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Nonadecane-1,19-dithiol

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.061
wR factor = 0.127
Data-to-parameter ratio = 16.3

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

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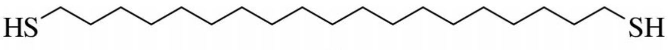
The title compound, $C_{19}H_{40}S_2$, has mercapto groups at both ends of the molecular skeleton, which has an all-*trans* conformation. The molecules form layers and the long axes of the molecules are inclined with respect to the layers in the crystal structure. This molecular arrangement is similar to that of the smectic C phase of liquid crystals.

Comment

Normal long-chain compounds can be regarded as having a rod-like shape, which is typical of some liquid crystals. In addition, the molecular arrangements in the crystalline state form a layer structure similar to the smectic phase of liquid crystals. Thus, these long-chain compounds have been studied from the viewpoint of being model compounds for smectic liquid crystals.

Compounds with mercapto groups have attracted attention because they form self-assembled monolayers on a metal substrate (Ulman, 1996). The melting-point alternation in alkane-α,ω-dithiols with 2–10 C atoms has been investigated by other researchers (Thalladi *et al.*, 2000). In that study, the crystal structures of alkane-α,ω-dithiols were analysed at 130 K by X-ray diffraction. Crystallographic data of only two homologs of alkane-α,ω-dithiols with more than 11 C atoms have been reported, namely dodecane-1,12-dithiol (Nakamura *et al.*, 2001*b*) and icosane-1,20-dithiol (Nakamura *et al.*, 2001*a*). Longer odd members of the alkane-α,ω-dithiol family have not yet been reported. In the present paper, the structure of nonadecane-1,19-dithiol, (I), is reported.



(I)

The molecular structure of (I) is shown in Fig. 1. The hydrocarbon skeleton has an all-*trans* conformation. Both terminal S1—H1*s* and S2—H2*s* bonds have a *gauche* conformation with respect to the skeleton [the C2—C1—S1—H1*s* and C18—C19—S2—H2*s* torsion angles are −90 (3) and −104 (2)°, respectively]. The projection of (I) along the *b* axis is shown in Fig. 2. The molecules form layers along the *c* axis and the long axes of the molecules are inclined relative to the layer plane. This packing is similar to that of the smectic C structure of liquid crystals.

The interlayer distances of the nearest neighboring mercapto S atoms are 3.5474 (18) Å for S1···S1^{i} and 3.6011 (19) Å for S2···S2^{ii} [symmetry code: (i) $2 - x$, $5 - y$, $2 - z$; (ii) $-x$, $-3 - y$, $1 - z$]. However, the S1—H1*s*···S1^{i} and S2—H2*s*···S2^{ii} angles are 80 (2) and 72.7 (19)°, respectively, which shows that these mercapto groups do not form classical hydrogen bonds.

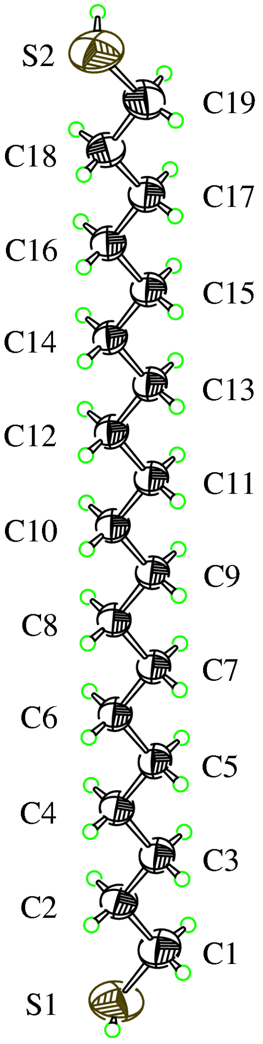


Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The crystal structure of (I) belongs to the triclinic system with space group $P\overline{1}$, whereas the crystal structures of odd-numbered alkane-α,ω-dithiols with 5–9 C atoms are monoclinic in the space group $P2/c$ from data collected at 130 K. Therefore, the packing motif of (I) is different from previously published data on the odd-numbered C-atom homologs; this difference may be the result of the experimental temperature and/or the length of the alkyl chain.

