

Table 1. Selected geometric parameters (Å, °)

| | | | |
|-------------|-------------|--------------|-------------|
| C1—O1 | 1.340 (2) | C7—O3 | 1.319 (2) |
| C1—C6 | 1.349 (3) | C8—O3 | 1.459 (3) |
| C1—C2 | 1.506 (3) | C9—O4 | 1.194 (2) |
| C2—C7 | 1.515 (3) | C9—O5 | 1.327 (2) |
| C2—C3 | 1.527 (3) | C10—O5 | 1.446 (3) |
| C3—C4 | 1.534 (2) | C11—O6 | 1.186 (3) |
| C4—C11 | 1.533 (2) | C11—O7 | 1.321 (2) |
| C4—C9 | 1.533 (3) | C12—O7 | 1.452 (3) |
| C4—C5 | 1.537 (3) | C13—O8 | 1.226 (2) |
| C5—C6 | 1.511 (3) | C13—O9 | 1.329 (2) |
| C6—C13 | 1.463 (3) | C14—O9 | 1.457 (2) |
| C7—O2 | 1.195 (3) | | |
| O1—C1—C6 | 125.1 (2) | O2—C7—O3 | 123.9 (2) |
| O1—C1—C2 | 111.3 (2) | O2—C7—C2 | 124.9 (2) |
| C6—C1—C2 | 123.6 (2) | O3—C7—C2 | 111.2 (2) |
| C1—C2—C7 | 110.7 (2) | O4—C9—O5 | 123.4 (2) |
| C1—C2—C3 | 112.5 (2) | O4—C9—C4 | 125.0 (2) |
| C7—C2—C3 | 108.92 (15) | O5—C9—C4 | 111.61 (14) |
| C2—C3—C4 | 111.14 (15) | O6—C11—O7 | 123.6 (2) |
| C11—C4—C9 | 109.23 (15) | O6—C11—C4 | 124.8 (2) |
| C11—C4—C3 | 108.13 (15) | O7—C11—C4 | 111.6 (2) |
| C9—C4—C3 | 111.47 (15) | O8—C13—O9 | 122.5 (2) |
| C11—C4—C5 | 109.43 (15) | O8—C13—C6 | 124.0 (2) |
| C9—C4—C5 | 108.90 (15) | O9—C13—C6 | 113.5 (2) |
| C3—C4—C5 | 109.7 (2) | C7—O3—C8 | 116.3 (2) |
| C6—C5—C4 | 111.90 (15) | C9—O5—C10 | 115.6 (2) |
| C1—C6—C13 | 118.3 (2) | C11—O7—C12 | 117.1 (2) |
| C1—C6—C5 | 122.3 (2) | C13—O9—C14 | 116.5 (2) |
| C13—C6—C5 | 119.3 (2) | | |
| C1—C2—C3—C4 | -43.4 (2) | C1—C2—C7—O3 | 131.4 (2) |
| C2—C3—C4—C5 | 61.7 (2) | C3—C4—C9—O4 | 132.1 (2) |
| C3—C4—C5—C6 | -48.7 (2) | C3—C4—C9—O5 | -46.4 (2) |
| C4—C5—C6—C1 | 20.1 (3) | C5—C4—C11—O6 | 112.4 (3) |
| C5—C6—C1—C2 | -2.3 (3) | C5—C4—C11—O7 | -66.3 (2) |
| C6—C1—C2—C3 | 14.0 (3) | C1—C6—C13—O8 | 4.6 (3) |
| C1—C2—C7—O2 | -51.2 (3) | C1—C6—C13—O9 | -175.1 (2) |

The methyl and hydroxyl H atoms were included at calculated positions and given a common isotropic displacement parameter [0.123 (5) Å²]. The coordinates and isotropic displacement parameters of the other H atoms were refined.

