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## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.056  
 $wR$  factor = 0.123  
Data-to-parameter ratio = 16.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Henicosane-1,21-dithiol

In the title compound,  $\text{C}_{21}\text{H}_{44}\text{S}_2$ , the molecular skeleton including both terminal S atoms has an all-*trans* conformation. The molecules form layers with a thickness of  $c/2$  and the long axis of the molecule is inclined to the  $ab$  plane in the crystal structure. This molecular arrangement is similar to that of the smectic C structure of liquid crystals.

## Comment

Long-chain aliphatic compounds have a simple structure of the molecular skeleton. Therefore, the structural study of these compounds has been performed from the viewpoint of basic polymer science. As the molecular shape of these compounds can be regarded as rod-like, the compounds have also been studied as a model of liquid crystalline molecules. The variation in melting point in alkane- $\alpha,\omega$ -dithiols with 2–10 C atoms has been investigated, and the crystal structures of these alkane- $\alpha,\omega$ -dithiols were analyzed at 130 K (Thalladi *et al.*, 2000). Recently, we reported the crystal structures of three alkane- $\alpha,\omega$ -dithiols, namely dodecane-1,12-dithiol (Nakamura *et al.*, 2001*b*), nonadecane-1,19-dithiol (Nakamura *et al.*, 2004) and icosane-1,20-dithiol (Nakamura *et al.*, 2001*a*). In this paper, the crystal structure of henicosane-1,21-dithiol, (I), is reported.

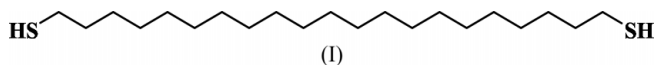


Fig. 1 shows the molecular structure of (I). The hydrocarbon skeleton has an all-*trans* conformation. The C–C distances are in the range 1.502 (4)–1.518 (3) Å and the C–C–C angles are in the range 112.8 (3)–114.8 (2)°. These values are normal compared with those of other dithiols reported previously. The two terminal S1–H1S and S2–H2S bonds have a *gauche* conformation with respect to the skeleton [the C2–C1–S1–H1S and C20–C21–S2–H2S torsion angles are  $-69$  (2)° and  $-98$  (2)°, respectively].

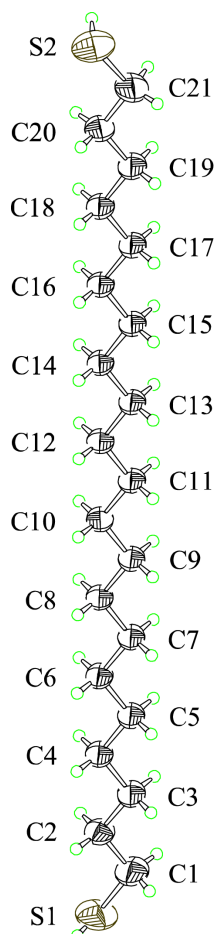
Fig. 2 shows the projection of (I) along the  $b$  axis. The molecules form layers along the  $c$  axis and the long axis of molecule is inclined to the layer plane. This packing is similar to that of the smectic C structure of liquid crystals. The interlayer distances between adjacent mercapto S atoms are 3.5401 (18) Å for S1 $\cdots$ S1<sup>i</sup> and 3.5919 (19) Å for S2 $\cdots$ S2<sup>ii</sup> [symmetry codes: (i)  $3 - x, -2 - y, 1 - z$ ; (ii)  $1 - x, 6 - y, 2 - z$ ]. These values are nearly the same as those observed for nonadecane-1,19-dithiol, which is another odd-numbered member of the series.

