

Fig. 1. Mean molecular dimensions (Å and deg) ($\sigma = 0.01\text{--}0.02$ Å and $0.6\text{--}1.1^\circ$); $C(2)\text{--}C(3)\text{--}C(9) = 112^\circ$, $C(4)\text{--}C(3)\text{--}C(10) = 109^\circ$.

Discussion. The geometry and dimensions* of the norbornane skeleton (Fig. 1) are generally normal; the one significant distortion (observed in both molecules) is an increase in the exocyclic angles at C(3), C(4), and C(5), to $114\text{--}116^\circ$, presumably as a result of steric repulsion between O(5) and C(9) (distance 2.94 Å).

Molecules are linked in the crystal by a double helical system of hydrogen bonds (Fig. 2).

We thank Dr T. Money for crystals, the Natural Sciences and Engineering Council Canada for financial support, and the University of British Columbia Computing Centre for assistance.

* See previous footnote.

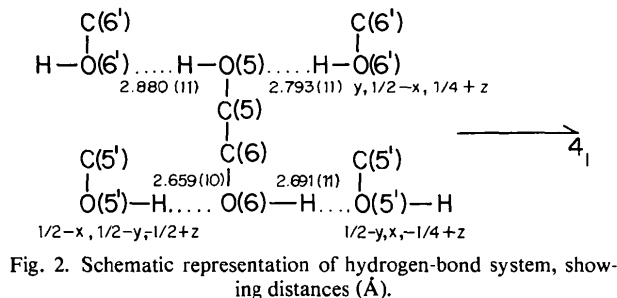
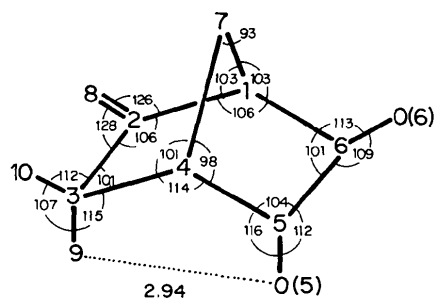


Fig. 2. Schematic representation of hydrogen-bond system, showing distances (Å).

Reference

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Acta Cryst. (1979). B35, 3111–3113

Decahydro-5-methylene-2-oxo-6 β -trimethylsiloxy-[3 α ,6 α ,8 $\alpha\beta$]-3 α ,6-methano-3 α -azulenecarboxylic Acid Methyl Ester

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(Received 2 July 1979; accepted 6 September 1979)

Abstract. $C_{17}H_{26}O_4Si$, monoclinic, $C2/c$, $a = 35.663$ (13), $b = 6.608$ (4), $c = 15.165$ (5) Å, $\beta = 94.44$ (3) $^\circ$, $M_r = 322.48$, $U = 3563.1$ Å 3 , $Z = 8$, $D_m = 1.205$ (floatation, aqueous KI), $D_c = 1.202$ Mg m $^{-3}$, $F(000) = 1392$; Mo $K\alpha$ radiation ($\lambda_{m1} = 0.70926$ Å, $\mu = 0.108$ mm $^{-1}$). The structure was solved by direct methods and refined by full-matrix least squares to $R = 0.063$ using 1614 diffractometer reflexions. The position of the methoxycarbonyl group on the azulene precursor has been established as 3 α .

Introduction. The title compound (Fig. 1) was prepared as an intermediate during studies toward the synthesis

of gibberellic acid (Stork, Still & Singh, 1979). The structure determination was undertaken to establish the position of the methoxycarbonyl group on the azulene precursor. The four possibilities were 1 α , 1 β , 3 α , or 3 β .