Data collection: AFC (Rigaku Corporation, 1974). Cell refinement: AFC. Data reduction: AFC. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1039). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 382–384

meso-3,6-Dimethyl-3,6-bis(tert-butylsilyloxy)-1,7-octadiyne

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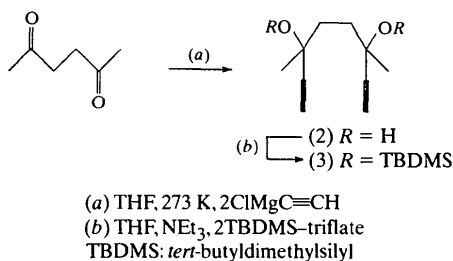
(Received 9 September 1997; accepted 14 November 1997)

Abstract

The title compound, C₂₂H₄₂O₂Si₂, shows a strictly antiperiplanar arrangement of the alkane chain with dihedral angles between the terminal alkyne groups and the alkane chains of -55 (6) and -60.7 (4)°. The central C—C bond contains the centre of inversion. The crystal packing shows interwoven meanders of the antiperiplanar 3,6-disubstituted diynes, with the methyl groups filling the space in between. The tert-butylsilyloxy groups of two meandering chains are oriented towards each other. The absolute values of the crystal data are compared with the data for *rac*-3,6-dimethyl-3,6-bis(tert-butylsilyloxy)-1,7-cyclododecadiyne [Boss *et al.* (1996). *Acta Cryst.* **C52**, 2370–2372].

Comment

The structure of 1,7-diynes are of interest due to their ability to react with a variety of 1,ω-alkylenedibromides to provide medium-sized ring compounds (Boss & Keese, 1996, 1997). The title compound, (3), prepared according to the scheme below, is an important intermediate in these ring-forming reactions and its structure was investigated for comparison with *rac*-3,6-dimethyl-3,6-bis(tert-butylsilyloxy)-1,7-cyclododecadiyne (Boss *et al.*, 1996).



The inversion centre of *meso*-(3) is apparent from the molecular as well as the crystal structure (see scheme

above and Fig. 1). The dihedral angles of the alkane chain show a strictly antiperiplanar arrangement ($C3-C4-C4^i-C3^i$ 180°) usually found for the most stable conformation of alkane chains (Dale, 1978). The terminal alkyne groups [$C2-C3-C4-C4^i$ $-60.7(4)^\circ$; symmetry code: (i) $2-x, -y, 2-z$] and the silyloxy substituents [$O1-C3-C4-C4^i$ $61.5(4)^\circ$] adopt *gauche* conformations. The cyclic analogue showed for these torsion angles the absolute values of -61.69 and 59.87° . The torsion angles at the silyloxy groups are $-139.06(19)$ ($Si1-O1-C3-C4$) and $-168.9(2)^\circ$ ($C8-Si1-O1-C3$). The other torsion angles are comparable in both compounds.

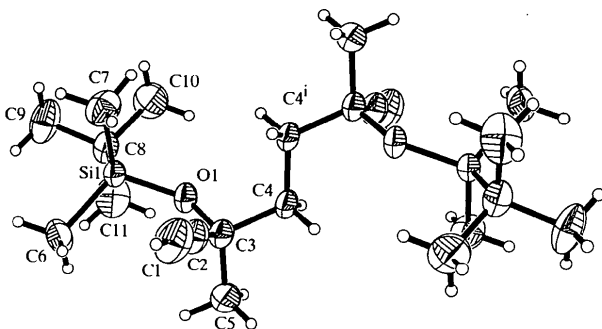


Fig. 1. Perspective view of *meso*-(3). Displacement ellipsoids are shown at the 50% probability level.

The bond angles in the alkane chain, $C5-C3-C4$ [$109.5(2)^\circ$] and $C4^i-C4-C3$ [$113.8(2)^\circ$], are in the expected range (Meyer & Keese, 1993), while the terminal alkyne group is non-linear by 3.6° [$C1-C2-C3$ $176.4(3)^\circ$]. The difference of 1.47° between the bond angles $O1-Si1-C6$ [$111.92(11)^\circ$] and $O1-Si1-C7$ [$110.45(12)^\circ$] is smaller than the difference between the analogous bond angles of cyclic 3,6-dimethyl-3,6-bis(*tert*-butyldimethylsilyloxy)-1,7-cyclo-dodecadiyne. The difference may be explained by the disorder observed for the silyl groups in the cyclic diyne (Boss *et al.*, 1996). The bond angle $C3-O-Si$, with a value of $132.28(18)^\circ$, lies within the range of similarly substituted silyl ethers. A search of the Cambridge Structural Database (Allen *et al.*, 1979) for the C—O—Si substructure in 179 compounds yielded a mean bond angle of 128.6° (range 118.5 – 143.3°).

