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(1R*,1'R*,2S*,2'S*,3R*,3'R*,5R*,5'R*,6S*,6'S*)-3-Hydroxy-3'-trimethylsilyloxy[3,3'-bitricyclo[4.2.1.0^{2,5}]non-7-enyl]-4,4'-dione, C₂₁H₂₆O₄Si

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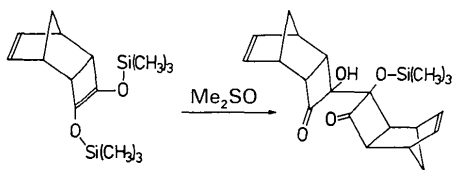
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Abstract. $M_r = 370.52$, triclinic, $P\bar{1}$, $Z = 2$, $a = 9.041$ (2), $b = 10.505$ (5), $c = 11.546$ (3) Å, $\alpha = 76.59$ (3), $\beta = 76.09$ (2), $\gamma = 67.54$ (3)°, $V = 971.5$ (5) Å³, $D_x = 1.266$ Mg m⁻³, $F(000) = 396$, Mo K α radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu = 0.137$ mm⁻¹, room temperature, 3124 non-equivalent diffractometer data up to $\sin\theta/\lambda = 0.58$ Å⁻¹, final $R(F) = 0.045$, $R_w(F) = 0.054$. The molecule consists of two *endo*-tricyclo[4.2.1.0^{2,5}]non-7-ene groups linked by a single C–C bond of 1.557 (2) Å. The norbornene groups show a bridging C–C–C angle of 93.6 (2)°. The molecules form dimers linked by hydrogen bonding.

Introduction. The title compound was obtained by an oxidative dimerization of *endo*-3,4-bis(trimethylsilyloxy)tricyclo[4.2.1.0^{2,5}]nona-3,7-diene with Me₂SO in acetic anhydride, accompanied by a partial hydrolysis (Bellinger, 1983). As a chemical analysis was not conclusive concerning the nature of the reaction product, an X-ray structure analysis was undertaken.

Experimental. Colorless crystals, recrystallization from diethyl ether. Crystal: 0.3 × 0.3 × 0.5 mm. Enraf–Nonius CAD-4 diffractometer. Cell constants from setting angles of 25 reflections with $6 < \theta \leq 12^\circ$. One hemisphere up to $2\theta = 49^\circ$, ω scan. Three standard reflections every 4000 s remained stable. 3846 reflections measured, 3281 unique, 3124 with $I > 0.4\sigma(I)$ used. No absorption correction. Weighting scheme: $w(I) = 1/[\sigma^2(I) + (0.03I)^2]$. Structure determination by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms from difference synthesis, H atoms included in refinement with fixed isotropic thermal parameters. Scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Extinction negligible. Calculations with SDP program system (Enraf–Nonius, 1981). Refinement on F . $(\Delta/\sigma)_{\max} = 0.2$. Final difference synthesis featureless. $R(F) = 0.045$, $R_w(F) = 0.054$, $S = 2.31$.

Discussion. The positional parameters are reported in Table 1.* Fig. 1 shows the bond distances and the numbering scheme of the atoms. The bond angles are



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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38910 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

reported in Table 2; a stereoscopic view of the molecule is shown in Fig. 2. The molecule contains two *endo*-tricyclo[4.2.1.0^{2,5}]non-7-ene groups linked by the C(8)–C(10) bond. The corresponding bond distances and angles in the two groups are very similar.

The geometry of the norbornene groups is in good agreement with other norbornene derivatives (Destro, Filippini, Gramaccioli & Simonetta, 1969; Filippini, Gramaccioli, Rovere & Simonetta, 1972). They show the characteristic value of 93.6 (2)° for the C–C–C angle around the bridging methyl group. The bond angles in the four-membered ring range from 86.8 (1) to 93.2 (1)° giving a small deviation from a rectangle. The ring is slightly puckered. The distortion of the four-membered rings is extended to the norbornene groups: the C(1)–C(5)–C(6) angle of 107.2 (1)° is

