

Fig. 2. Projection of the crystal structure down *b*.

C(12) and C(14). This interaction is also responsible for the flattening of ring *B* at C(9). Analogously, the widening of angle C(9)–C(8)–C(13) to 114.2 (4)° is a demand of the interaction C(12)···C(13), while the short contact (1.96 Å) between two H atoms at C(1) and C(11) causes the angle C(1)–C(10)–C(9) to widen to 114.4 (3)°.

Otherwise, the widening of the angle C(9)–C(11)–C(16) to 119.1 (4)° is probably due to requirements of the packing of the hydroquinone fragment which, in this way, becomes perpendicular to the mean plane through the sesquiterpene system

[interplanar angles: 91 (1) for molecule 1 and 86 (1)° for molecule 2].

The crystal packing, illustrated in Fig. 2, shows weak van der Waals contacts.

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Structure of *N*-Benzoyl-5'-*O*-*tert*-butyldimethylsilyl-2'-deoxyadenosine Monohydrate

BY S. K. BURLEY

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA and Harvard Medical School (Health and Sciences and Technology Division), 25 Shattuck Street, Boston, MA 02115, USA

AND A. H.-J. WANG

Department of Biology, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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Abstract. C₂₃H₃₁N₅O₄Si.H₂O, *M*_r = 487.6, orthorhombic, *P*2₁2₁2₁, *a* = 18.642 (2), *b* = 8.032 (1), *c* = 16.825 (2) Å, *V* = 2519.3 (1) Å³, *Z* = 4, *D*_x = 1.286 g cm⁻³, λ(Cu *K*α) = 1.5418 Å, μ = 10.85 cm⁻¹, *F*(000) = 1040, *T* = 283 K, *R* = 0.067 for 1664 unique observed reflections. The glycosidic torsion angle, χ = 161.8 (10)°, is in the *anti* conformation. The deoxyribose ring has a C3'-*exo* (C2'-*endo*) pucker and the conformation around the C5'–C4' bond is *gauche*–

gauche. The mean Si–C bond length is 1.861 (6) Å (three evaluations), and the Si–O5' bond length is 1.658 (6) Å. The crystal structure is stabilized by a fully satisfied hydrogen-bond network involving the water of crystallization and by stacking interactions between the phenyl ring and the base. Finally, there are weakly polar C–H···O interactions between C8 and O5' and between the δ(+) edge of the phenyl ring and the water of crystallization.

Introduction. The crystal structures of 2'-deoxyadenosine monohydrate (Watson, Sutor & Tollin, 1965) and 2'-deoxyadenosine (Sato, 1984) have been reported. We describe the solution of the structure of a monohydrate of a protected form of 2'-deoxyadenosine, which is part of a series of crystallographic investigations of the reagents for oligonucleotide synthesis.

Experimental. Rectangular crystals from a water/methanol mixture by slow evaporation, $0.2 \times 0.2 \times 0.8$ mm, Nicolet P3 diffractometer, Ni-filtered radiation, ω -scan method, $(\sin\theta)/\lambda < 0.58 \text{ \AA}^{-1}$, lattice parameters from the 2θ values of ten reflections with $30 < 2\theta < 50^\circ$, no absorption corrections, $h = 0$ to 20, $k = 0$ to 8, $l = 0$ to 19, three reflections measured as intensity standards with variation $< 2\%$. 2395 unique reflections measured, 731 excluded during refinement [$F < 3\sigma(F)$]. Structure solved by heavy-atom phasing from silicon atom, first F map revealed the positions of all non-hydrogen atoms, least-squares refinement using SHELX76 (Sheldrick, 1976), F magnitudes, unit weights; isotropic and then anisotropic temperature factors gave $R = 0.067$ and $S = 1.77$ [calculated with $\sigma(F)$]. 311 parameters varied: x, y, z, U_{ij} for non-H atoms and H atoms at calculated positions allowed to 'ride' on non-H atom, with a U varied for each group of H atoms bound to the phenyl ring, the base, the sugar and the methyl carbons, respectively. In final cycle $(\Delta/\sigma)_{\max} = 0.015$. Final difference synthesis $(\Delta\rho)_{\max} = 0.29$, $(\Delta\rho)_{\min} = -0.48 \text{ e \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1* gives the final atom parameters, and Fig. 1 shows the molecular structure drawn by ORTEPII (Johnson, 1976) and the atomic numbering scheme.