The lengths of the $Si1-C6$ [$1.852(3)$ Å] and $Si1-C7$ [$1.855(3)$ Å] bonds are consistent with expected values. In the cyclic diyne, these bond lengths are shorter because of the larger thermal movement of the protecting groups (Boss *et al.* 1996). The other bond lengths are comparable in both compounds.

The unit-cell contains two molecules of (3) and is packed so that the triple bonds and the protecting groups are built up in layers (Fig. 2). The alkyne groups of three

successive molecules are packed in such a way that the silyloxy groups of the two triple bonds sitting on the edges of the unit cell belong to the same layer, whereas the silyloxy groups of the triple bond in the middle of the cell are part of the layer below. Thus, the distance between the two triple bonds in the *c* direction is $c/2$ (6.384 Å), hence there is no interaction between the π systems.

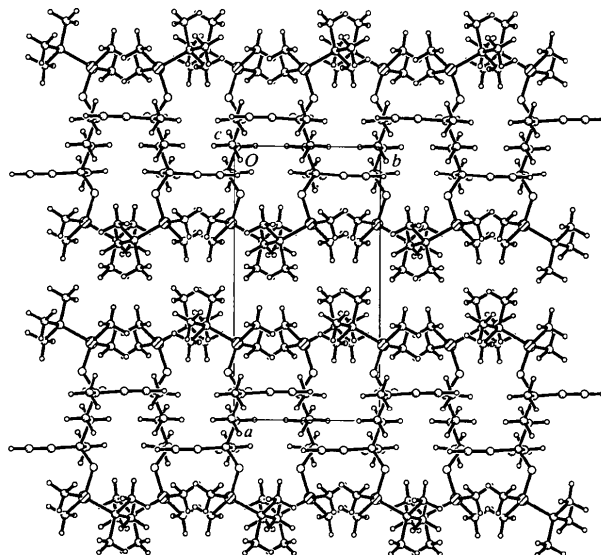


Fig. 2. Packing diagram of *meso*-(3).

Experimental

Compound (3) was prepared in a two-step sequence from acetonylacetone [(1), see scheme] and ethynylmagnesium chloride (Boss, 1996). Silylation of the hydroxy groups with *tert*-butyldimethylsilyl trifluoromethanesulfonate yielded (3) as a 1:1 mixture of diastereomers. Flash chromatography and recrystallization from hexane-ether (1:1) at room temperature gave pure *meso*-(3) as colourless hexagonal plates (m.p. 307 K).

Crystal data

$C_{22}H_{42}O_2Si_2$

$M_r = 394.74$

Monoclinic

$P2_1/c$

$a = 14.458(1)$ Å

$b = 7.569(1)$ Å

$c = 12.768(1)$ Å

$\beta = 105.80(1)^\circ$

$V = 1344.4(2)$ Å³

$Z = 2$

$D_x = 0.975$ Mg m⁻³

$D_m = 0.94(1)$ Mg m⁻³

D_m measured by flotation in water-ethanol

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3153

reflections

$\theta = 1.46$ – 26.60°

$\mu = 0.143$ mm⁻¹

$T = 293(2)$ K

Hexagonal plate

$0.55 \times 0.37 \times 0.28$ mm

Colourless

Data collection

| | |
|-------------------------------------|-------------------------------------|
| Siemens SMART CCD | 2522 independent reflections |
| System diffractometer | 1964 reflections with |
| ω scans (1271 frames, 0.30°) | $I > 2\sigma(I)$ |
| 10 s, detector distance | $R_{\text{int}} = 0.060$ |
| 5.5 cm, detector angle | $\theta_{\text{max}} = 26.60^\circ$ |
| 23.0°) | $h = -17 \rightarrow 18$ |
| Absorption correction: none | $k = -6 \rightarrow 8$ |
| 6368 measured reflections | $l = -15 \rightarrow 16$ |