Table 1. *Positional parameters and equivalent isotropic temperature parameters*

$$B_{eq} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Si	0.92743 (5)	0.38540 (5)	0.27057 (5)	3.62 (1)
O(1)	0.6483 (1)	0.5489 (1)	0.1130 (1)	3.25 (3)
O(2)	0.3152 (1)	0.5207 (1)	0.1151 (1)	3.83 (3)
O(3)	0.4415 (1)	0.2974 (1)	0.4558 (1)	3.88 (3)
O(4)	0.7591 (1)	0.3462 (1)	0.3202 (1)	3.09 (2)
C(1)	0.2558 (2)	0.8234 (2)	0.1589 (2)	4.47 (5)
C(2)	0.4044 (2)	0.8183 (2)	0.1564 (2)	4.40 (5)
C(3)	0.4454 (2)	0.7592 (2)	0.2816 (2)	3.61 (4)
C(4)	0.2761 (2)	0.8163 (2)	0.3579 (2)	4.22 (4)
C(5)	0.1928 (2)	0.7660 (2)	0.2846 (2)	3.83 (4)
C(6)	0.2930 (2)	0.6068 (2)	0.3060 (1)	3.07 (4)
C(7)	0.4667 (2)	0.6021 (1)	0.3110 (1)	2.79 (3)
C(8)	0.5442 (2)	0.5062 (1)	0.2119 (1)	2.64 (3)
C(9)	0.3691 (2)	0.5355 (1)	0.1947 (1)	2.81 (3)
C(10)	0.6316 (2)	0.3532 (1)	0.2682 (1)	2.64 (3)
C(11)	0.5080 (2)	0.2897 (2)	0.3534 (1)	2.95 (3)
C(12)	0.5125 (2)	0.2069 (2)	0.2600 (2)	3.40 (4)
C(13)	0.6589 (2)	0.2482 (2)	0.1825 (1)	3.10 (4)
C(14)	0.7998 (2)	0.1042 (2)	0.1888 (2)	4.16 (5)
C(15)	0.7073 (3)	0.0127 (2)	0.1755 (2)	4.98 (5)
C(16)	0.5851 (2)	0.0451 (2)	0.2916 (2)	4.63 (5)
C(17)	0.6993 (3)	0.0127 (2)	0.3784 (2)	4.96 (5)
C(18)	0.8248 (3)	0.0493 (2)	0.3185 (2)	4.85 (5)
C(19)	0.8871 (2)	0.5729 (2)	0.2621 (2)	5.25 (5)
C(20)	1.0362 (2)	0.3257 (2)	0.1250 (2)	5.18 (5)
C(21)	1.0504 (2)	0.2866 (3)	0.3903 (2)	5.90 (6)
H(O)	0.641 (2)	0.530 (2)	0.050 (2)	4.0†
H(1)	0.195 (2)	0.847 (2)	0.098 (2)	5.5
H(2)	0.477 (2)	0.840 (2)	0.088 (2)	5.5
H(3)	0.531 (2)	0.775 (2)	0.301 (2)	4.5
H(4)	0.239 (2)	0.919 (2)	0.348 (2)	5.5
H(5)	0.268 (2)	0.776 (2)	0.445 (2)	5.5
H(6)	0.083 (2)	0.785 (2)	0.307 (2)	4.5
H(7)	0.244 (2)	0.556 (2)	0.376 (2)	4.5
H(8)	0.507 (2)	0.559 (2)	0.387 (1)	4.0
H(9)	0.419 (2)	0.238 (2)	0.223 (2)	4.5
H(10)	0.648 (2)	0.296 (2)	0.099 (2)	4.5
H(11)	0.891 (2)	0.105 (2)	0.129 (2)	5.5
H(12)	0.773 (3)	−0.084 (2)	0.182 (2)	6.0
H(13)	0.658 (2)	0.045 (2)	0.108 (2)	6.0
H(14)	0.507 (2)	0.003 (2)	0.313 (2)	5.5
H(15)	0.673 (2)	−0.017 (2)	0.464 (2)	6.0
H(16)	0.911 (2)	0.055 (2)	0.349 (2)	5.5
H(17)	0.823 (2)	0.632 (2)	0.205 (2)	6.0
H(18)	0.831 (2)	0.600 (2)	0.348 (2)	6.0
H(19)	0.977 (3)	0.585 (2)	0.250 (2)	6.0
H(20)	1.084 (3)	0.221 (2)	0.138 (2)	6.0
H(21)	0.969 (2)	0.350 (2)	0.067 (2)	6.0
H(22)	1.121 (2)	0.353 (2)	0.100 (2)	6.0
H(23)	0.987 (3)	0.308 (2)	0.470 (2)	6.5
H(24)	1.153 (3)	0.301 (2)	0.378 (2)	6.5
H(25)	1.062 (3)	0.202 (2)	0.401 (2)	6.5

† Not refined.

significantly smaller than the corresponding C(2)–C(3)–C(7) angle of 110.1 (2)°.