Similar space groups were observed within the odd- or the even-numbered alkane- $\alpha,\omega$ -dithiols with 4–10 C atoms, while the compounds with two to three C atoms belonged to the

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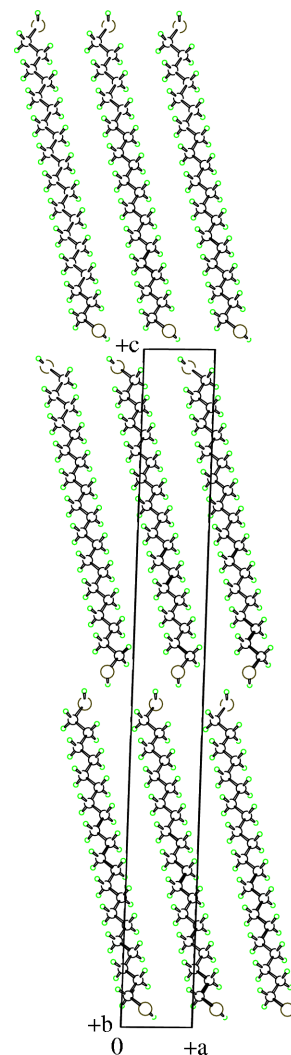


**Figure 1**

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

orthorhombic system. The odd members containing more than five C atoms are monoclinic with space group  $P2_1/c$ , and the even ones with more than four C atoms are triclinic system with space group  $P\bar{1}$ . These results suggest that the crystal system is monoclinic and the space group is  $P2_1/c$  in the higher odd members, such as (I) and nonadecane-1,19-dithiol. However, these members crystallize in the triclinic space group  $P\bar{1}$ , which is the same as the lower even members, not the lower odd members. This fact adds special interest to the situation where the crystal system and space group change from odd to even members. Consideration of this is now in progress. The space group of dodecane-1,12-dithiol and icosane-1,20-dithiol is  $P\bar{1}$  (Nakamura *et al.*, 2001a, b), the same as the lower even members. Therefore, the even members of alkane- $\alpha,\omega$ -dithiols with 14–18 C atoms probably crystallize in the same space group,  $P\bar{1}$ . It is considered that the crystal system and space group may be the same throughout the series of even members.

In the lower members, the nearest S $\cdots$ S distances between layers are in the range 3.48–3.51 Å, and the C–S $\cdots$ S angles seem more nearly linear in the odd members (*ca* 173°) than in the even members (*ca* 162°) (Thalladi *et al.*, 2000). In the title compound, (I), the C1–S1 $\cdots$ S1<sup>i</sup> angle is 160.19 (13)°, which is similar to the even members. On the other hand, the C21–



**Figure 2**

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

S2 $\cdots$ S2<sup>ii</sup> angle is 179.21 (14)°, which is close to that of the odd members and more linear than C1–S1 $\cdots$ S1<sup>i</sup>. Consequently, the crystal structure of (I) has both features observed in the lower members of the series with odd and even numbers of C atoms.

## Experimental

The title compound was synthesized from henicoseane-1,21-dioic acid (Tokyo Kasei Co.) according 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 1,2-dichloroethane and 2-propanol (4:3).

### Crystal data

C<sub>21</sub>H<sub>44</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 360.70  
 Triclinic,  $P\bar{1}$   
*a* = 4.7477 (5) Å  
*b* = 5.5680 (11) Å  
*c* = 44.455 (5) Å  
 $\alpha$  = 87.619 (13)°  
 $\beta$  = 87.920 (9)°  
 $\gamma$  = 77.733 (11)°  
*V* = 1146.9 (3) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.044 Mg m<sup>-3</sup>  
 Cu *K* $\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 10.0–18.8°  
 $\mu$  = 2.07 mm<sup>-1</sup>  
*T* = 296 (1) K  
 Plate, colourless  
 0.65 × 0.22 × 0.01 mm

Data collection

Rigaku AFC-5R diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.640$ ,  $T_{\max} = 0.977$   
 5611 measured reflections  
 4187 independent reflections  
 1926 reflections with  $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.019$   
 $\theta_{\text{max}} = 70.1^\circ$   
 $h = -5 \rightarrow 5$   
 $k = -1 \rightarrow 6$   
 $l = -54 \rightarrow 54$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 12.4%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.123$   
 $S = 1.00$   
 4187 reflections  
 257 parameters  
 H-atom parameters constrained

$w = (4F_o^2)/[0.0001F_o^2 + 3.3\sigma^2(F_o) + 0.55]$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.60 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{Å}^{-3}$   
 Extinction correction:  
 Larson (1970)  
 Extinction coefficient: 23.4 (1)

Because the molecule is non-centrosymmetric, a longer data-collection time was needed; the intensity decay was therefore somewhat high. The 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: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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