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Acta Cryst. (1999). C**55**, 630–632

(*E*)-Dimethyl 4-isopropyl-3-[tris(trimethylsilyl)silylmethylene]-1,1-cyclohexanedicarboxylate

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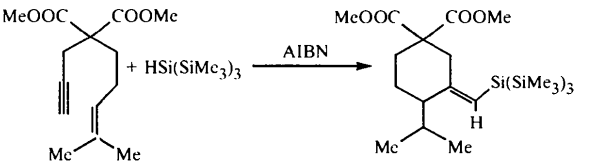
(*Received 16 April 1998; accepted 21 October 1998*)

Abstract

The title isomer carbocyclic compound, $C_{23}H_{48}O_4Si_4$, was prepared by treatment of the 1,7-enyne system dimethyl (4-methylpent-3-enyl)propanodioate with tris(trimethylsilyl)silicon hydride in the presence of azobisisobutyronitrile. The C=C distance is 1.335 (4) Å, the C=C—Si bond angle is 132.6 (2)° and the C—C=C—Si torsion angle is 6.2 (5)°. The *E* configuration of the exocyclic double bond has been confirmed by the present X-ray study.

Comment

Tris(trimethylsilyl)silane (TTMS) has emerged as an alternative to the more common tri-*n*-butyltin hydride in free-radical chain processes (Curran, 1988; Chatgilialoglu, 1992, 1995). The hydrosilylating ability of TTMS with alkenes and alkynes (Chatgilialoglu *et al.*, 1992) has been used in particular for intramolecular addition of the corresponding alkyl (Kulicke *et al.*, 1992) or vinyl (Miura *et al.*, 1993) radicals generated on the other additional double bond. As a result of synthetic work in the free-radical cyclization of 1,6- and 1,7-enyne systems through silylation of the triple bond with TTMS, the six-membered cyclic compound, (*E*)-dimethyl 4-isopropyl-3-[tris(trimethylsilyl)-silylmethylene]-1,1-cyclohexanedicarboxylate, (2), has been isolated in 51% yield as a colourless crystal with a melting point of 356 (1) K.



(1) (2)

No other compounds in which the bulky 'supersilyl' $(Me_3Si)_3Si$ group is bonded to the methylene exocyclic double bond of the cyclohexane ring such as (2) are available in the literature. The enol system formed by 2,2-dimethyl-1-tris(trimethylsilyl)silylethanol (Frey *et al.*, 1994), compound (3), is however the most similar one to compare with some parameters of the title compound. Parameters of the title compound can also be compared with 1-tris(trimethylsilyl)silyl-3,4,5,6-tetrakis-(trimethylsilyl)cyclohex-1-ene (Puranik & Fink, 1994), compound (4), where the supersilyl group is bonded to an endocyclic double bond of the cyclohexene ring. The crystal-structure determination of compound (2) was undertaken to confirm the *E* configurations of the exocyclic double bond. The Si—Si and C—Si distances of the tris(trimethylsilyl)silane of the title compound are close to the distances reported for the 'supersilyl' $(Me_3Si)_3Si$ group (Frey *et al.*, 1994). The C1—C7 distance reveals the existence of a double bond. The C7—Si1 distance changes from 1.94 Å in compound (3) and 1.904 (3) Å in compound (4) to 1.888 (3) Å in the title compound. This difference suggests that compounds (3) and (4) have more steric strains due to the presence of large pendant groups in their structures. The C1—C7—Si1 angle is 133.2° in compound (3). This value is close to the value found in the present structure [132.6 (2)°]. This relatively large bond angle is likely to be due to the steric effects of the bulky groups in both compounds. A torsion angle of 6.2 (5)° for C6—C1—C7—Si1 shows the *E* configuration of compound (2). The cyclohexane backbone adopts a chair conformation with θ = 174 (1)° and φ = 85 (1)° (Cremer & Pople, 1975). The geminal carboethoxy groups bonded to C5 of the cyclohexane ring are oriented in such a way that the C=O groups maintain

the smallest repulsion among them. The angle C10—C5—C8 of 107.5 (2)° indicates a small decrease with regard to the tetrahedral angle due to the presence of the supersilyl group in the present molecule. The torsion angles which define this geometric disposition are given in Table 1.

