Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Racemic 3,6-Dimethyl-3,6-bis(*tert*-butyldimethylsilyloxy)-1,7-cyclododecadiyne

Christoph Boss,[a] Reinhart Keese[a] and Marcel Förtsch[b]

[a]*Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland, and* [b]*Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland. E-mail: keese@ioc.unibe.ch*

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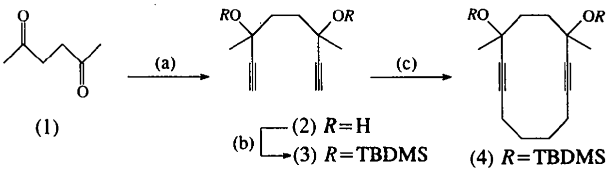
Abstract

The title compound, $C_{26}H_{48}O_2Si_2$, has been prepared and its structure determined. The bond angles at the triple bond are close to 174.5° (average) and the length of the triple bond is 1.179 (3) Å. The alkylene chains maintain a screw-type arrangement similar to that found in unsubstituted cyclododecane.

Comment

Medium-sized ring compounds are of considerable interest because of their unique structure and transannular reactivity (Dunitz & Meyer, 1965; Johnson, 1986; Gleiter, Merger, Irngartinger & Nuber, 1993). The title cyclododecadiyne, (4), has been prepared in order to investigate the reactions of juxtaposed triple bonds with doubly functionalized reagents.



(*a*) THF, 273K, 2 eq. ClMgC≡CH
(*b*) THF, NEt_3, 2 eq. TBDMS-triflate
(*c*) (i) THF, 253K, 2 eq. *n*-BuLi;
(ii) 298K, DMPU, 1 eq. 1,4-dibromobutane

TBDMS: *tert*-butyldimethylsilyl
DMPU: 1,3-dimethyl-3,4,5,6-tetrahydro-2 (1*H*)-pyrimidinone

The expected C_2 symmetry of racemic compound (4) is apparent from the structural analysis (Fig. 1). The orientation of the two alkylene chains relative to each other corresponds to the screw-type arrangement found in unsubstituted cyclododecane (Dale, 1978). The length of the triple bond is 1.179 (3) Å.

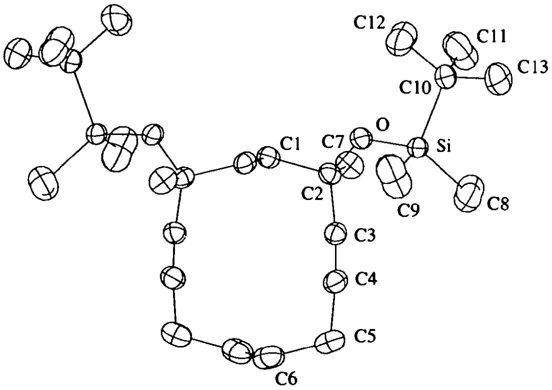


Fig. 1. The molecular structure of title compound (site occupancy 0.799) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 20% probability level.

The bond angles at the triple bond are 174.2 (3) (C2—C3—C4) and 174.7 (3)° (C3—C4—C5), which deviate only slightly from 180°. The transannular distance of the two alkyne units is 3.871 (4) Å [C3···C3*A* 3.891 (4) and C4···C4*A* 3.886 (4) Å]. These structural features are well within the range found in cyclododecadiynes and cyclodecadiynes, extracted from the Cambridge Structural Database (Allen *et al.*, 1979). The silyloxy groups are highly disordered. For every Si, C8, C9, C10, C11, C12 and C13 atom, two different positions with acceptable geometric and displacement parameters have been found. The unit cell contains two pairs of enantiomeric molecules of (4). The value of the density of (4) is rather low. It is apparent from the crystal

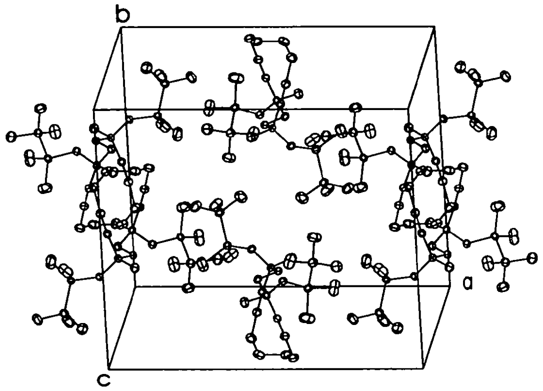


Fig. 2. Packing diagram of title compound (site occupancy 0.799) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 10% probability level.

structure (*cf.* Fig. 2), that the bulky *tert*-butyldimethylsilyl groups are juxtaposed in the unit cell, preventing a more dense packing. This is enhanced by the disorder of these groups.