The 2'-deoxyribose ring adopts a C3'-*exo* ($_3T^2$) (C2'-*endo*) pucker with a pseudorotation angle $P \simeq 190^\circ$, which is often found in 2'-deoxynucleosides and nucleotides (Olson & Sussman, 1982). The glycosidic torsion angle defined by O4'-C1'-N9-C4, $\chi = 161.8 (10)^\circ$, is in the *anti* conformation, giving a close contact between sugar and base [O4'...C8 = 2.799 (11) Å] similar to that seen in 2'-deoxyadenosine (Sato, 1984). In addition, the conformation about the C4'-C5' bond defined by O5'-C5'-C4'-C3', $\gamma = 56.0 (11)^\circ$, is *gauche-gauche* (+sc), which is stabilized by an intramolecular 'hydrogen bond' [C8-H...O5' = 3.241 (11) Å] that is only rarely observed in

purine nucleotides and nucleosides (Amidon, Anik & Rubin, 1975). The bond lengths in the adenine base are in good agreement with the mean values for the neutral base calculated by Taylor & Kennard (1982), except for C2-N3 = 1.359 (13) Å and C6-N6 = 1.386 (10) Å, which exceed their mean values, and C4-C5 = 1.353 (12) Å and C6-N1 = 1.317 (11) Å, which are less than their mean values. The three Si-C bond lengths vary between 1.857 (11) and 1.864 (11) Å [mean = 1.861 (6) Å] and the Si-O5'

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
M1	0.3011 (8)	0.2071 (16)	0.3222 (7)	0.103
M2	0.2498 (7)	0.592 (2)	0.3139 (8)	0.117
M3	0.3762 (7)	0.6115 (19)	0.3548 (7)	0.107
M4	0.3434 (10)	0.6973 (15)	0.2141 (7)	0.126
M5	0.4356 (6)	0.304 (2)	0.2299 (8)	0.119
Si	0.33964 (15)	0.3555 (4)	0.24887 (16)	0.055
CSi	0.3278 (6)	0.5723 (14)	0.2850 (6)	0.065
O5'	0.2931 (4)	0.3234 (9)	0.1663 (3)	0.058
C1'	0.2194 (5)	0.0114 (11)	0.0185 (6)	0.055
C2'	0.2952 (5)	-0.0615 (13)	0.0059 (6)	0.058
C3'	0.3415 (5)	0.0697 (12)	0.0516 (5)	0.051
O3'	0.4137 (3)	0.0688 (9)	0.0288 (4)	0.063
C4'	0.3028 (5)	0.2325 (12)	0.0312 (5)	0.050
O4'	0.2275 (3)	0.1886 (7)	0.0283 (4)	0.050
C5'	0.3134 (6)	0.3729 (13)	0.0899 (5)	0.059
N1	0.0799 (5)	-0.4738 (10)	0.1375 (4)	0.056
C2	0.1086 (6)	-0.4494 (16)	0.0660 (6)	0.066
N3	0.1472 (4)	-0.3169 (11)	0.0398 (4)	0.057
C4	0.1517 (5)	-0.2040 (12)	0.0983 (5)	0.047
C5	0.1255 (5)	-0.2126 (13)	0.1732 (5)	0.046
C6	0.0899 (5)	-0.3620 (13)	0.1937 (5)	0.048
N7	0.1408 (4)	-0.0676 (10)	0.2160 (4)	0.050
C8	0.1764 (5)	0.0243 (14)	0.1637 (5)	0.057
N9	0.1857 (4)	-0.0513 (11)	0.0924 (4)	0.050
N6	0.0658 (4)	-0.3844 (10)	0.2709 (4)	0.049
C	0.0566 (5)	-0.5394 (14)	0.3083 (5)	0.054
O	0.0708 (5)	-0.6717 (10)	0.2752 (4)	0.079
C1(B)	0.0296 (5)	-0.5314 (13)	0.3894 (5)	0.045
C2(B)	0.0477 (5)	-0.6596 (14)	0.4389 (5)	0.058
C3(B)	0.0232 (6)	-0.6615 (16)	0.5181 (6)	0.070
C4(B)	-0.0198 (6)	-0.5335 (16)	0.5465 (6)	0.074
C5(B)	-0.0377 (6)	-0.4038 (16)	0.4945 (6)	0.070
C6(B)	-0.0133 (5)	-0.4010 (14)	0.4160 (6)	0.056
O(W)	0.0701 (3)	-0.0728 (8)	0.3611 (3)	0.052

