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Key indicators

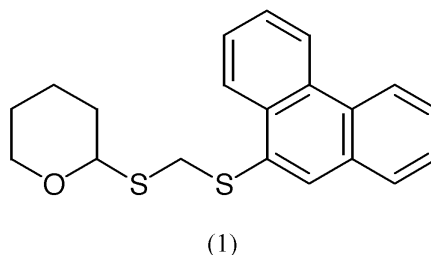
Single-crystal X-ray study
T = 193 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.035
wR factor = 0.099
Data-to-parameter ratio = 14.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-(Phenanthren-9-ylthiomethylthio)tetrahydropyran at 193 K

The title compound, $\text{C}_{20}\text{H}_{20}\text{OS}_2$, crystallizes in the monoclinic space group $P2_1/c$. The S-side chain at the 2-position of the tetrahydropyran (THP) group is axial with a C—O—C—S torsion angle of $66.77(19)^\circ$. The C—S—C—S torsion angle at the THP side of the dithioacetal group is $78.31(12)^\circ$ and at the phenanthrene side is $-176.73(10)^\circ$.

Comment

The title compound, 2-(phenanthren-9-ylthiomethylthio)-tetrahydropyran, (1), is thus far the only crystalline starting material used for lithiations during the study of the syntheses and structures of novel *O,S,S*-acetal compounds. The crystal structures of several hydroxyalkylated derivatives have been determined, namely (1*S*,2*S*,2'*R*)-X, (2) (Kansikas *et al.*, 1996), (1*S*,2*R*,2'*S*)-X, (3), and (1*S*,2*S*,2'*S*)-X, (4) (Kansikas & Sipilä, 2000*a*), (1*R**,2*S**,2'*S**)-X, (5) (Sipilä *et al.*, 2002), (1*S**,2*S**,-2'*R**)-Y, (6) (Kansikas *et al.*, 1995), (1*S**,2*R**,-2'*R**)-Y, (7) (Kansikas & Sipilä, 2001), (1*R*,2*S*,2'*R*)-Z, (8), and (1*R*,2*S*,2'*S*)-Z, (9) (Sipilä & Kansikas, 2002), where X = 1-phenyl-2-phenylthio-2-(tetrahydropyran-2-ylthio)ethanol, Y = 2-phenyl-1-phenylthio-1-(2-tetrahydropyran-2-ylthio)propan-2-ol and Z = 1-phenyl-2-(2-naphthylthio)-2-(tetrahydropyran-2-ylthio)ethanol. In these compounds [(2)–(9)], the O atom belongs to the tetrahydropyran (THP) ring with the S-side chain at the 2-position and the other S atom of the dithioacetal moiety is substituted by an aryl group. Alkylations of lithiated *O,S,S*-acetals showed remarkable diastereoselectivity, which was rationalized by the locked conformation of the five-membered ring, caused by lithium-to-oxygen coordination (Sipilä *et al.*, 2002). Compound (1) crystallized in a supposedly monoclinic crystal system, but triclinic data were collected at 193 K. Data reduction and further structure refinement confirmed the space group to be $P2_1/c$. The molecule with crystallographic atom labels is shown in Fig. 1.



The S-side chain at the THP ring is axial, with a C—O—C—S torsion angle of $66.77(19)^\circ$. The C—S—C—S torsion angle at the THP side is $78.31(12)^\circ$ and at the phenanthrene side is $-176.73(10)^\circ$. The distances of atom S2 from the C atom of the THP ring are 1.845 (2) and 1.797 (2) Å from the central

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atom C15. The distances of the other S atom from the aromatic C atom are 1.765 (2) and 1.810 (2) Å from the central C atom. The S—C(aromatic) distance is somewhat shorter than the mean value of 1.781 Å found in other 2-S-(THP) *O,S,S*-acetals (2)–(9), where the aromatic group is phenyl or naphthyl. However, in 9-S-alkyl phenanthrenes, where alkyl is methyl, ethyl, propyl or butyl (Kansikas & Sipilä, 1997), dodecyl or tetradecyl (Kansikas & Sipilä, 2000*b*) and *tert*-butyl (Sipilä *et al.*, 1999), the S—C(phenanthrene) distances, varying between 1.764 and 1.777 Å, are equal or slightly longer than in (1). The S—C(THP) distances are, as expected, longer in axially than equatorially substituted compounds (2)–(9), with mean values of 1.834 and 1.808 Å, respectively. In six out of nine 2-S-(THP) *O,S,S*-acetals [(1)–(9)], the S-side chain is axial, with C—O—C—S torsion-angle values ranging from 65.3 (6) to 71.6 (2)°. In other 2-S-(THP) structures, even slightly related to the compounds (1)–(9) found in the Cambridge Structural Database (CSD, Version 5.22 of October 2001; Allen & Kennard, 1993), the equatorial S-side chain was far more common. Among those sugar-like *O,S*-acetals only one otherwise unsubstituted 2-S-(THP) ring (CSD refcode DUMHAU; Block *et al.*, 1986) was found. In the compounds with an axial S-side chain, the C—O—C—S torsion angles varied from 62.5 (KUHNEG; Durier *et al.*, 1992) to 87.4° (GUNTAK; Liberek *et al.*, 2000). The S—C(THP) distances in both axial and equatorial substituents showed large variations, ranging for axial compounds from 1.784 Å in DUMHAU (Block *et al.*, 1986) to 1.855 Å in