The quality of the crystal used for data collection (approximate dimensions $0.2 \times 0.6 \times 0.3$ mm) was examined on the diffractometer, by taking ω scans of several strong low-angle reflexions, and judged to be acceptable. The average width of the peaks at half height was 0.23° . Intensity data, in the range $3 \leq 2\theta \leq 55^\circ$, were collected at 301 K employing the ω - 2θ scan technique on an Enraf-Nonius CAD-4F κ -geometry

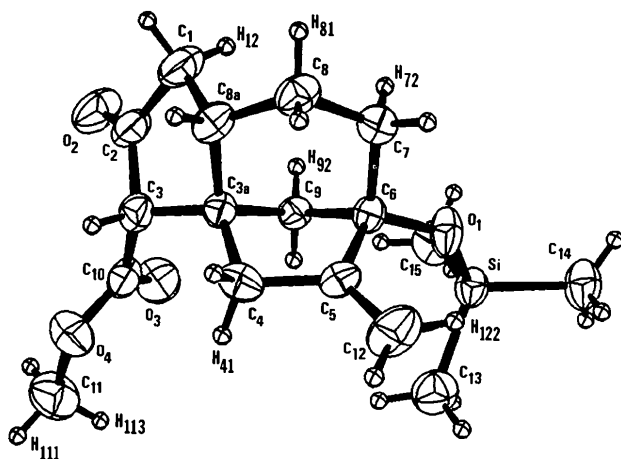


Fig. 1. ORTEP II diagram of the title compound showing the atom-numbering scheme. For atoms C(1) to C(8a) this is the *Chemical Abstracts* numbering scheme. H atoms are labelled such that H(*i*,*j*) is the *j*th H on C(*i*). The 40% probability thermal ellipsoids are depicted.

diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Scan rates varied from 5 to 20° min⁻¹ in ω and scan ranges were calculated according to $\Delta\omega = (0.9 + 0.35 \tan \theta)^\circ$. Three standard reflexions, 113, 204, and 18,4,0, measured after each 3600 s of X-ray exposure time (approximately after each 170 reflexions), were used to scale the data for a 7% isotropic decay during the course of the data collection. 4242 unique reflexions ($\pm h, +k, +l$) were scanned, the 1614 having $F_o > 4\sigma(F_o)$ being used in the structure solution and refinement. Unit-cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflexions with $2\theta > 30^\circ$. Data were corrected for Lorentz and polarization effects but not for absorption since the maximum and minimum transmission factors were 0.980 and 0.965 respectively.

Systematic absences were $hkl, h + k \neq 2n$ and $h0l, l \neq 2n$, determining the space group as $C2/c$ or Cc ; the former was assumed, since the compound was a racemic mixture, and this choice was vindicated by the successful solution and refinement of the structure. A sharpened Patterson map failed to reveal, uniquely, the position of the Si atom and the structure was solved using *MULTAN* 76 (Main, Lessinger, Woolfson, Germain & Declercq, 1976). The E map with the highest combined figure of merit, based on 170 reflexions having $|E| > 2.10$ and using 2500 unique phase relationships, revealed the positions of 11 of the 22 non-H atoms. Earlier attempts to solve the structure using the 500 largest E values, with 4000 phase relationships, proved fruitless. Further calculations were performed with *SHELX* (Sheldrick, 1978). At this stage R was 0.47. Two subsequent difference-Fourier maps revealed the remaining non-H atom positions and refinement with isotropic temperature factors gave $R =$

0.15. At this stage most of the H atoms could be located from difference maps; however, for simplicity they were treated as follows. Methyl groups were set up and refined as rigid groups (C–H 0.95 Å, H–C–H 109.5°) as were the two H atoms on C(12) (C–H 0.95 Å, H–C–H 120°). All these H atoms were assigned a common isotropic temperature factor which refined to $U = 0.111(7) \text{ \AA}^2$. The remaining H atoms were placed in calculated positions and refined subject to the constraint that the C–H vectors were constant in magnitude (C–H 0.95 Å) and direction but not position (*i.e.* a riding model). A common isotropic temperature factor for these H atoms converged at $U = 0.061(4) \text{ \AA}^2$.