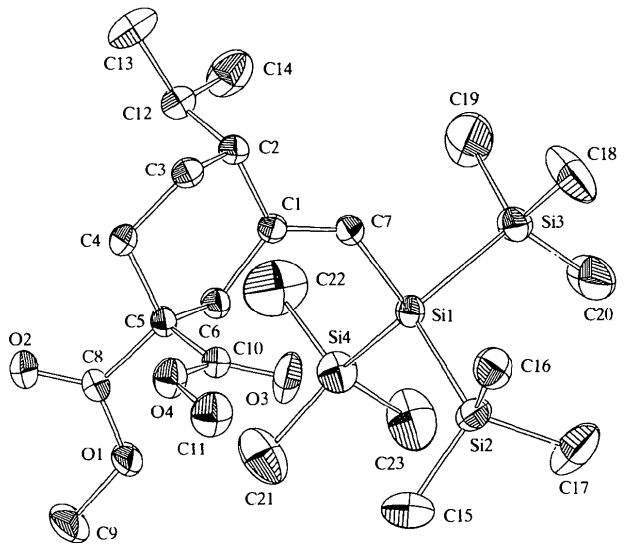


Fig. 1. A perspective view (*ZORTEP*; Zsolnai, 1995) of compound (2) with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Compound (2) was prepared using the following procedure. To a solution degassed with argon of the enyne precursor (1) (0.8 mmol, 0.025 *M*) and azobisisobutyronitrile (AIBN) (0.24 eq) in toluene, TTMS (1.2 eq) was added by syringe. Under an argon atmosphere, the solution was heated to 363–368 K (silicone oil bath) until no starting material was observed by thin-layer chromatography. After cooling to room temperature, the reaction mixture was concentrated in vacuum and the residue was purified by flash column chromatography to give the carbocyclic compound (2).

Compound (2) was characterized by IR, ^{1}H and ^{13}C NMR and MS. ^{1}H NMR (300 MHz; $CDCl_3$): δ 5.25 (1H, *d*, *J* = 1.5 Hz), 3.7 (3H, *s*), 3.67 (3H, *s*), 2.85 (1H, *dd*, *J* = 1.5, 14.4 Hz), 2.47 (1H, *dd*, *J* = 1.8, 14.4 Hz), 2.1 (1H, *dt*, *J* = 1.8, 12.6 Hz), 1.97 (1H, *td*, *J* = 3.6, 12.6 Hz), 1.82–1.72 (3H, *m*), 1.64 (1H, *dd*, *J* = 3.6, 12.6 Hz), 0.89 (3H, *d*, *J* = 6.0 Hz), 0.81 (3H, *d*, *J* = 6.0 Hz), 0.195 p.p.m. (27H, *s*); ^{13}C NMR (75 MHz; $CDCl_3$): δ 172.4, 170.9, 152.0, 118.0, 56.0, 53.8, 52.3, 37.0, 26.7, 26.3, 24.3, 21.9, 20.2, 1.0 p.p.m.; IR (neat) 2952, 2894, 1738, 1602, 1455, 1434, 1245, 1070, 839 cm^{-1}; CIMS: *m/e* 427 (M^+ −73), 485 (M^+ −15), 501 (M^+ +1); HRMS 500.2726 (calculated for $C_{23}H_{48}O_4Si_4$ 500.2629).

Crystal data

$C_{23}H_{48}O_4Si_4$
M_r = 500.97
Monoclinic
$P2_1/n$
a = 9.6682 (9) Å
b = 33.169 (2) Å
c = 9.9711 (8) Å
β = 98.82 (1)°
V = 3159.8 (4) Å^3
Z = 4
D_x = 1.053 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.89–17.97°
μ = 0.21 mm^{-1}
T = 293 (2) K
Transparent plate
0.24 × 0.20 × 0.16 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6781 measured reflections
6402 independent reflections
4289 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 26.30°
h = 0 → 12
k = −41 → 0
l = −12 → 12
3 standard reflections
frequency: 120 min
intensity decay: 1.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.180
S = 1.097
6401 reflections
281 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 2.6905P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Si1—C7	1.888 (3)	Si1—Si2	2.3625 (13)
Si1—Si3	2.3551 (12)	C1—C7	1.335 (4)
Si1—Si4	2.3590 (13)	C2—C12	1.558 (4)
C10—C5—C8	107.5 (2)	C1—C7—Si1	132.6 (2)
C6—C1—C7—Si1	6.2 (5)	C6—C5—C10—O3	0.9 (5)
C4—C5—C8—O2	8.5 (5)	C6—C5—C10—O4	−180.0 (2)
C4—C5—C8—O1	−171.8 (3)		

