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Icosane-1,20-dithiol

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.057
wR factor = 0.159
Data-to-parameter ratio = 19.1

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, $C_{20}H_{42}S_2$, (I), the skeleton of the hydrocarbon has an all-*trans* conformation. The terminal S—H bond is in a *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. This packing is very similar to that of the smectic C structure of liquid crystals. Except for the length of the *c* axis, no big difference was observed between the crystal data obtained here and those of homologues with even numbers of C atoms already reported.

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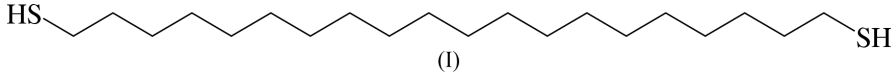
Comment

As is well known, the mercapto group plays an important role in maintaining the structure of a protein or hormone, for example, making a disulfide bond in a living body. Alkane-α,ω-dithiols have the mercapto groups at both ends of the hydrocarbon skeleton, and the melting-point alternation in alkane-α,ω-dithiols containing less than 10 C atoms was investigated (Thalladi *et al.*, 2000). In the study, the crystal structures of nine members of the alkane-α,ω-dithiol family were analyzed by single-crystal X-ray diffraction. Alkane-α,ω-dithiols containing more than four C atoms have $P\bar{1}$ as a space group for an even number of C atoms and $P2/c$ for an odd number of C atoms. Crystallographic data for alkane-α,ω-dithiols containing more than 11 C atoms have not yet been reported to our knowledge. In this paper, the crystal structure of icosane-1,20-dithiol, (I), is reported.



(I)

Fig. 1 shows the molecular structure of (I). The skeleton of the hydrocarbon has an all-*trans* conformation. The molecule is centrosymmetric. The C—C distances are in the range 1.509 (3)–1.518 (3) Å and the C—C—C angles are in the range 112.8 (2)–114.6 (2)°. The terminal S1—H1*s* bond has a *gauche* conformation with respect to the skeleton [C2—C1—S1—H1*s* torsion angle 67 (1)°]. This is one of the characteristic points in this compound, because no such conformation has been observed in alkane-α,ω-diols. In the crystal 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 interlayer S1···S1 distance is 3.551 (1) Å. This value is too long to make a hydrogen bond. Except for the length of the *c* axis, the

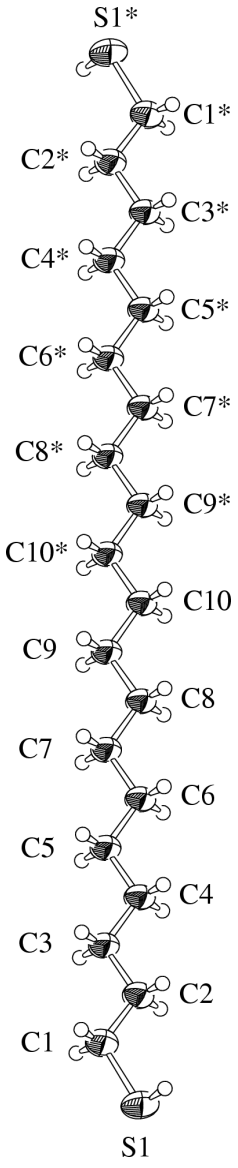


Figure 1
An *ORTEP*II (Johnson, 1976) view of the molecule of (I) showing the crystallographic numbering scheme [symmetry code: (*) $-x$, $2-y$, $1-z$]. Displacement ellipsoids are drawn at the 50% probability level.