The angle C(10)–O(4)–Si of 135.30 (9)° is rather large and possibly a result of a repulsion between the trimethylsilyl group and the hydrocarbon skeleton. Si–O–C angles of 130.5 (3) and 131.9 (3)° have been observed by Cheng & Nyburg (1976) and Cheng, Wong-Ng, Nyburg & Van der Heijden (1976) in ring systems and show that large values are not uncommon.

Table 2. *Bond angles (°); e.s.d.'s in parentheses*

C(5)–C(1)–C(2)	108.1 (2)	C(16)–C(17)–C(18)	107.5 (2)
C(1)–C(2)–C(3)	108.0 (2)	C(17)–C(18)–C(14)	108.1 (2)
C(2)–C(3)–C(4)	100.0 (1)	C(18)–C(14)–C(15)	99.5 (2)
C(2)–C(3)–C(7)	110.1 (2)	C(18)–C(14)–C(13)	109.4 (2)
C(4)–C(3)–C(7)	98.5 (1)	C(15)–C(14)–C(13)	98.8 (2)
C(3)–C(4)–C(5)	93.6 (2)	C(14)–C(15)–C(16)	93.6 (2)
C(1)–C(5)–C(4)	99.9 (2)	C(17)–C(16)–C(15)	100.1 (2)
C(1)–C(5)–C(6)	107.2 (1)	C(17)–C(16)–C(12)	107.2 (2)
C(4)–C(5)–C(6)	98.6 (1)	C(15)–C(16)–C(12)	99.6 (1)
C(5)–C(6)–C(7)	103.7 (2)	C(16)–C(12)–C(13)	103.9 (1)
C(5)–C(6)–C(9)	117.0 (1)	C(16)–C(12)–C(11)	116.4 (2)
C(7)–C(6)–C(9)	87.4 (1)	C(13)–C(12)–C(11)	88.2 (2)
C(3)–C(7)–C(6)	101.5 (1)	C(14)–C(13)–C(12)	101.4 (1)
C(3)–C(7)–C(8)	121.3 (1)	C(14)–C(13)–C(10)	121.1 (1)
C(6)–C(7)–C(8)	91.0 (1)	C(12)–C(13)–C(10)	90.5 (1)
O(1)–C(8)–C(7)	116.4 (1)	O(4)–C(10)–C(13)	120.3 (1)
O(1)–C(8)–C(9)	117.5 (1)	O(4)–C(10)–C(11)	114.9 (1)
O(1)–C(8)–C(10)	109.8 (1)	O(4)–C(10)–C(8)	110.2 (1)
C(7)–C(8)–C(9)	86.8 (1)	C(13)–C(10)–C(11)	87.2 (1)
C(7)–C(8)–C(10)	110.8 (1)	C(13)–C(10)–C(8)	111.5 (1)
C(9)–C(8)–C(10)	113.9 (1)	C(11)–C(10)–C(8)	110.9 (1)
O(2)–C(9)–C(6)	133.8 (1)	O(3)–C(11)–C(12)	133.9 (2)
O(2)–C(9)–C(8)	132.6 (1)	O(3)–C(11)–C(10)	133.5 (2)
C(6)–C(9)–C(8)	93.2 (1)	C(12)–C(11)–C(10)	92.5 (1)
C(8)–O(1)–H(O)	112 (1)	C(10)–O(4)–Si	135.30 (9)
O(4)–Si–C(19)	111.91 (7)	C(19)–Si–C(20)	111.21 (9)
O(4)–Si–C(20)	112.28 (9)	C(19)–Si–C(21)	108.76 (13)
O(4)–Si–C(21)	102.52 (9)	C(20)–Si–C(21)	109.77 (9)

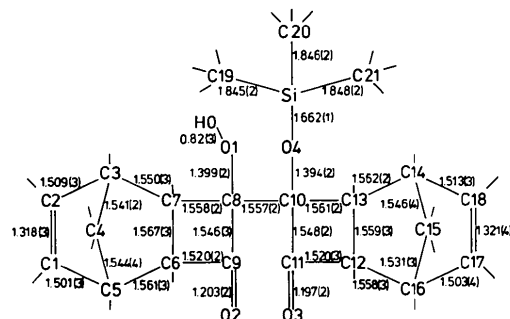


Fig. 1. Bond distances (Å) and numbering scheme of the atoms.

