dithiol is reported.



(I)

The molecular structure of (I) is depicted in Fig. 1. The hydrocarbon skeleton has an all-*trans* conformation and the molecule is centrosymmetric. The terminal S1—H1*s* bond is in the *gauche* conformation with respect to the skeleton [the C2—C1—S1—H1*s* torsion angle is 65 (1)°]. In the crystal

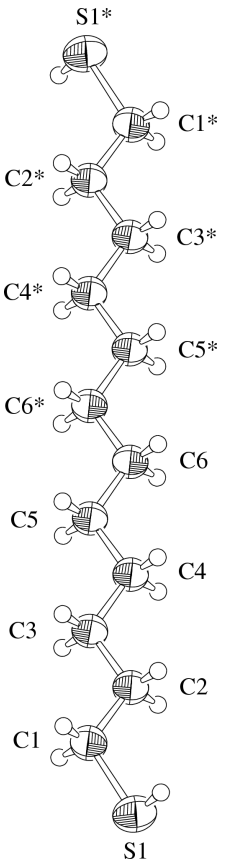


Figure 1
An *ORTEP*II (Johnson, 1976) view of the molecule of (I) showing the crystallographic numbering scheme [symmetry code: (*) $-x$, $2-y$, $2-z$]. Displacement ellipsoids are drawn at the 50% probability level.

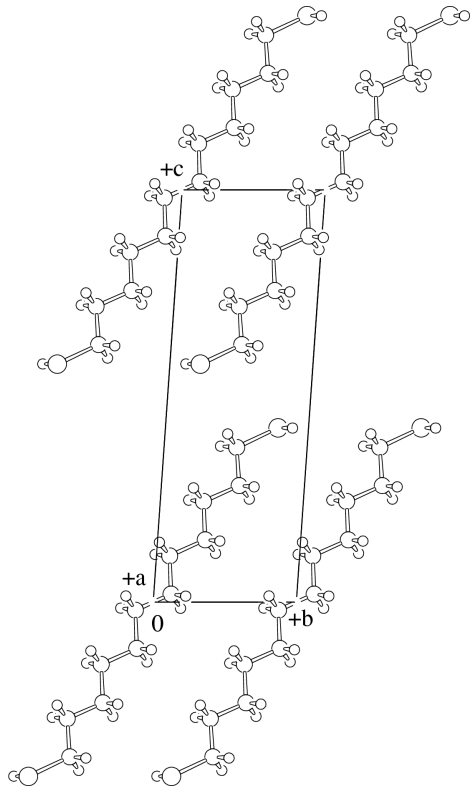


Figure 2
The projection of the crystal structure of (I) along the *a* axis.

structure of (I), the molecules are arranged along the *c* axis forming layers in which the long axis of the molecule is inclined to the layer plane, as is shown in Fig. 2. This packing is very similar to that of the smectic C structure of liquid crystals. The nearest neighboring mercapto S atom distance is the interlayer $S1\cdots S1^{i}$ [symmetry code: (i) $2-x$, $-y$, $1-z$], whose value is 3.5552 (8) Å; the $S1-H1s\cdots S1^{i}$ angle is 80 (1)°. These results show the mercapto groups do not form hydrogen bonds. Apart from the length of the *c* axis, the longest axis, no major differences were observed between the crystal data obtained here and those of homologues with an even number of C atoms containing more than four C atoms (Thalladi *et al.*, 2000; Nakamura *et al.*, 2001*a*).

Investigations of model compounds for smectic liquid crystals have been reported. The molecular and crystal structures of eleven alkane-α,ω-diols with 10–19 and 21 C atoms have been analyzed by single-crystal X-ray diffraction in our laboratory. The structural differences between compounds with an even number of C atoms and those with an odd number of C atoms were analysed and discussed from the viewpoint of smectic liquid crystals. In the alkane-α,ω-diols with an even number of C atoms, the molecules form layers in a herring-bone arrangement, just as in the chiral smectic C mesophase of liquid crystals (Nakamura & Sato, 1999*a*, *b*; Nakamura & Setodoi, 1997; Nakamura & Yamamoto, 1994; Nakamura & Watanabe, 2001). On the other hand, in the alkane-α,ω-diols with an odd number of C atoms, the molecules form a layer structure which is very similar to that of the smectic A mesophase in liquid crystals (Nakamura *et al.*, 1997, 1999; Nakamura, Uno, Watanabe *et al.*, 2000; Nakamura, Uno & Ogawa, 2000; Nakamura *et al.*, 2001*b*,*c*).

As a result, alkane-α,ω-diols with an odd number of C atoms, alkane-α,ω-dithiols with an even number of C atoms, and alkane-α,ω-diols with an even number of C atoms could be regarded as model compounds for smectic A, smectic C and chiral smectic C liquid crystals, respectively.

Experimental

Dodecane-1,12-dithiol was synthesized from 1,12-dibromododecane (Tokyo Kasei Co.) according to the procedure of Urquhart *et al.* (1955). The single crystal used for analysis was grown by slow evaporation from a benzene–ethanol (1:3) solution at low temperature (283 K).

Crystal data

$C_{12}H_{26}S_2$	$Z = 1$
$M_r = 234.46$	$D_x = 1.099$ Mg m^{-3}
Triclinic, $P\overline{1}$	Cu Kα radiation
$a = 4.221$ (1) Å	Cell parameters from 22 reflections
$b = 5.430$ (1) Å	$\theta = 9.7$–$21.4°$
$c = 15.615$ (2) Å	$\mu = 3.12$ mm^{-1}
$\alpha = 85.65$ (1)°	$T = 296.2$ K
$\beta = 86.68$ (2)°	Plate, colorless
$\gamma = 83.51$ (1)°	0.60 × 0.25 × 0.17 mm
$V = 354.1$ (1) Å^3	

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.406, T_{max} = 0.589
1972 measured reflections
1287 independent reflections
1173 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.041
θ_{max} = 70.6°
$h = -4 \rightarrow 5$
$k = -6 \rightarrow 2$
$l = -19 \rightarrow 19$
3 standard reflections every 150 reflections intensity decay: 9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.138
S = 1.67
1287 reflections
68 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + \{0.07[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.31 (9)

The methylene H atoms were positioned at idealized positions and were allowed to ride on the parent C atoms. The mercapto H atom was located in a difference map and the positional parameters were allowed to refine during the final refinement. All H-atom isotropic displacement parameters were fixed at $1.2U_{eq}$ of the parent atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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