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Structure of *endo*-(5*R**,6*R**,10*R**,11*S**)-10-(*tert*-Butyldimethylsiloxy)-5,6,10,11-tetrahydro-5-hydroxy-4,11-dimethoxy-7,7,9-trimethyl-6,10-methano-(7*H*)-benzocyclononene-8-carbaldehyde

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Abstract

The seven-membered ring adopts a chair-like conformation with an axial hydroxy group and an equatorial methoxy group; the cyclohexene ring is in a half-chair conformation. There is an intermolecular hydrogen bond between O(2) of the aldehyde group and O(4) of the hydroxy group of the neighboring molecule at $\frac{1}{2}+x$, $-\frac{1}{2}-y$, z [O(2)···O(4) 2.788 (4) Å].

Comment

The structure determination of the title compound was undertaken to confirm the tricarbocyclic skeleton and the conformation of the side chains. An X-ray analysis was required for the determination of the seven-membered ring conformation. The compound was obtained by Lewis-acid-promoted seven-membered ring cyclization reaction between C(9) and C(13). Details of the synthetic work will be published elsewhere (Morihira, Seto, Furukawa, Horiguchi & Kuwajima, 1993).

The seven-membered ring adopts a chair-like conformation (Fig. 1), while NMR spectra of a structurally related compound that we have synthesized suggested a boat-like seven-membered ring. The cyclohexene ring is in a half-chair conformation with a twisted C=C double bond. The largest torsion angle, C(10)—C(11)—C(12)—C(18), is 11.1 (5)°. A search of the January 1992 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed no structure determinations for bicyclo[4.3.1]dec-7-ene fragments.

The arrangement of the molecules in the unit cell is presented in Fig. 2. O(2) of the aldehyde group is hydrogen bonded to O(4) of the hydroxy group in the neighboring molecule at $\frac{1}{2}+x$, $-\frac{1}{2}-y$, z [O(2)···O(4) 2.788 (4) Å].

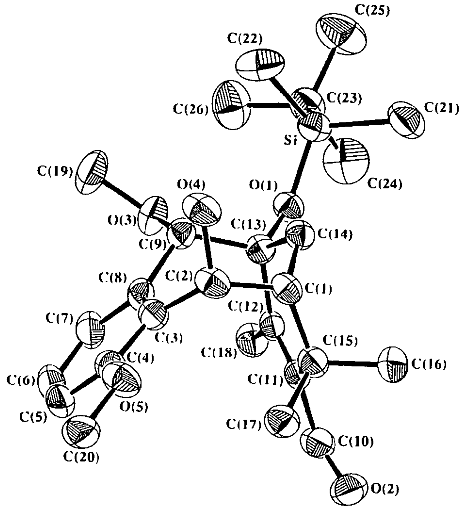

Fig. 1. A perspective view of the molecule (30% probability ellipsoids) with the numbering scheme, excluding H atoms.

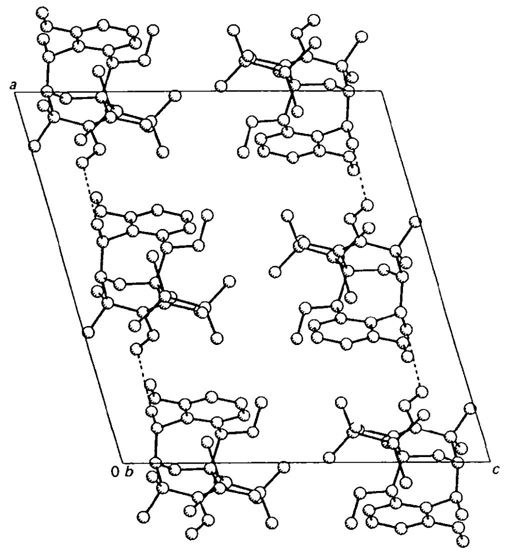

Fig. 2. Crystal structure viewed along the *b* axis. Hydrogen bonds are represented as dashed lines.