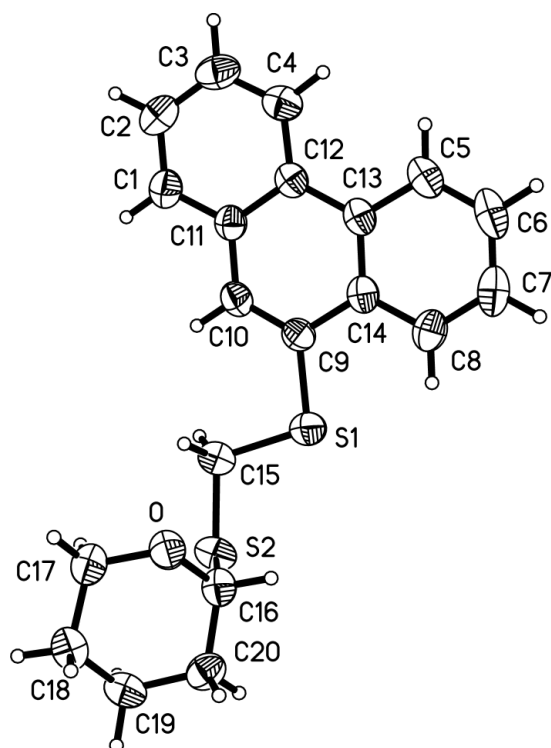


Figure 1
View of (1) with the crystallographic atom labels. Displacement ellipsoids are drawn at the 50% probability level.

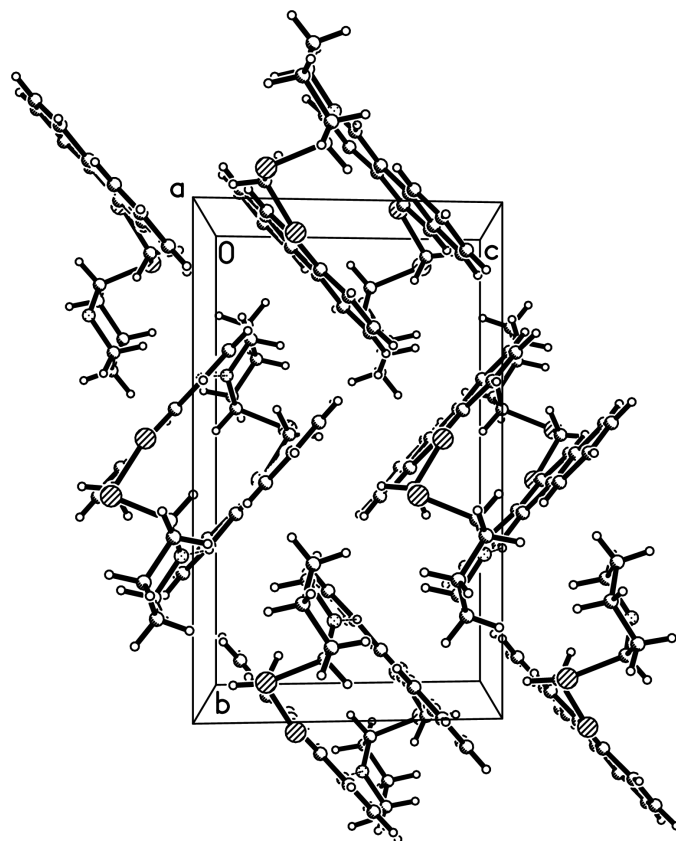


Figure 2
The molecular packing of (1), viewed along the *a*-axis direction.