Experimental

Compound (4) was prepared in a three-step sequence. Addition of hexane-2,5-dione, (1), to ethynylmagnesium chloride gave a 1:1 mixture of *meso* and racemic (2). After silylation of the hydroxy groups with *tert*-butyldimethylsilyl trifluoromethanesulfonate, compound (3) was deprotonated with ^{n}BuLi and alkylated with 1,4-dibromobutane to give compound (4) in 43% isolated yield. Pure racemic (4) was obtained by flash chromatography and recrystallization from pentane/ether (1:1) solution at room temperature (m.p. 353 K).

Crystal data

$C_{26}H_{48}O_2Si_2$
$M_r = 448.82$
Orthorhombic
Pbcn
$a = 17.242 (4)$ Å
$b = 15.244 (3)$ Å
$c = 11.406 (5)$ Å
$V = 2997.9 (16)$ Å^3
$Z = 4$
$D_x = 0.994$ Mg m^{-3}
$D_m = 0.95 (2)$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 14 reflections
$\theta = 10.7–16.3°$
$\mu = 0.135$ mm^{-1}
$T = 173 (2)$ K
Prism
0.45 × 0.36 × 0.36 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
3876 measured reflections
2956 independent reflections
1721 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0606$
$\theta_{max} = 24.97°$
$h = -1 \rightarrow 20$
$k = -1 \rightarrow 18$
$l = -1 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 1.4%

Refinement

Refinement on F^2
$R(F) = 0.0435$
$wR(F^2) = 0.1454$
$S = 1.091$
2418 reflections
170 parameters
H atoms refined with group U_{iso}
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.9495P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.286$ e Å^{-3}
$\Delta\rho_{min} = -0.142$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0044 (7)
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)*

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

	x	y	z	U_{eq}
Si†	0.34929 (8)	0.68701 (8)	−0.00944 (14)	0.0644 (4)
Si*A*‡	0.3613 (7)	0.6785 (9)	−0.0333 (12)	0.219 (8)
O	0.43305 (9)	0.67990 (10)	0.0564 (2)	0.0696 (6)
C1	0.52857 (13)	0.7174 (2)	0.1988 (2)	0.0688 (8)
C2	0.49251 (14)	0.7424 (2)	0.0807 (2)	0.0653 (7)
C3	0.46205 (15)	0.8331 (2)	0.0894 (2)	0.0694 (8)
C4	0.4429 (2)	0.9066 (2)	0.1031 (3)	0.0810 (9)
C5	0.4223 (2)	0.9981 (2)	0.1312 (3)	0.1008 (11)
C6	0.4558 (2)	1.0233 (2)	0.2494 (3)	0.1015 (11)
C7	0.5532 (2)	0.7376 (2)	−0.0167 (3)	0.0965 (10)
C8†	0.3462 (3)	0.7628 (3)	−0.1313 (5)	0.159 (3)
C8*A*‡	0.3973 (10)	0.6877 (13)	−0.1885 (13)	0.116 (7)
C9†	0.2778 (2)	0.7218 (4)	0.1056 (5)	0.168 (3)
C9*A*‡	0.2881 (9)	0.7718 (9)	−0.0100 (16)	0.097 (5)
C10†	0.3259 (3)	0.5740 (3)	−0.0538 (5)	0.0806 (13)
C10*A*‡	0.3074 (11)	0.5795 (12)	−0.0126 (18)	0.087 (9)
C11†	0.3889 (3)	0.5423 (4)	−0.1406 (5)	0.158 (3)
C11*A*‡	0.3659 (11)	0.5067 (14)	−0.040 (2)	0.113 (7)
C12†	0.3268 (3)	0.5119 (3)	0.0522 (5)	0.141 (3)
C12*A*‡	0.2763 (11)	0.5797 (14)	0.1122 (15)	0.130 (7)
C13†	0.2454 (5)	0.5700 (8)	−0.1133 (10)	0.124 (5)
C13*A*‡	0.2437 (17)	0.567 (2)	−0.105 (3)	0.071 (10)

† Site occupancy of 0.799. ‡ Site occupancy of 0.201.