In the final stages of refinement, with all non-H atoms refining anisotropically, the weighting scheme $w = [\sigma^2(F_o) + 0.0018F_o^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with data sectioned both with respect to $|F_o|$ and $(\sin \theta)/\lambda$. At convergence, no parameter shift was > 0.007 of its estimated standard deviation and a final difference-Fourier map showed no peaks with electron density $> 0.32 \text{ e \AA}^{-3}$. The final R was 0.063 and $R' = \{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\} 0.082$. The $|F_o| - |F_c|$ values for strong low-order reflexions were randomly positive and negative and no corrections for secondary extinction were therefore applied. Complex neutral-atom scattering factors for the non-H atoms were those of Cromer & Mann (1968). Scattering factors for neutral H atoms were taken from Stewart, Davidson & Simpson (1965). Final atomic coordinates are given in Table 1, bond lengths and angles in Table

Table 1. Non-hydrogen atom coordinates ($\times 10^5$ for Si, $\times 10^4$ for O and C) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Si	55672 (4)	77650 (20)	39349 (9)
O(1)	5690 (1)	7979 (6)	2921 (2)
O(2)	7472 (1)	9156 (8)	3237 (3)
O(3)	6950 (1)	11192 (7)	4534 (3)
O(4)	7023 (1)	14220 (7)	3911 (3)
C(1)	7010 (2)	8541 (11)	2004 (4)
C(2)	7188 (2)	9626 (10)	2806 (4)
C(3)	6945 (1)	11438 (8)	2957 (3)
C(3a)	6557 (1)	10787 (7)	2550 (3)
C(4)	6256 (1)	12399 (8)	2371 (4)
C(5)	5890 (1)	11219 (8)	2308 (3)
C(6)	5982 (1)	9037 (8)	2532 (3)
C(7)	6061 (1)	7833 (8)	1709 (3)
C(8)	6339 (1)	8879 (9)	1152 (3)
C(8a)	6670 (1)	9831 (9)	1689 (3)
C(9)	6354 (1)	9250 (8)	3101 (3)
C(10)	6972 (1)	12241 (10)	3886 (4)
C(11)	7069 (2)	15166 (12)	4769 (4)
C(12)	5552 (2)	11951 (12)	2101 (5)
C(13)	5505 (2)	10264 (10)	4450 (4)
C(14)	5117 (2)	6386 (10)	3807 (4)
C(15)	5916 (2)	6260 (10)	4630 (4)

Table 2. *Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses*

Si—O(1)	1.637 (4)	C(3a)—C(4)	1.522 (7)
Si—C(13)	1.848 (7)	C(3a)—C(8a)	1.531 (7)
Si—C(14)	1.842 (6)	C(3a)—C(9)	1.534 (7)
Si—C(15)	1.855 (6)	C(4)—C(5)	1.518 (7)
O(1)—C(6)	1.419 (6)	C(5)—C(6)	1.512 (7)
O(2)—C(2)	1.201 (7)	C(5)—C(12)	1.312 (8)
O(3)—C(10)	1.210 (7)	C(6)—C(7)	1.525 (7)
O(4)—C(10)	1.321 (8)	C(6)—C(9)	1.531 (6)
O(4)—C(11)	1.442 (8)	C(7)—C(8)	1.517 (7)
C(1)—C(2)	1.508 (8)	C(8)—C(8a)	1.518 (7)
C(1)—C(8a)	1.529 (8)	O(2)···C(11 ^h)	3.357 (8)
C(2)—C(3)	1.507 (8)	O(2)···C(31 ^h)	3.378 (7)
C(3)—C(3a)	1.532 (6)	O(2)···H(31 ^h)	2.557 (6)
C(3)—C(10)	1.502 (7)	O(3)···H(112 ^h)	2.772 (8)
O(1)—Si—C(13)	111.7 (3)	C(8a)—C(3a)—C(9)	111.0 (4)
O(1)—Si—C(14)	103.8 (2)	C(3a)—C(4)—C(5)	104.1 (4)
O(1)—Si—C(15)	111.3 (2)	C(4)—C(5)—C(6)	107.7 (4)
C(13)—Si—C(14)	110.7 (3)	C(4)—C(5)—C(12)	126.5 (5)
C(13)—Si—C(15)	109.7 (3)	C(6)—C(5)—C(12)	125.8 (5)
C(14)—Si—C(15)	109.6 (3)	O(1)—C(6)—C(5)	114.2 (4)
Si—O(1)—C(6)	133.8 (3)	O(1)—C(6)—C(7)	105.8 (4)
C(10)—O(4)—C(11)	117.4 (5)	O(1)—C(6)—C(9)	116.2 (4)
C(2)—C(1)—C(8a)	105.1 (5)	C(5)—C(6)—C(7)	111.4 (4)
O(2)—C(2)—C(1)	126.9 (6)	C(5)—C(6)—C(9)	101.7 (4)
O(2)—C(2)—C(3)	126.3 (5)	C(7)—C(6)—C(9)	107.5 (4)
C(1)—C(2)—C(3)	106.8 (4)	C(6)—C(7)—C(8)	112.9 (4)
C(2)—C(3)—C(3a)	103.1 (4)	C(7)—C(8)—C(8a)	113.8 (4)
C(2)—C(3)—C(10)	115.3 (4)	C(1)—C(8a)—C(3a)	102.6 (4)
C(3a)—C(3)—C(10)	117.9 (4)	C(1)—C(8a)—C(8)	120.1 (5)
C(3)—C(3a)—C(4)	118.5 (4)	C(3a)—C(8a)—C(8)	112.6 (4)
C(3)—C(3a)—C(8a)	99.9 (4)	C(3a)—C(9)—C(6)	100.4 (3)
C(3)—C(3a)—C(9)	114.7 (4)	O(3)—C(10)—O(4)	124.2 (5)
C(4)—C(3a)—C(8a)	111.4 (4)	O(3)—C(10)—C(3)	123.8 (6)
C(4)—C(3a)—C(9)	101.7 (4)	O(4)—C(10)—C(3)	112.0 (5)

