

Monoclinic

$P2_1/c$
 $a = 6.383$ (2) Å
 $b = 23.443$ (4) Å
 $c = 8.031$ (2) Å
 $\beta = 107.92$ (2)°
 $V = 1143$ (1) Å³
 $Z = 4$
 $D_x = 1.543$ Mg m⁻³
 D_m not measured

Data collection

Rigaku AFC diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 Gaussian (SHELX76;
 Sheldrick, 1976)
 $T_{\min} = 0.156$, $T_{\max} = 0.514$
 2084 measured reflections
 1928 independent reflections
 1173 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.211$
 $S = 0.910$
 1928 reflections
 149 parameters
 Only H-atom U 's refined
 $w = 1/[\sigma^2(F_o^2) + (0.1473P)^2 + 0.136P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 25 reflections

$\theta = 18.8$ – 30.5 °
 $\mu = 7.00$ mm⁻¹
 $T = 293$ (2) K
 Platelet
 $0.194 \times 0.192 \times 0.052$ mm
 Colourless

$R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 65.0$ °
 $h = -10 \rightarrow 10$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 14$
 3 standard reflections
 every 100 reflections
 intensity decay: <1.7%

$(\Delta/\sigma)_{\text{max}} = 0.014$
 $\Delta\rho_{\text{max}} = 0.446$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.413$ e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 2. Selected bond lengths (Å) for (4)

C1—C8a	1.521 (7)	C5—C6	1.515 (6)
C1—C2	1.551 (5)	C6—C7	1.321 (4)
C2—C3	1.542 (8)	C6—C16	1.749 (5)
C3—C3a	1.507 (7)	C7—C8	1.525 (7)
C3a—C4	1.473 (7)	C8—C8a	1.520 (7)
C3a—C9	1.507 (6)	C8a—C9	1.518 (5)
C3a—C8a	1.540 (6)	C9—C19'	1.750 (3)
C4—C5	1.513 (7)	C9—C19	1.761 (4)
C5—O5	1.196 (4)		

As crystals of (3) were unstable in the X-ray beam, two crystals were used for the intensity measurements. The crystal dimensions and absorption corrections for the second crystal are given in parentheses in the experimental data.

For both compounds, data collection: *AFC/MSD Data Collection and Refinement Software* (Rigaku Corporation, 1974); cell refinement: *AFC/MSD Data Collection and Refinement Software*; data reduction: *AFC/MSD Data Collection and Refinement Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELX76* (Sheldrick, 1976); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1196). Services for accessing these data are described at the back of the journal.

References

- Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.
 Banwell, M. G., Gable, R. W., Halton, B. & Phyland, J. R. (1994). *Aust. J. Chem.* **47**, 1879–1884.
 Banwell, M. G., Gable, R. W., Peters, S. C. & Phyland, J. R. (1995). *J. Soc. Chem. Commun.* pp. 1395–1397.
 Banwell, M. G. & Pallich, S. (1997). Unpublished results.
 Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. I, pp. 18–199. New York: Plenum Press.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Mackay, M. F., Banwell, M. G. & Phyland, J. R. (1997). *Acta Cryst.* **C53**, 1497–1499.
 Rigaku Corporation (1974). *AFC/MSD Data Collection and Refinement Software*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). **C54**, 380–382

Cyclohexanone-2,4,4,6-tetramethyl Ester†

ANDREW B. HUGHES AND MAUREEN F. MACKAY

School of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083. E-mail: xraymm2@lure.latrobe.edu.au

(Received 7 July 1997; accepted 31 October 1997)

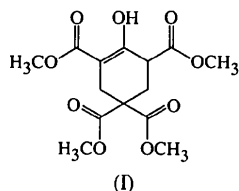
Abstract

The title compound, C₁₄H₁₈O₉, was isolated as a minor by-product (2.6%) from the benzene mother liquors of a preparation of Meerwein's ester. The molecule is present in the crystal in the enol configuration with the cyclohexene ring adopting a half-chair conformation.

Comment

In the course of a preparation of Meerwein's ester (Meerwein & Schurmann, 1913), the main compound was isolated in the published manner (Schaefer & Honig, 1968) from a benzene recrystallization. The mother liquors were left to stand for a few days and a highly crystalline second crop precipitated. As the ¹H NMR spectrum of the latter did not agree with that of the major compound, an X-ray analysis was undertaken to identify the minor product. A perspective view of the title compound, (I), is illustrated in Fig. 1.

† Alternative name: tetramethyl 2-hydroxycyclohexene-1,3,5,5-tetracarboxylate.



The cyclohexene ring adopts a half-chair conformation, with atoms C5, C6, C1 and C2 planar to within 0.009 (1) Å and with C3 and C4 on opposite sides of the plane at distances of 0.301 (4) and 0.451 (4) Å, respectively; the asymmetry parameter (Duax & Norton, 1975) $\Delta C_2^{1,6}$ is 5.7°. The C2 methyl ester group occupies an equatorial position and the C6 ester group lies within the four-atom plane as reflected in the torsion angles C5—C6—C13—O8 of -178.1 (2)° and C5—C6—C13—O9 of 2.1 (3)°. The C1—C6 bond of 1.349 (3) Å

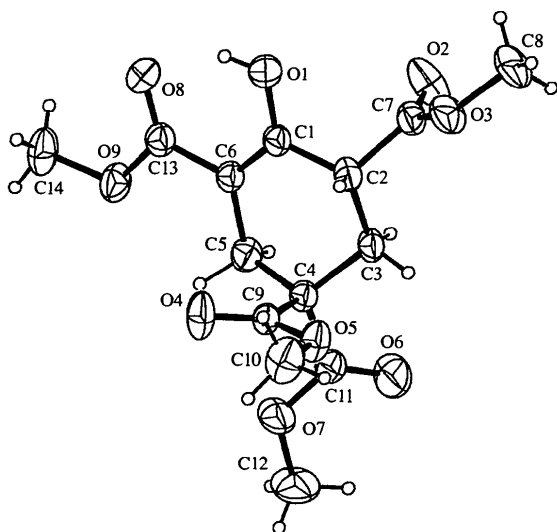


Fig. 1. Perspective view of the molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. The H atoms are denoted by spheres of arbitrary radii.