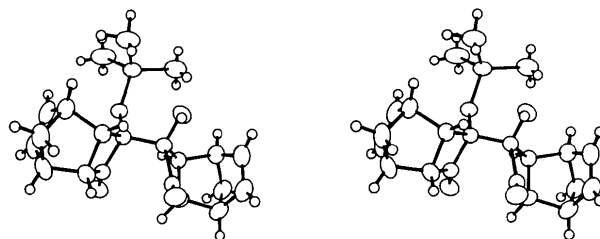


Fig. 2. A stereoscopic view of the molecule. The thermal ellipsoids are the 50% probability surfaces.

The two symmetry-related molecules form a dimer linked by two equivalent O(1)—H(O)···O(2') hydrogen bonds, with characteristic values: H(O)···O(2') 2.00 (3) Å, O(1)···O(2') 2.806 (2) Å, O(1)—H(O)—O(2') 165 (1)°. No other short intermolecular contact distances occur in the structure.

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Structure of 5,2'-Anhydro-5-(*p*-toluenesulfonamido)-1-(3'-*O*-tosyl- β -D-arabinofuranosyl)imidazole-4-carbonitrile, C₂₃H₂₂N₄O₇S₂

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Abstract. $M_r = 530.57$, monoclinic, $P2_1$, $a = 11.099$ (1), $b = 11.015$ (1), $c = 10.114$ (1) Å, $\beta = 92.27$ (2)°, $V = 1235.6$ (3) Å³, $Z = 2$, $D_m = 1.404$ (1), $D_x = 1.426$ Mg m⁻³, Zr-filtered Mo $K\alpha$, $\lambda = 0.70924$ Å, $\mu = 0.267$ mm⁻¹, $F(000) = 552$, $T = 293$ K, final $R = 0.033$ for 2764 reflections. The glycosyl torsion angle $\chi[C(2)-N(1)-C(1')-O(4')]$ is -74.2 (2)° and the furanose ring is in the C(4')-endo-C(3')-exo (⁴T₃) conformation.

Introduction. The present study is one of a series of crystal structure analyses of nucleosides containing the imidazole ring. The title compound is the first nucleoside to be solved as a cyclic nucleoside formed between imidazole and the furanose ring through the N atom. The effect of stereochemical restriction by such a cyclization was investigated by comparison with the previously solved structure of 1-(5'-*O*-acetyl-2',3'-*O*-isopropylidene- β -D-ribofuranosyl)-5-ditosylaminoimidazole-4-carbonitrile (Kitamura, Mizuno, Sugio, Okabe, Ikehara & Tomita, 1983).

Experimental. Colorless prismatic crystals from water-ethanol solution at room temperature; density by flotation. Cell dimensions by least-squares refinement of 2θ values of 19 reflections with $18^\circ \leq 2\theta \leq 34^\circ$. Crystal $0.2 \times 0.2 \times 0.3$ mm. Rigaku–Denki AFC-4 automated diffractometer, Zr-filtered Mo $K\alpha$ radiation, $2\theta_{\max} = 55^\circ$, θ - 2θ scan technique. 3000 independent

reflections, $0 \leq h \leq 14$, $0 \leq k \leq 14$ and $-13 \leq l \leq 13$, 2764 with $|F_o| > 3\sigma(F_o)$. Three standard reflections (500, 040 and 004) monitored after every 61 reflections; <0.9 (6)% intensity fluctuation. Intensities corrected for Lorentz and polarization factors but not for absorption. Direct methods (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Positional and anisotropic thermal parameters for all non-H atoms refined by block-diagonal least squares (*HBLSSV*; Ashida, 1979); $w(|F_o| - k|F_c|)^2$ minimized; $w = [\sigma^2(F_o) + 0.0042|F_o| + 0.0001|F_o|^2]^{-1}$. All H atoms located on a difference Fourier map; their positional parameters included in the refinement with a fixed isotropic thermal parameter of 3.0 Å². Final R and R_w for 2764 reflections 0.033 and 0.043; S for 414 parameters (nine for each non-H atom, four for each H atom and two for overall scale and thermal parameters) = 1.385. In final cycle $(\Delta/\sigma)_{\text{mean}}$ and $(\Delta/\sigma)_{\text{max}}$, 0.020 and 0.083, respectively for non-H atoms. Maximum and minimum heights on final difference Fourier map 0.17 and -0.16 e Å⁻³; no other significant features observed. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. The final atomic coordinates for non-H atoms with their estimated standard deviations are