Experimental

Crystal data

$C_{26}H_{40}O_5Si$
M_r = 460.69

Cu *Kα* radiation
λ = 1.541840 Å

0108-2701/93/061201-03$06.00

Monoclinic
$P2_1/c$
$a = 16.430$ (4) Å
$b = 10.819$ (1) Å
$c = 15.536$ (4) Å
$\beta = 105.52$ (1)°
$V = 2661$ (2) Å^3
$Z = 4$
$D_x = 1.150$ Mg m^{-3}

Cell parameters from 18 reflections
$\theta = 19$–28°
$\mu = 1.01$ mm^{-1}
$T = 296.15$ K
Plate-like
0.40 × 0.30 × 0.10 mm
Colorless
Crystal source: hexane

Data collection

Rigaku AFC-4 four-circle diffractometer
Profile data from $\theta/2\theta$ scans
Absorption correction: none
4683 measured reflections
4508 independent reflections
3418 observed reflections [$F > 3.0\sigma(F)$]

$\theta_{\max} = 62.5°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 12$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 50 reflections intensity variation: 8.3%

Refinement

Refinement on F
Final $R = 0.064$
$wR = 0.079$
$S = 1.01$
3418 reflections
362 parameters
$w^{-1} = \sigma(F_o)^2 + 0.004F^2$

$(\Delta/\sigma)_{\max} = 0.25$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

H atoms were located geometrically. Non-H atoms refined with anisotropic thermal parameters, and H atoms refined as rigid groups, except for H(O4) which refined freely, with isotropic thermal parameters.

Data collection: AFC-4 software. Cell refinement: AFC-4 software. Data reduction: *PROCESS* in *TEXSAN* program package (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *DIRDIF* in *TEXSAN* program package. Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976).

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

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si	0.05050 (6)	0.22594 (9)	0.75124 (6)	0.0658
O(1)	0.05323 (13)	0.0756 (2)	0.73645 (14)	0.0587
O(2)	0.19068 (16)	−0.3913 (3)	0.8709 (2)	0.0880
O(3)	−0.08302 (14)	−0.0046 (3)	0.62172 (15)	0.0778
O(4)	−0.14193 (17)	−0.0509 (2)	0.8797 (2)	0.0833
O(5)	−0.17705 (17)	−0.3857 (2)	0.8605 (2)	0.0874
C(1)	−0.0012 (2)	−0.1247 (3)	0.9107 (2)	0.0592
C(2)	−0.0950 (2)	−0.1623 (3)	0.8787 (2)	0.0658
C(3)	−0.12279 (19)	−0.2277 (3)	0.7888 (2)	0.0617
C(4)	−0.1606 (2)	−0.3445 (3)	0.7835 (3)	0.0684
C(5)	−0.1796 (2)	−0.4118 (4)	0.7051 (3)	0.0780
C(6)	−0.1622 (2)	−0.3627 (4)	0.6307 (3)	0.0834
C(7)	−0.1296 (2)	−0.2444 (4)	0.6324 (3)	0.0757
C(8)	−0.11065 (18)	−0.1758 (3)	0.7108 (2)	0.0614
C(9)	−0.07775 (19)	−0.0440 (3)	0.7096 (2)	0.0607
C(10)	0.1546 (2)	−0.3172 (3)	0.8140 (3)	0.0718
C(11)	0.09216 (18)	−0.2248 (3)	0.8235 (2)	0.0558
C(12)	0.06828 (17)	−0.1403 (3)	0.7578 (2)	0.0519
C(13)	0.01527 (18)	−0.0281 (3)	0.7673 (2)	0.0547
C(14)	0.0182 (2)	−0.0089 (3)	0.8649 (2)	0.0573
C(15)	0.0668 (2)	−0.2238 (3)	0.9119 (2)	0.0624
C(16)	0.1455 (3)	−0.1931 (4)	0.9883 (3)	0.0807
C(17)	0.0366 (3)	−0.3540 (3)	0.9317 (3)	0.0760
C(18)	0.0890 (2)	−0.1468 (4)	0.6682 (2)	0.0687
C(19)	−0.1648 (3)	0.0373 (6)	0.5740 (4)	0.1076
C(20)	−0.2135 (3)	−0.5036 (4)	0.8615 (4)	0.0926
C(21)	0.1290 (3)	0.2718 (4)	0.8568 (3)	0.0946
C(22)	−0.0557 (3)	0.2825 (5)	0.7541 (4)	0.1062
C(23)	0.0807 (3)	0.2916 (4)	0.6518 (3)	0.0799
C(24)	0.1633 (4)	0.2336 (6)	0.6436 (4)	0.1168
C(25)	0.0944 (6)	0.4321 (5)	0.6632 (5)	0.1293
C(26)	0.0125 (4)	0.2631 (7)	0.5661 (3)	0.1156

Table 2. *Geometric parameters* (Å, °)