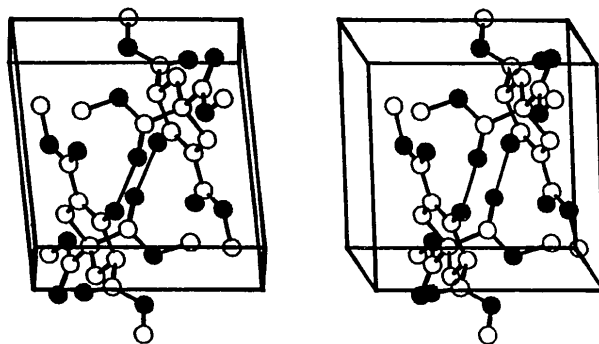


Fig. 2. Stereoview of the crystal packing viewed down the *b* axis. The *c* axis is horizontal.

is close to the value expected for a C=C bond and the the C1—O1 bond of 1.340 (2) Å is similar to values reported for a single C_{sp^2} —O bond. These dimensions, together with the angles subtended at atoms C1 and C6 (Table 1), and the coplanarity of atoms C5, C6, C1 and C2, indicate that the molecule adopts the enol configuration in the crystal. The crystal packing is illustrated in Fig. 2. Weak intermolecular hydrogen bonds in which the hydroxyl group donates its proton to the C9 carbonyl O atom link the molecules into centrosymmetric dimers, graph set $R_2^2(14)$ (Etter, 1990). The O1...O4(1 - *x*, -*y*, 1 - *z*), O1—H1 and H1...O4 distances are 3.067 (2), 0.82 and 2.60 Å, respectively, with the O1—H1...O4 angle 117.7°.

Experimental

Crystals of (I) were obtained from a benzene solution.

Crystal data

$C_{14}H_{18}O_9$
 $M_r = 330.3$
 Triclinic
 $P\bar{1}$
 $a = 9.906$ (3) Å
 $b = 10.635$ (3) Å
 $c = 8.126$ (1) Å
 $\alpha = 90.56$ (2)°
 $\beta = 94.84$ (3)°
 $\gamma = 116.49$ (2)°
 $V = 762.4$ (3) Å³
 $Z = 2$
 $D_x = 1.439$ Mg m⁻³
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54180$ Å
 Cell parameters from 25 reflections
 $\theta = 19.1$ –34.8°
 $\mu = 1.051$ mm⁻¹
 $T = 293$ (2) K
 Prismatic
 0.375 × 0.300 × 0.275 mm
 Colourless

Data collection

Rigaku AFC diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 Gaussian (SHELX76;
 Sheldrick, 1976)
 $T_{min} = 0.671$, $T_{max} = 0.794$
 2773 measured reflections
 2571 independent reflections
 2355 reflections with
 $I > 2\sigma(I)$

$R_{int} = 0.014$
 $\theta_{max} = 65.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = 0 \rightarrow 9$
 3 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.121$
 $S = 1.092$
 2355 reflections
 236 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.4613P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.34$ e Å⁻³
 $\Delta\rho_{min} = -0.22$ e Å⁻³
 Extinction correction:
 SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.026 (2)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

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.

References

- Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. 1, pp. 18–199. New York: Plenum Press.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Meerwein, H. & Schurmann, A. (1913). *Liebigs Ann. Chem.* **398**, 196–250.
- Rigaku Corporation (1974). AFC. *Diffraction Control Program System*. Rigaku Corporation, Tokyo, Japan.
- Schaefer, J. P. & Honig, L. M. (1968). *J. Org. Chem.* **33**, 2655–2659.
- Sheldrick, G. M. (1976). SHELX76. *Program for Crystal Structure Determination*. University of Cambridge, England.
- Sheldrick, G. M. (1985). SHELXS86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). SHELXL93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). **C54**, 382–384

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

ANDREAS WICKI,^a SABINE GRÜSCHOW,^a THERESE LÜTHI,^a JULIA VON GROTHE,^a SILVIA CAPELLI,^b JÜRGEN HAUSER^b AND REINHART KEESE^a

^aDepartement für Chemie und Biochemie, Universität Bern, Freiestr. 3, CH-3012 Bern, Schweiz, and ^bLaboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern, Schweiz. E-mail: rk@ioc.unibe.ch

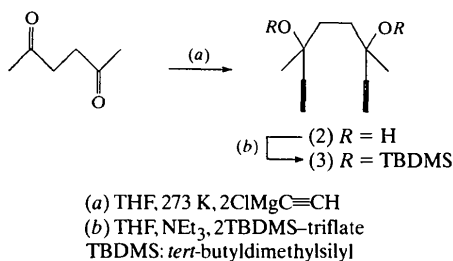
(Received 9 September 1997; accepted 14 November 1997)

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