C10	0.4312 (6)	0.1462 (4)	−0.1920 (4)	0.157 (3)
N11	0.2438 (2)	0.2722 (2)	−0.06674 (14)	0.0661 (8)
C12	0.2369 (2)	0.2595 (2)	0.0000 (2)	0.0615 (9)
N13	0.2968 (2)	0.2861 (2)	0.0500 (2)	0.0717 (8)
C14	0.3059 (2)	0.2571 (3)	0.1210 (2)	0.0650 (9)
C15	0.3252 (2)	0.1761 (3)	0.1338 (2)	0.0778 (11)
C16	0.3339 (3)	0.1522 (4)	0.2038 (3)	0.1033 (15)
C17	0.3248 (4)	0.2061 (5)	0.2586 (2)	0.110 (2)
C18	0.3072 (3)	0.2835 (5)	0.2457 (2)	0.102 (2)
C19	0.2974 (3)	0.3114 (3)	0.1768 (2)	0.0811 (12)
C20	0.2746 (4)	0.3979 (4)	0.1661 (3)	0.119 (2)
C21	0.3524 (6)	0.4537 (4)	0.1680 (5)	0.155 (3)
C22	0.3391 (4)	0.1175 (4)	0.0737 (3)	0.112 (2)
C23	0.4111 (5)	0.0598 (4)	0.0835 (5)	0.159 (3)
N24	0.1649 (2)	0.2150 (2)	0.02549 (14)	0.0636 (7)
C25	0.1112 (2)	0.1770 (3)	−0.0295 (2)	0.0710 (10)
C26	0.0447 (3)	0.1201 (3)	0.0045 (2)	0.0849 (11)
O27	−0.0116 (2)	0.1614 (2)	0.0527 (2)	0.0979 (9)
C28	0.0404 (3)	0.1972 (4)	0.1067 (2)	0.0971 (14)
C29	0.1060 (3)	0.2563 (3)	0.0769 (2)	0.0839 (12)

Table 2. *Selected geometric parameters (Å, °)*

C1—N11	1.414 (5)	N13—C14	1.430 (5)
N11—C12	1.280 (4)	N24—C25	1.458 (4)
C12—N13	1.376 (5)	N24—C29	1.481 (5)
C12—N24	1.395 (5)		
C12—N11—C1	123.6 (3)	C12—N13—C14	126.4 (3)
N11—C12—N13	124.5 (3)	C12—N24—C25	114.4 (3)
N11—C12—N24	119.3 (3)	C12—N24—C29	115.9 (3)
N13—C12—N24	116.2 (3)	C25—N24—C29	109.9 (3)
C12—N11—C1—C2	106.4 (4)	N13—C12—N24—C25	−170.5 (3)
C12—N13—C14—C15	58.8 (5)	N13—C12—N24—C29	60.1 (4)
C12—N24—C25—C26	171.0 (3)	N24—C12—N11—C1	−179.3 (3)
C12—N24—C29—C28	−172.0 (3)	N24—C12—N13—C14	16.8 (5)
N11—C12—N13—C14	−162.4 (4)	C1—C2—C9—C10	158.0 (6)
N11—C12—N24—C25	8.8 (5)	C1—C6—C7—C8	−83.9 (7)
N11—C12—N24—C29	−120.7 (4)	C14—C15—C22—C23	139.5 (6)
N13—C12—N11—C1	−0.1 (6)	C14—C19—C20—C21	−99.4 (6)

H atoms bonded to C atoms were refined using a riding model, with the torsion angles of the methyl groups defined by the expected staggered conformation (*SHELXL*93; Sheldrick, 1993). H-atom displacement parameters were restricted to be 1.2U of the parent atom, except for the methyl groups, in which $U_H = 1.5U_C$. The H(N) atom was located from a difference Fourier calculation and was then treated using the riding model. The positioning of H(N) at N13 and not at N11 is supported by the C12—N bond lengths [C12—N13 1.376 (5) and C12=N11 1.280 (4) Å] and by the modes of intermolecular interactions; N13—H is involved in a hydrogen bond, with N13···O27($\frac{1}{2}+x$, $\frac{1}{2}-y$, z) 3.000 (4) Å, whereas N11 has no potential hydrogen-bond acceptor within a radius of 4 Å. This treatment of H atoms was used because displacement parameters of the structure are generally very high. Since the structure contains only light atoms, the orientation of the polar axis (z) cannot be unambiguously determined from the Flack parameter (Flack, 1983).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexakis(mercaptomethyl)benzene: a Structure Possessing Well Ordered Homodromic [SH···S]$_6$ Interactions

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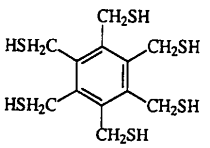
Abstract

In the molecular crystal of the title compound, 1,2,3,4,5,6-phenylhexakis(methanethiol), $C_{12}H_{18}S_6$, an intermolecular [SH]$_6$ grouping around a point of $\bar{3}$ symmetry is found between molecules which are stacked infinitely along the c-axial direction.