Si—O(1)	1.645 (2)	C(4)—C(5)	1.381 (6)
Si—C(21)	1.862 (4)	C(5)—C(6)	1.371 (7)
Si—C(22)	1.860 (6)	C(6)—C(7)	1.385 (6)
Si—C(23)	1.884 (5)	C(7)—C(8)	1.389 (5)
O(1)—C(13)	1.427 (4)	C(8)—C(9)	1.527 (5)
O(2)—C(10)	1.223 (5)	C(9)—C(13)	1.561 (4)
O(3)—C(9)	1.410 (4)	C(10)—C(11)	1.467 (5)
O(3)—C(19)	1.423 (5)	C(11)—C(12)	1.349 (4)
O(4)—C(2)	1.433 (4)	C(11)—C(15)	1.537 (5)
O(4)—H(O4)	0.90 (5)	C(12)—C(13)	1.524 (4)
O(5)—C(4)	1.369 (5)	C(12)—C(18)	1.522 (5)
O(5)—C(20)	1.411 (5)	C(13)—C(14)	1.519 (5)
C(1)—C(2)	1.542 (5)	C(15)—C(16)	1.539 (5)
C(1)—C(14)	1.516 (5)	C(15)—C(17)	1.551 (5)
C(1)—C(15)	1.545 (5)	C(23)—C(24)	1.531 (8)
C(2)—C(3)	1.523 (5)	C(23)—C(25)	1.540 (7)
C(3)—C(4)	1.400 (5)	C(23)—C(26)	1.524 (6)
C(3)—C(8)	1.398 (5)		
O(1)—Si—C(21)	110.36 (16)	O(3)—C(9)—C(13)	108.6 (3)
O(1)—Si—C(22)	112.90 (18)	C(8)—C(9)—C(13)	113.0 (2)
O(1)—Si—C(23)	103.60 (16)	O(2)—C(10)—C(11)	126.2 (4)
C(21)—Si—C(22)	108.9 (3)	C(10)—C(11)—C(12)	117.0 (3)
C(21)—Si—C(23)	110.5 (2)	C(10)—C(11)—C(15)	117.3 (3)
C(22)—Si—C(23)	110.5 (2)	C(12)—C(11)—C(15)	125.3 (3)
Si—O(1)—C(13)	134.4 (2)	C(11)—C(12)—C(13)	121.6 (3)
C(9)—O(3)—C(19)	113.9 (3)	C(11)—C(12)—C(18)	124.8 (3)
C(2)—O(4)—H(O4)	107. (3)	C(13)—C(12)—C(18)	113.5 (3)
C(4)—O(5)—C(20)	119.2 (4)	O(1)—C(13)—C(9)	110.0 (2)
C(2)—C(1)—C(14)	112.5 (2)	O(1)—C(13)—C(12)	106.3 (3)
C(2)—C(1)—C(15)	118.5 (3)	O(1)—C(13)—C(14)	109.1 (2)
C(14)—C(1)—C(15)	109.7 (3)	C(9)—C(13)—C(12)	110.7 (2)
O(4)—C(2)—C(1)	105.6 (3)	C(9)—C(13)—C(14)	110.7 (3)
O(4)—C(2)—C(3)	111.7 (3)	C(12)—C(13)—C(14)	109.8 (2)
C(1)—C(2)—C(3)	116.6 (3)	C(1)—C(14)—C(13)	113.7 (3)
C(2)—C(3)—C(4)	119.5 (3)	C(1)—C(15)—C(11)	111.2 (3)
C(2)—C(3)—C(8)	122.1 (3)	C(1)—C(15)—C(16)	108.3 (3)
C(4)—C(3)—C(8)	118.4 (3)	C(1)—C(15)—C(17)	111.3 (3)
O(5)—C(4)—C(3)	115.5 (3)	C(11)—C(15)—C(16)	108.5 (3)
O(5)—C(4)—C(5)	123.2 (3)	C(11)—C(15)—C(17)	110.4 (3)
C(3)—C(4)—C(5)	121.3 (4)	C(16)—C(15)—C(17)	106.9 (3)
C(4)—C(5)—C(6)	119.4 (4)	Si—C(23)—C(24)	110.3 (3)
C(5)—C(6)—C(7)	120.6 (4)	Si—C(23)—C(25)	109.8 (4)
C(6)—C(7)—C(8)	120.4 (4)	Si—C(23)—C(26)	110.3 (4)
C(3)—C(8)—C(7)	119.7 (3)	C(24)—C(23)—C(25)	108.0 (5)
C(3)—C(8)—C(9)	121.3 (3)	C(24)—C(23)—C(26)	107.8 (4)
C(7)—C(8)—C(9)	119.0 (3)	C(25)—C(23)—C(26)	110.6 (4)
O(3)—C(9)—C(8)	111.3 (3)		