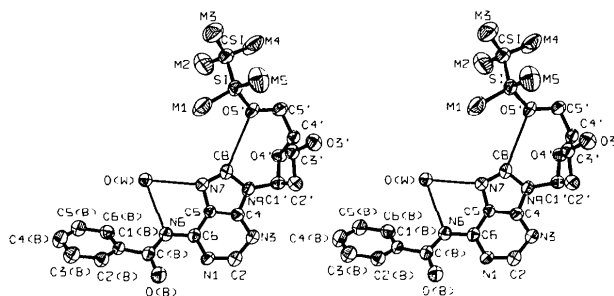


Fig. 1. Stereodrawing of the molecular geometry with the atom numbering. The thermal ellipsoids are drawn at the 50% level.

* Lists of structure-factor amplitudes, anisotropic thermal parameters, bond lengths and bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43678 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

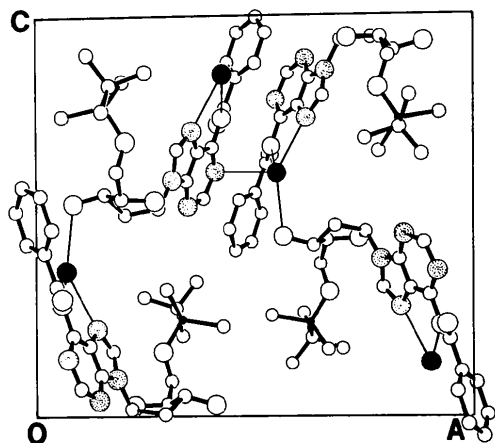


Fig. 2. Packing of the molecules in the unit cell. Atoms are identified by the following: N = large shaded circles, O = large open circles, H₂O = large black circles, C = small open circles, Si = small black circles. Hydrogen bonds are indicated with narrow lines.

bond length is 1.658 (6) Å, which are in good agreement with previously published values for Si–X distances given in *International Tables for X-ray Crystallography* (1974).

The crystal structure is illustrated in Fig. 2. All available H atoms participate in hydrogen bonds [N6–H···O(W) = 2.929 (11), N7···H–O(W) = 2.775 (11) Å, O3'–H···O(W') = 2.838 (10) and N1···H–O(W'') = 2.907 (11) Å], and there are no adenine–adenine base pairs. There is a stacking interaction between the phenyl ring and the base

[C5···C1(B) = 3.339 (11), C8···C6(B) = 3.377 (10), N9···C5(B) = 3.339 (11), N9···C6(B) = 3.435 (11) Å]. Finally, there is a close contact between C6 of the phenyl ring and O of the water of crystallization [C6(B)–H···O(W) = 3.197 (11) Å], which brings the δ(–) oxygen atom close to one of the δ(+) hydrogen atoms of the phenyl ring and is enthalpically favorable (Thomas, Smith, Thomas & Feldman, 1982).

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Structure and Stereochemistry of the Methyl Ester of (5 α ,13 α ,14 β ,17 α ,20S,24Z)-3-Oxolanosta-7,24-dien-26-oic Acid (Masticadienonic Acid)*†

BY M. SORIANO-GARCÍA,‡ R. A. TOSCANO, B. ORTÍZ, A. NAVARRETE, R. SÁNCHEZ-OBREGÓN, H. BARRIOS AND F. YUSTE

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, Mexico DF

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Abstract. C₃₁H₄₈O₃, *M_r* = 468.7, orthorhombic, *P*2₁2₁2₁, *a* = 7.118 (1), *b* = 10.165 (3), *c* =

38.244 (10) Å, *V* = 2767 (1) Å³, *Z* = 4, *D_x* = 1.125 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 0.065 mm⁻¹, *F*(000) = 1032, *T* = 293 K. Final *R* = 0.066 for 1636 observed reflections. The molecular structure determined from the X-ray data confirms the structure previously assigned on the basis of chemical and spectroscopic evidence. All the rings are *trans*

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† Note that the crystallographic numbering differs from that used to name the compound.

‡ To whom correspondence should be addressed.