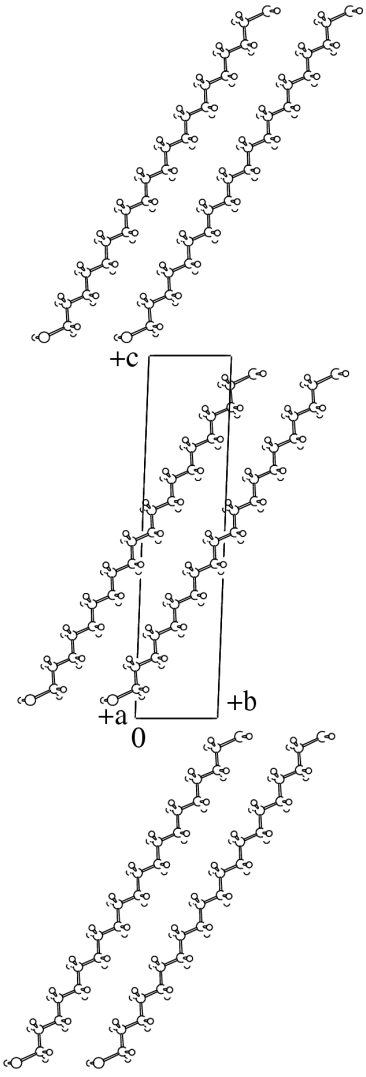


Figure 2
The projection of the crystal structure of (I) along the *a* axis.

longest axis, no major difference was observed between the crystal data obtained here and those of homologues with an even number of C atoms already reported by Thalladi *et al.* (2000).

The molecular and crystal structures of ten alkane-α,ω-diols containing 10–18 and 21 C atoms have been analyzed by single-crystal X-ray diffraction. The structural differences between the compounds with an even number of C atoms and those with an odd number of C atoms were determined and were studied from a structural point of view as a model of polymers and/or smectic liquid crystals by Nakamura and his co-workers. In the alkane-α,ω-diols with an even number of C atoms, the hydroxyl groups located at both ends of the hydrocarbon skeleton showed a *trans* conformation. As a result, the molecule is constructed by an all-*trans* conformation. In this case, these molecules form layers in a herringbone fashion, just like the chiral smectic C of liquid crystals (Nakamura & Sato, 1999*a*,*b*; Nakamura & Setodoi, 1997; Nakamura & Yamamoto, 1994; Nakamura & Watanabe, 2001). On the other hand, for the alkane-α,ω-diols with an odd number of C atoms, one hydroxyl group had a *gauche* conformation with respect to the all-*trans* hydrocarbon skeleton, whereas the other hydroxyl group had a *trans* conformation. The molecules formed a layer structure which was very similar to that of the smectic A in liquid crystals (Nakamura *et al.*, 1997, 1999, 2001; Nakamura, Uno, Watanabe *et al.*, 2000; Nakamura, Uno & Ogawa, 2000).

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

Experimental

Icosane-1,20-dioic acid (Tokyo Kasei Co.) was converted to its methyl ester, which was further reduced to the alcohol with $LiAlH_4$. The alcohol was heated with aqueous 48% hydrobromic acid and converted to the corresponding bromide. Icosane-1,20-dithiol was synthesized from the bromide according to reported procedures (Urquhart *et al.*, 1955). The single crystal used for analysis was grown by slow evaporation from a solution containing a mixture of toluene and ethanol (1:3).

Crystal data

$C_{20}H_{42}S_2$
M_r = 346.67
Triclinic, $P\overline{1}$
a = 4.2261 (6) Å
b = 5.4283 (6) Å
c = 23.819 (3) Å
α = 87.43 (1)°
β = 86.56 (1)°
γ = 83.37 (1)°
V = 541.4 (1) Å^3
Z = 1
D_x = 1.063 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 9.8–17.5°
μ = 2.17 mm^{-1}
T = 296.2 K
Plate, colorless
0.70 × 0.15 × 0.01 mm

Data collection

Rigaku AFC-5R diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.767, T_{max} = 0.996
3008 measured reflections
1967 independent reflections
1453 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.045
θ_{max} = 70.5°
$h = -4 \rightarrow 5$
$k = -6 \rightarrow 2$
$l = -29 \rightarrow 29$
2 standard reflections every 150 reflections intensity decay: 11.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.159
S = 1.77
1966 reflections
103 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + \{0.05[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

The methylene H atoms were located at idealized positions and were allowed to ride on the parent C atoms. The mercapto H atom was located on difference syntheses and the positional parameters were allowed to refine for the final refinements. All H-atom isotropic displacement parameters were set to be $1.2U_{eq}$ 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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