Comment

The title compound, (1), was selected as an attractive candidate for *ab initio* and experimental electron-density studies owing to the potentially high site symmetry in its molecular crystal. The resulting small 'covalently anchored' asymmetric unit was expected to exhibit attenuated thermal motion effects compared with a corresponding smaller molecule containing the functional entity of interest, for example, CH_3SH (m.p. 150 K).



(1)

The molecular conformation, which is of the *ababab* type, generated by crystallographic $\bar{3}$ symmetry, is shown in Fig. 1. Adjacent molecules along the *c* axis are involved in interactions between the SH groups and S atoms of pairs such that the six S atoms adopt a chair-like arrangement. The $\bar{3}$ symmetry of the $[SH]_6$ grouping imposes a homodromic (Saenger, 1984) arrangement on the hydrogen-bonded network. The measured S—H distance of 1.24 (3) Å is somewhat shortened, a value of *ca* 1.35 Å being expected. A similar effect has been reported for 4-*p*-mercaptophenyl-2,2,4-trimethylchroman in its CCl_4 clathrate (Hardy, McKendrick, MacNicol & Wilson, 1979). The $H\cdots S^{iii}$ and $S\cdots S^{iii}$ interatomic distances are 2.838 (2) and 4.053 (1) Å, respectively, and the $S—H\cdots S^{iii}$ angle is 165.7 (5)° (see Table 2 for symmetry code).

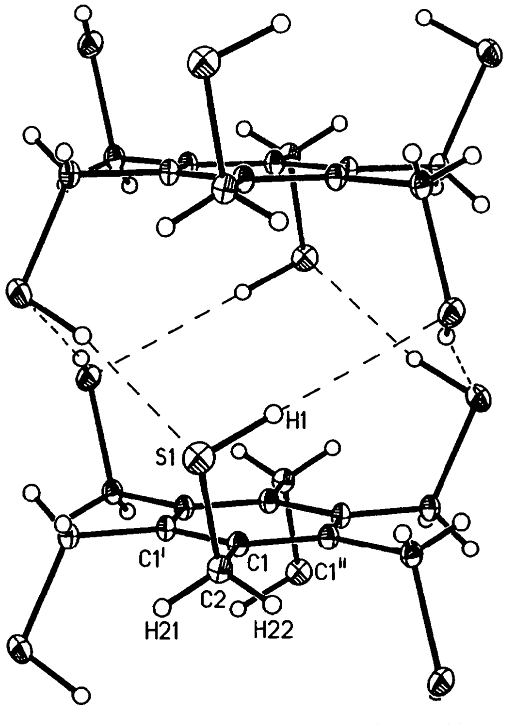


Fig. 1. A view normal to the *c* axis showing the juxtaposition of molecules of (1) along **c**. Displacement ellipsoids are drawn at the 50% probability level. The S—H···S hydrogen bonds are represented by dashed lines.

While the S···S distance is essentially a van der Waals contact, it is interesting to note that the S—H bond appears to lie in the expected direction of an acceptor S lone pair. This is reflected in the IR S—H stretching peak which is observed at 2510 cm^{-1} compared with 2610 cm^{-1} for an isolated S—H bond (Paul, 1974).

Close contacts exist between S atoms in adjacent molecules in the *xy* plane. These are shown as dashed lines in Fig. 2, in which the S···H interactions are also indicated. The intermolecular $S\cdots S(\frac{1}{3}-y, \frac{2}{3}+x-y, z-\frac{1}{3})$ distance of 3.623 (1) Å is considerably shorter than the S···S van der Waals distance of 3.70 Å (Pauling, 1960).

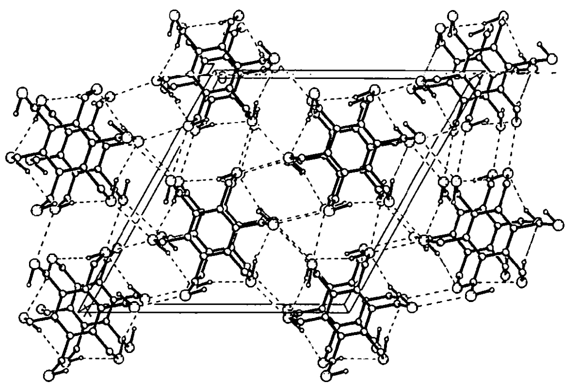


Fig. 2. A view along **c** showing the packing of (1) in its molecular crystal. S—H···S hydrogen bonds and S···S intermolecular interactions are indicated by dotted/dashed and dashed lines, respectively.