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 0.452P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.154$ | $(\Delta/\sigma)_{\text{max}} = 0.033$ |
| $S = 1.063$ | $\Delta\rho_{\text{max}} = 0.376 \text{ e } \text{Å}^{-3}$ |
| 2522 reflections | $\Delta\rho_{\text{min}} = -0.171 \text{ e } \text{Å}^{-3}$ |
| 125 parameters | Extinction correction: none |
| H atoms treated by a | Scattering factors from |
| mixture of independent | <i>International Tables for</i> |
| and constrained refinement | <i>Crystallography</i> (Vol. C) |

Table 1. Selected geometric parameters (Å, °)

| | | | |
|--------------|--------------|--------------|-----------|
| Si1—O1 | 1.6485 (16) | O1—C3 | 1.437 (3) |
| Si1—C6 | 1.852 (3) | C1—C2 | 1.168 (5) |
| Si1—C7 | 1.855 (3) | C2—C3 | 1.474 (5) |
| Si1—C8 | 1.874 (3) | C3—C5 | 1.527 (4) |
| O1—Si1—C6 | 111.92 (11) | C1—C2—C3 | 176.4 (3) |
| O1—Si1—C7 | 110.45 (12) | C2—C3—C4 | 110.2 (2) |
| O1—Si1—C8 | 103.73 (10) | C5—C3—C4 | 109.5 (2) |
| C3—O1—Si1 | 132.28 (18) | C4—C3—C5 | 113.8 (2) |
| C8—Si1—O1—C3 | -168.9 (2) | C1—C2—C3—C5 | 66 (6) |
| Si1—O1—C3—C2 | -18.2 (3) | C1—C2—C3—C4 | -55 (6) |
| Si1—O1—C3—C5 | 103.2 (3) | O1—C3—C4—C4' | 61.5 (4) |
| Si1—O1—C3—C4 | -139.06 (19) | C2—C3—C4—C4' | -60.7 (4) |
| C1—C2—C3—O1 | -174 (6) | C5—C3—C4—C4' | 178.5 (3) |

Symmetry code: (i) 2 - x, -y, 2 - z.

H-atom positions were calculated from idealized geometries and refined as riding on the corresponding C atoms.

Data collection: SMART (Siemens 1996a). Cell refinement: SAINT (Siemens 1996a). Data reduction: SAINT. Program(s) used to solve structure: SHELXS90 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTL (Siemens, 1996b). Software used to prepare material for publication: SHELXL97.

This work has been supported by the Swiss National Science Foundation (Project No. 20.43565.95). The diffraction data have been collected within an undergraduate trainee program, organized by Prof. H.-B. Bürgi, whom the authors thank for his generous support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1151). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C54, 384–386

Ammonium Hydrogen Tartronate

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(Received 4 July 1997; accepted 3 November 1997)

Abstract

The title compound, ammonium hydrogen hydroxypropanedioate, NH₄⁺.C₃H₃O₅⁻, has a very short non-centrosymmetric O—H...O hydrogen bond [2.443 (2) Å] between the carboxyl and carboxylate groups. The hydroxyl group attached to C1 forms a bifurcated hydrogen bond with intra- and intermolecular O atoms. The NH₄⁺ cation forms six N—H...O hydrogen bonds including two bifurcated hydrogen bonds, by which a layer composed of the cations and anions is formed.

Comment

It has been found that acid salts of carboxylic acids form very short O—H...O hydrogen bonds (Macdonald *et al.*, 1972; Videnova *et al.*, 1980; Kroon & Kanters, 1982; Hermansson & Tellgren, 1983; Misaki *et al.*, 1986). The structure of ammonium hydrogen tartronate, (I), is expected to be suitable for a detailed investigation of the bonding behavior of the H atom, because the molecule contains only a few light atoms with low atomic numbers.