GUNTAK (Liberek *et al.*, 2000) and from 1.773 Å in DARSUK01 (Battacharjee & Jeffrey, 1983) to 1.835 Å in GUNTAK (Liberek *et al.*, 2000) for equatorially substituted 2-S-(THP) compounds. The molecular packing of (1) has a zigzag motif composed of the phenanthrene groups, which are stacked pairwise with a mean distance of 3.51 Å between the nearly planar and parallel phenanthrene groups, when viewed from the *a*-axis direction (Fig. 2).

Experimental

Compound (1) was prepared from hydrolyzed thioacetic acid, *S*-(2-tetrahydropyranyl) ester and 9-(chloromethylthio)phenanthrene (Sipilä *et al.*, 2002). The crude product was purified with flash chromatography (silica gel, dichloromethane) and recrystallized from ethanol.

Crystal data

$C_{20}H_{20}OS_2$
 $M_r = 340.48$
 Monoclinic, $P2_1/c$
 $a = 12.793$ (3) Å
 $b = 14.890$ (3) Å
 $c = 8.9570$ (18) Å
 $\beta = 99.42$ (3)°
 $V = 1683.2$ (6) Å³
 $Z = 4$

$D_x = 1.344$ Mg m⁻³
 Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 4$ –12°
 $\mu = 2.87$ mm⁻¹
 $T = 193$ (2) K
 Prism, colourless
 0.21 × 0.20 × 0.19 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 5817 measured reflections
 2995 independent reflections
 2427 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$

$\theta_{\text{max}} = 67.8^\circ$
 $h = -15 \rightarrow 15$
 $k = -1 \rightarrow 17$
 $l = -10 \rightarrow 10$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.099$
 $S = 1.02$
 2995 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.5652P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------|-------------|--------------|--------------|
| O—C16 | 1.410 (2) | S1—C15 | 1.810 (2) |
| O—C17 | 1.441 (3) | S2—C15 | 1.797 (2) |
| S1—C9 | 1.765 (2) | S2—C16 | 1.845 (2) |
| C16—O—C17 | 114.09 (15) | C14—C9—S1 | 116.61 (15) |
| C9—S1—C15 | 103.17 (10) | S2—C15—S1 | 109.29 (12) |
| C15—S2—C16 | 100.66 (10) | O—C16—C20 | 111.72 (17) |
| C10—C9—S1 | 123.42 (15) | O—C16—S2 | 112.90 (14) |
| C15—S1—C9—C10 | −11.0 (2) | C9—S1—C15—S2 | −176.73 (10) |
| C15—S1—C9—C14 | 169.89 (14) | C17—O—C16—S2 | 66.77 (19) |
| C16—S2—C15—S1 | 78.31 (12) | C15—S2—C16—O | 46.56 (16) |

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: WINGX (Farrugia,

1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXL97.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Battacharjee, S. & Jeffrey, G. A. (1983). *Mol. Cryst. Liq. Cryst.* **101**, 247–260.
- Block, E., Laffitte, J.-A. & Eswarakrishnan, V. (1986). *J. Org. Chem.* **51**, 3428–3465.
- Bruker (1997). SHELXTL. Release 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Durier, V., Driguez, H., Rollin, P., Duce, E. & Buisson, G. (1992). *Acta Cryst.* **C48**, 1791–1794.
- Enraf–Nonius (1994). CAD-4 EXPRESS. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Kansikas, J., Leskelä, M., Sipilä, K. & Hase, T. (1995). *Acta Chem. Scand.* **49**, 809–812.
- Kansikas, J. & Sipilä, K. (1997). *Acta Cryst.* **C53**, 1127–1131.
- Kansikas, J. & Sipilä, K. (2000a). *Acta Cryst.* **C56**, 1383–1385.
- Kansikas, J. & Sipilä, K. (2000b). *Acta Cryst.* **C56**, 69–71.
- Kansikas, J. & Sipilä, K. (2001). *Acta Cryst.* **E57**, o335–o337.
- Kansikas, J., Sipilä, K. & Hase, T. (1996). *Acta Chem. Scand.* **50**, 1147–1152.
- Liberek, B., Konitz, A., Frankowski, R. & Smiatacz, Z. (2000). *Carbohydr. Res.* **326**, 151–158.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–373.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Sipilä, K., Hase, T., Koskimies, J., Matikainen, J. & Kansikas, J. (2002). *Phosphorus Sulfur Silicon*. In the press.
- Sipilä, K. & Kansikas, J. (2002). *Phosphorus Sulfur Silicon*. In the press.
- Sipilä, K., Kansikas, J. & Mesilaakso, M. (1999). *J. Chem. Soc. Perkin Trans. 2*, pp. 1841–1845.