Experimental

Nonadecane-1,19-dioic acid (Tokyo Kasei Co.) was converted to the methyl ester, which was further reduced to the alcohol using $LiAlH_4$. The alcohol was heated with aqueous 48% hydrobromic acid to form the corresponding bromide. Nonadecane-1,19-dithiol was synthesized from the bromide according to reported procedures (Urquhart *et al.*, 1955). A mixture of the bromide, thiourea, and ethanol was refluxed. An aqueous solution of sodium hydroxide was added to the mixture, and the mixture was refluxed again. The title compound was obtained by cooling in an ice bath and was purified by recrystallization from ethanol (yield 45%). Thin plate-like crystals of (I) were obtained by slow evaporation of a solution in a 2:1 mixture of 1,2-dichloroethane and 2-propanol.

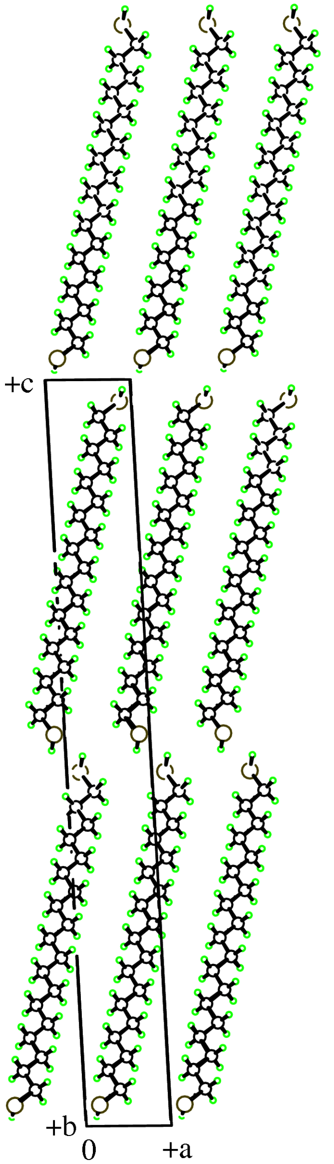


Figure 2
The projection of the crystal structure of (I) along the *b* axis.

Crystal data

$C_{19}H_{40}S_2$
$M_r = 332.65$
Triclinic, $P\overline{1}$
$a = 4.7557\ (6)$ Å
$b = 5.5781\ (13)$ Å
$c = 40.930\ (4)$ Å
$\alpha = 92.452\ (12)^\circ$
$\beta = 92.094\ (9)^\circ$
$\gamma = 102.365\ (13)^\circ$
$V = 1058.5\ (3)$ Å^3

$Z = 2$
$D_x = 1.044$ Mg m^{-3}
Cu Kα radiation
Cell parameters from 24 reflections
$\theta = 9.4$–18.2°
$\mu = 2.21$ mm^{-1}
$T = 296\ (1)$ K
Plate, colorless
0.68 × 0.15 × 0.01 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.748$, $T_{\max} = 0.977$
5132 measured reflections
3825 independent reflections
1834 reflections with $F^2 > 2\sigma(F^2)$

$R_{\rm int} = 0.024$
$\theta_{\max} = 70.1^\circ$
$h = -5 \rightarrow 5$
$k = -1 \rightarrow 6$
$l = -49 \rightarrow 49$
3 standard reflections every 150 reflections intensity decay: 21.5%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.127$
$S = 1.00$
3822 reflections
234 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = (4F_o^2)/[0.0001F_o^2 + 7.6\sigma^2(F_o) + 0.19]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

A longer time was needed to collect the reflection data because the molecule is non-centrosymmetric. Therefore, the intensity decay was somewhat high (21.5%). The methylene H atoms were placed at idealized positions (C—H = 0.95 Å)and made to ride on their parent C atoms. The mercapto H atoms were located in difference syntheses and their positional parameters were allowed to refine freely. The isotropic displacement parameters of all H atoms were fixed at $1.2U_{\rm eq}$ of the parent atoms.

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 Corporation, 2001); program(s) used to solve structure: *SIR*92 (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*.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation & Rigaku (2001). *CrystalStructure.* Version 3.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196–8666, Japan.

Nakamura, N., Uno, K. & Ogawa, Y. (2001*a*). *Acta Cryst.* E**57**, o505–o507.

Nakamura, N., Uno, K. & Ogawa, Y. (2001*b*). *Acta Cryst.* E**57**, o508–o510.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Thalladi, V. R., Boese, R. & Weiss, H. C. (2000). *J. Am. Chem. Soc.* **122**, 1186–1190.

Ulman, A. (1996). *Chem. Rev.* **96**, 1533–1554.

Urquhart, G. G., Gates, J. W. & Connor, R. (1955). *Org. Synth.* **III**, pp. 363–365.

Watkin, D. J., Prout, C. K., Carruthers, J. R. & Betteridge, P. W. (1996). *CRYSTALS.* Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.

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