The ring, vinyl, isopropyl and methyl H atoms were added at calculated positions. The H atoms treated with a riding model with *SHELXL*93 (Sheldrick, 1993) defaults (C—H 0.93–0.98 Å) were not refined. An isotropic displacement parameter of 0.075 Å^2 was assigned to all H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP-VAX* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SDP-VAX*.

The authors want to acknowledge Universidad del Valle and COLCIENCIAS (Colombia) for partial financial support. The authors also thank Brazilian agencies FAPESP and FINEP.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1141). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 632–633

FF-β-D-Arabinofuranosyluracil

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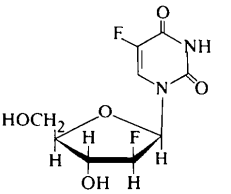
(*Received 28 September 1998; accepted 23 November 1998*)

Abstract

In the title compound, 1-(2-deoxy-2-fluoro-β-D-arabinofuranosyl)-5-fluoropyrimidine-2,4(1*H*,3*H*)-dione, $C_9H_{10}F_2N_2O_5$, the furanosyl ring adopts the twisted conformation (*T*) with O1′ *endo* and C1′ *exo*. The crystal structure is characterized by a three-dimensional hydrogen-bond network involving the three H atoms bonded to heteroatoms.

Comment

FF-β-D-Arabinofuranosyluracil (FFaraU) was synthesized for possible use in positron-emission-tomography (PET) imaging of *Herpes-simplex*-virus-transformed cells and tumors. Expression of the *Herpes simplex* thymidine kinase gene in tumors, after transfection with a gene therapy retroviral vector, could be monitored through the use of positron-emitting ^{18}F-labeled nucleosides which are incorporated preferentially into the target cells. The antiviral properties of FFaraU suggest it is 5′-monophosphorylated by the viral kinase; the phosphorylated compound is known to bind to thymidylate synthetase (Coderre *et al.*, 1983), and it is not phosphorylated by host-cell thymidine kinase, indicating its suitability for these studies. We undertook the structure elucidation of FFaraU in conjunction with biological testing of a series of fluorinated nucleosides (Shields *et al.*, 1996) in order to correlate structural characteristics with cellular activity.



FFaraU

The molecular structure is presented in Fig. 1. The molecule can be described as having an *anti* orientation of the base with respect to the sugar ring; the χ torsion angle O1′—C1′—N1—C6 is 21.4 (3)° (the ring oxygen O1′ is often designated O4′ by organic chemists). The sugar moiety adopts a twisted conformation (*T*) with O1′ *endo* and C1′ *exo*. The deviations of the two atoms from the best plane containing the remaining sugar ring atoms are: 0.56 (1) and 0.54 (1) Å for O1′ and C1′, respectively. Puckering parameters for the sugar moiety are: $Q(2)$ = 0.388 (3) Å and $\varphi(2)$ = 12.1 (4)° (Cremer & Pople, 1975). Pseudorotation parameters are: P = 101.6 (2) and $\tau(M)$ = 43.2 (1)° for reference bond C2′—C3′ (Rao *et al.*, 1981). The sugar pucker differs from that observed in 5-nitro-1-β-D-arabinofuranosyluracil (Biswas *et al.*, 1988) and uracil-β-D-arabinofuranoside (Tollin *et al.*, 1973), where the puckering is C2′-*endo*, and 1-β-D-arabinofuranosyl-4-thiouracil (Saenger, 1972), where the puckering is C3′-*endo*. The 2′-F atom is axial to the ring. The uracil ring is planar and the bond lengths and angles for the whole molecule conform to accepted values with no significant deviations. In the crystal structure, the molecules are held together through hydrogen bonds from the donating heteroatoms (N3, O3′ and O5′ to O3′, O4 and O5′), forming a three-dimensional infinite network.