Experimental

The title hexathiol was prepared according to the literature method of Backer (1935) and purified by conversion to its hexathioacetate $C_6(CH_2SCOCH_3)_6$ (m.p. 507–508 K) by refluxing in acetic anhydride and pyridine. Conversion back to the hexathiol (m.p. 499–500 K) was then effected by refluxing in MeOH/conc. HCl.

Crystal data

$C_{12}H_{18}S_6$	Mo $K\alpha$ radiation
$M_r = 354.62$	$\lambda = 0.71073$ Å
Trigonal	Cell parameters from 25 reflections
$R\bar{3}$	$\theta = 16.57–19.21°$
$a = 16.088$ (2) Å	$\mu = 0.860$ mm^{-1}
$c = 5.197$ (1) Å	$T = 120$ (1) K
$V = 1164.9$ (3) $Å^3$	Needle
$Z = 3$	0.4 × 0.1 × 0.1 mm
$D_x = 1.517$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.0648$
	$\theta_{max} = 49.92°$

ω–2θ scans
Absorption correction:
none
2715 measured reflections
2705 independent reflections
1261 observed reflections
$[I > 2\sigma(I)]$

$h = -34 \rightarrow 0$
$k = 0 \rightarrow 34$
$l = 0 \rightarrow 11$
5 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0554$
$wR(F^2) = 0.1040$
$S = 1.076$
2701 reflections
40 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.12756 (2)	0.42611 (2)	−0.00817 (6)	0.01645 (8)
C1	0.25648 (7)	0.57146 (7)	−0.3339 (2)	0.0108 (2)
C2	0.17428 (8)	0.46913 (8)	−0.3324 (2)	0.0125 (2)
H1	0.2075 (17)	0.4515 (17)	0.088 (5)	0.039 (6)
H21	0.1199 (12)	0.4625 (13)	−0.428 (4)	0.013 (4)
H22	0.1942 (14)	0.4292 (14)	−0.405 (4)	0.019 (5)

Table 2. *Selected geometric parameters (Å, °)*

S1—C2	1.8340 (13)	C1—C1$^{\rm i}$	1.4074 (10)
S1—H1	1.24 (3)	C1—C2	1.5107 (15)
C2—S1—H1	94.7 (11)	C1—C2—S1	112.72 (8)
C1$^{\rm i}$—C1—C1$^{\rm ii}$	120	S1$^{\rm iii}\cdots$H1—S1	165.7 (5)
C1$^{\rm i}$—C1—C2	119.77 (9)		

Symmetry codes: (i) $\frac{2}{3}+x-y, \frac{1}{3}+x, -\frac{2}{3}-z$; (ii) $y-\frac{1}{3}, \frac{1}{3}-x+y, -\frac{2}{3}-z$; (iii) $\frac{2}{3}+x-y, \frac{1}{3}+x, \frac{1}{3}-z$.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *Express*. Data reduction: *GX* (Mallinson & Muir, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 4-Hydroxy-3-[4-methoxy-2-(methoxymethyleneoxy)phenyl]-2-{[4-methoxy-2-(methoxymethyleneoxy)phenyl]methyl}-5-oxo-2,5-dihydrofuran-2-carboxylate

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Abstract

The title compound, $C_{25}H_{28}O_{11}$, is formed by a homo-aldol condensation of methyl [4-methoxy-2-(methoxymethyleneoxy)phenyl]pyruvate followed by lactonization. The structure consists of a butenolide ring substituted at the 2 position by an arylmethyl and a methyl carboxylate group, at the 3 position by an aryl group and at the 2 position by a hydroxyl group. The solid-state structure contains a hydrogen-bonded cyclic dimer. The hydrogen bonds are formed between the enol H atom of one molecule and the lactone carbonyl O atom of another.

Comment

In a continuing effort towards the synthesis of some sponge secondary metabolites (Boehlow & Spilling 1995), we proposed a synthetic route involving methyl [4-methoxy-2-(methoxymethyleneoxy)phenyl]pyruvate, (2), as the key intermediate. A Wadsworth–Emmons reaction of 4-methoxy-2-(methoxymethyleneoxy)benzaldehyde with methyl 2-dimethoxyphosphoryl-2-(*tert*-butyldimethylsilyloxy)acetate (Plantier-Royon, Anker & Robert-Baudouy, 1991) gave the silylenol ether (1) in quantitative yield. Treatment of (1) with the complex triethylamine tris(hydrogen fluoride) in methanol yielded methyl [4-methoxy-2-(methoxymethyleneoxy)-phenyl]pyruvate. Attempted isolation of pyruvate (2) by SiO_2 chromatography yielded a white crystalline solid,