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

Si—O	1.631 (2)	C2—C3	1.482 (3)
Si—C8	1.808 (4)	C2—C7	1.528 (4)
Si—C10	1.840 (4)	C3—C4	1.179 (3)
Si—C9	1.877 (4)	C4—C5	1.475 (4)
O—C2	1.427 (3)	C5—C6	1.517 (4)
C1—C1^i	1.528 (5)	C6—C6^i	1.523 (5)
C1—C2	1.531 (3)		
O—Si—C8	115.0 (2)	C10—Si—C9	108.2 (3)
O—Si—C10	105.0 (2)	C2—O—Si	133.0 (2)
C8—Si—C10	112.4 (2)	C4—C3—C2	174.2 (3)
O—Si—C9	106.1 (2)	C3—C4—C5	174.7 (3)
C8—Si—C9	109.7 (3)		
C2—C3—C4—C5	−27 (6)	C5^i—C6^i—C6—C5	−148.1 (4)
C2^i—C1^i—C1—C2	−148.4 (3)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick 1991). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1231). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Carboxy- and 2,7-Dicarboxy-4,5-benzotropone: Hydrogen-Bonding Patterns of a β-Keto Acid and a Related β-Keto 1,5-Diacid

Hugh W. Thompson, Roger A. Lalancette* and Marie L. Coté

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA. E-mail: lalancette@hades.rutgers.edu

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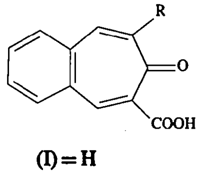
Abstract

The two title compounds exhibit strikingly different hydrogen-bonding modes. The monoacid $C_{12}H_8O_3$, (I) (alternative systematic name: 7-oxo-7*H*-benzocycloheptene-6-carboxylic acid), adopts a nearly planar conformation with the carboxyl internally hydrogen-bonded to the ketone; the molecules pack in stacks at an interplanar distance of 3.397 (4) Å with six lateral C═O···H—C close contacts. In the diacid $C_{13}H_8O_5$, (II) (alternative systematic name: 7-oxo-7*H*-benzocycloheptene-6,8-dicarboxylic acid), the ketone carbonyl, which is not involved in hydrogen bonding, lies out of the general molecular plane, while the carboxylic acids are paired by hydrogen bonding with those of neighboring molecules, forming flat zigzag chains. Both (I) and (II) adopt slightly asymmetric conformations.

Comment

The crystalline states of acetic and formic acids involve chains (catemers) created by repeating intermolecular O—H···O═C hydrogen bonds (Jones & Templeton, 1958; Nahringbauer, 1978). This pattern is otherwise unusual among carboxylic acids, which typically form hydrogen-bonding dimers (Leiserowitz, 1976). Our interest in the X-ray structures of simple keto carboxylic acids concerns such hydrogen-bonding motifs, of which four are known. The most common has acid dimers, in which the ketone is not involved. Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds repeat along one cell axis to yield a catemer. A third, rare arrangement is an internal hydrogen bond, and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed numerous examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

The geometry of β-keto acids appears attractive for internal hydrogen bonding (Toffoli, Khodadad & Rodier, 1988), consistent with the six-centered internal H-atom transfer underlying their thermal decarboxylation (Logue, Pollack & Vitullo, 1975). However, crystallographically, this hydrogen-bonding mode has been found only in γ-keto acids (and one ε-keto acid), requiring larger hydrogen-bonding rings. Internal six-membered hydrogen-bonding does occur in several α,β-unsaturated acids where a β′-oxo function is part of a vinylogous amide or ester and thus more negative than in ketones, but evidence for it in simple crystalline β-keto acids has been lacking. In our study of these patterns, we have examined the title compounds, 2-carboxy-4,5-benzotropone, (I), and 2,7-dicarboxy-4,5-benzotropone, (II), which include the first case of a true β-keto acid with internal hydrogen bonding.



(I) = H
(II) = COOH

Fig. 1 presents a view of molecule (I) with its atomic numbering. The internal angles in a planar heptagon average 128.57°; these angles in (I) are