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

2, and selected torsion angles in Table 3.* An *ORTEP* II (Johnson, 1976) diagram of the molecule is given in Fig. 1.

Discussion. The methoxycarbonyl group has been shown to be at position 3 α of the title compound.

* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34745 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected torsion angles (°) with estimated standard deviations in parentheses*

C(1)—C(2)—C(3)—C(3a)	-26.4 (5)	C(3a)—C(9)—C(6)—C(7)	-72.6 (4)
C(1)—C(8a)—C(3a)—C(3)	-45.3 (5)	C(4)—C(3a)—C(9)—C(6)	-48.3 (4)
C(2)—C(1)—C(8a)—C(3a)	29.7 (6)	C(4)—C(5)—C(6)—C(9)	-24.6 (5)
C(2)—C(3)—C(3a)—C(8a)	44.1 (5)	C(5)—C(4)—C(3a)—C(9)	32.9 (5)
C(3)—C(2)—C(1)—C(8a)	-2.1 (6)	C(6)—C(7)—C(8)—C(8a)	-42.0 (6)
C(3a)—C(4)—C(5)—C(6)	-5.2 (5)	C(6)—C(9)—C(3a)—C(8a)	70.3 (4)
C(3a)—C(8a)—C(8)—C(7)	37.8 (6)	C(8)—C(7)—C(6)—C(9)	61.5 (5)
C(3a)—C(9)—C(6)—C(5)	44.5 (4)	C(8)—C(8a)—C(3a)—C(9)	-54.5 (5)

Distances within the trimethylsilyl ether group agree with those previously determined by Weeks, Hauptman & Norton (1972) who obtained Si—O, 1.623 (7) Å and Si—C(av.), 1.87 (1) Å. The closest intermolecular non-H atom contact of the structure is O(2)···C(11^h), 3.357 (8) Å. The shortest intermolecular O···H distances [O(2)···H(31^h), 2.557 (6) Å and O(3)···H(112^h), 2.772 (8) Å] are too long to be considered hydrogen-bonding interactions (Hamilton & Ibers, 1968). The packing of the molecules is thus determined by van der Waals forces. There are no intramolecular hydrogen bonds.

I wish to thank Professor S. J. Lippard for the use of his X-ray diffraction facilities.

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