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55971 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1027]

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Structure of a Triazaoxabicyclodecatriene Derivative

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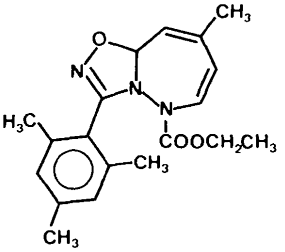
Abstract

The structure of ethyl 5-methyl-10-(2,4,6-trimethylphenyl)-8-oxa-1,2,9-triazabicyclo[5.3.0]deca-3,5,9-triene-2-carboxylate (I) has been determined. The 1,2-diazepine ring has a twisted-sofa form and the 1,2,4-oxadiazole ring has an envelope conformation, with the bridgehead C7 atom out of the plane of the ring. The terminal methyl group of the side chain is disordered, being split over two different positions.

Comment

Compound (I) has been obtained as the main adduct, along with two minor products, from the cycloaddition reaction between 2,4,6-trimethylphenylnitrile oxide and ethyl 5-methyl-1,2-diazepine-1-carboxylate (Beltrame, Cadoni, Carnasciali, Gelli, Lai, Mugnoli & Pani, 1992). The crystal structure determination of (I) has been performed to confirm the C=N diazepine bond as the preferred reaction site (in the competition between one C=N and two C=C bonds) and to define the regioselectivity of the cycloaddition reaction.



Apart from the disordered end of the ethoxycarbonyl chain, the bond lengths are in good agreement with the average literature values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987); the only significant differences concern the observed bond distances N2—C3 [1.409 (6) Å] and N9=C10 [1.267 (6) Å]. However, these values compare well with the corresponding bond distances found in a 1,2-diazepine derivative similar to (I) [1.408 (3) Å; Allmann & Debaerdemaeker (1974)] and in recent structure determinations of 1,2,4-oxadiazoles retrieved from the Cambridge Structural Database, version 4.6 [1.280 (9) Å, sample e.s.d.; Allen, Kennard & Taylor (1983)]. In the disordered part of the molecule the bond lengths O13—C14, and C14—C15 and C14—C15′ refine to long and short distances, respectively, while the bond angles O13—C14—C15 and O13—C14—C15′ have fairly normal values. The puckering parameters (Cremer & Pople, 1975) calculated for the seven- and five-membered rings [q_2 = 0.415 (4), q_3 = 0.285 (4) Å, φ_2 = −149.0 (6), φ_3 = −175 (1)°; q_2 = 0.269 (4) Å, φ_2 = 35.7 (9)°, respectively] correspond to an approximate twisted sofa (Boessenkool & Boeyens, 1980) and an envelope conformation, respectively. In the oxadiazole ring, the N1, O8, N9 and C10 atoms are coplanar within 0.005 (4) Å, with a deviation of 0.429 (5) Å for the C7 atom. Intermolecular distances are in the normal range. There is just one contact appreciably shorter than the sum of the van der Waals radii (Pauling, 1960): C14···C15($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$) 3.64 (2) Å.

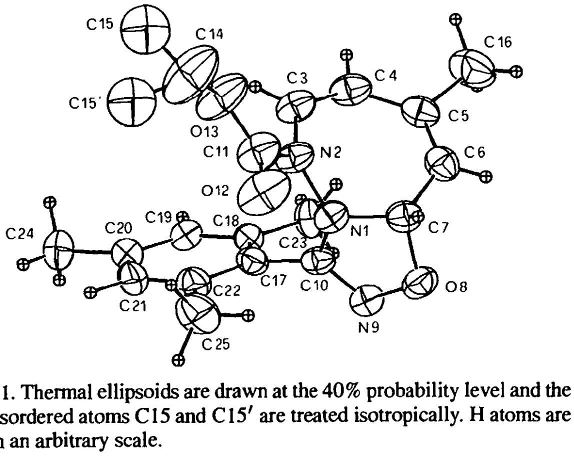


Fig. 1. Thermal ellipsoids are drawn at the 40% probability level and the disordered atoms C15 and C15′ are treated isotropically. H atoms are on an arbitrary scale.

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