

3',5'-O-(Tetraisopropyl-1,3-disiloxanediyl)cytidine*

BY C. H. M. VERDEGAAL

Organic Chemistry Section, Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

A. J. DE KOK AND H. P. WESTERINK

X-ray and Electron Diffraction Section, Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

J. H. VAN BOOM

Organic Chemistry Section, Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

AND C. ROMERS

X-ray and Electron Diffraction Section, Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

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Abstract. $C_{21}H_{39}N_3O_6Si_2$, $M_r = 485.7$, orthorhombic, $P2_12_12_1$, $a = 8.942(2)$, $b = 10.324(3)$, $c = 27.576(7)$ Å at 113 K, $Z = 4$. The structure was solved with direct methods and refined by least squares, using 2043 diffractometer-measured reflexions, including 1481 significant ones ($R_w = 6.03\%$). The ribose ring has an envelope conformation [$C(3')$ -endo] with the pseudorotation angle $P = 16.1^\circ$, and $\phi_{max} = 46.3^\circ$. The cytosine base has an *anti* orientation ($\chi = 21.4^\circ$) with respect to the five-membered ring. The eight-membered ring containing two Si atoms has an irregular shape.

Introduction. The tetraisopropyl-1,3-disiloxanediyl group of the title compound protects simultaneously the alcoholic functions at O(3') and O(5') of the ribose ring. The molecular structure of the solid title compound was determined in order to verify the conformation considered to be present [$C(3')$ -endo] under acidic conditions, particularly the orientation of the O(2') function (Verdegaal, Jansse, de Rooij & van Boom, 1980). Proton coupling between H(1') and H(2') being absent, the NMR data suggest this conformation with dihedral angle $\alpha [H(1')-C(1')-C(2')-H(2')] \approx 90^\circ$. The numbering of the atoms is indicated in Fig. 1.

$C_{21}H_{39}N_3O_6Si_2$ was crystallized from acetonitrile. A crystal with dimensions $0.2 \times 0.2 \times 0.2$ mm was used during all diffraction measurements on a Nonius CAD-4 diffractometer.

* Nucleic Acid Constituents. XVIII. Part XVII: Olsthoorn, Bostelaar, de Rooij, van Boom & Altona (1981).

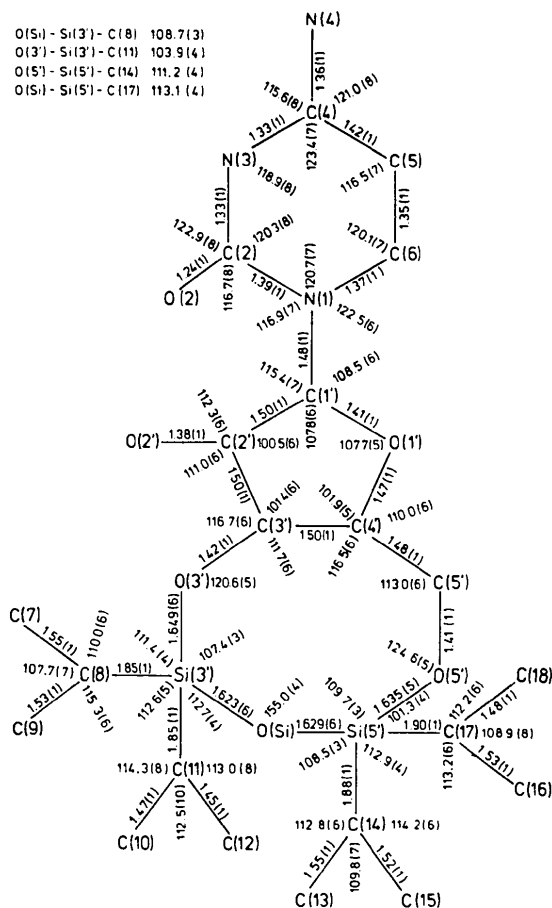


Fig. 1. Numbering of atoms, intramolecular distances (Å) and valency angles ($^\circ$). Estimated standard deviations in units of the last digit are given in parentheses.

If 030, 050 and 007 are disregarded, the reflexions $h00$, $0k0$ and $00l$ are absent for h , k , l odd, respectively, and indicate space group $P2_12_12_1$. This assumption was confirmed by the successful analysis. Therefore, the deviations from space-group symmetry must be negligible. The measured density at room temperature is 1.21 Mg m^{-3} . The cell contains four molecules, resulting in $d_{\text{calc}} = 1.268 \text{ Mg m}^{-3}$ at 113 K.

The reflexion intensities were measured with the ω scanning mode in the range between $\theta = 2$ and $\theta = 23^\circ$, with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). A total of 2043 symmetry-independent reflexions were measured, of which 1481 had intensities with $I > 2\sigma$. At intervals, repeated measurements of standard reflexions were used to correct for the loss of scattering power of the crystal during the total exposure. An absorption correction was not applied.

The structure was determined with direct methods using the multiple-solution program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq &

Woolfson, 1978). Nine heavy atoms, including the two Si atoms, were located. The remaining heavy atoms and 28 H atoms were found in Fourier and difference Fourier maps. The remaining 11 H atoms were introduced at fixed calculated positions (tetrahedral valency angles at sp^3 , trigonal valency angles at sp^2 C atoms, and C—H = 1.0 \AA).

The scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Using 2043 reflexions, including the non-observed ones, the positions and anisotropic vibrational parameters of the heavy atoms were refined with full-matrix least squares, with a program developed and modified by Mrs E. W. Rutten-Keulemans, but the H positions and their isotropic temperature factors ($B = 3 \text{ \AA}^2$) were not refined. Using the expressions for anisotropic temperature factors and the definitions of reliability indices as given by de Graaff, Martens & Romers (1978), the final weighted and unweighted indices are $R_w = 6.03$ and $R = 9.16\%$.* The positional parameters and their e.s.d.'s are given in Table 1.

Table 1. *Fractional positional parameters and equivalent isotropic B values*

Estimated standard deviations in units of the last digit are given in parentheses.

$$B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
C(1')	0.4501 (10)	0.0752 (7)	0.1494 (3)	2.5 (4)
C(2')	0.3537 (9)	-0.0134 (7)	0.1792 (3)	2.2 (4)
C(3')	0.2302 (9)	-0.0410 (8)	0.1438 (3)	2.0 (4)
C(4')	0.3168 (8)	-0.0617 (7)	0.0979 (3)	1.8 (4)
C(5')	0.2309 (9)	-0.0542 (7)	0.0520 (3)	2.0 (4)
C(2)	0.4808 (10)	0.2719 (9)	0.1975 (3)	3.4 (5)
C(4)	0.3776 (9)	0.4663 (8)	0.1749 (3)	2.7 (4)
C(5)	0.3161 (9)	0.4138 (8)	0.1316 (3)	2.2 (4)
C(6)	0.3370 (9)	0.2857 (8)	0.1242 (3)	2.2 (4)
O(1')	0.4272 (6)	0.0441 (5)	0.1000 (1)	2.3 (3)
O(2')	0.4272 (7)	-0.1256 (5)	0.1921 (2)	3.6 (3)
O(3')	0.1366 (6)	-0.1477 (5)	0.1544 (2)	2.3 (3)
O(5')	0.1349 (6)	0.0537 (5)	0.0500 (1)	1.7 (3)
O(Si)	-0.0847 (6)	-0.0496 (5)	0.1029 (2)	2.4 (3)
O(2)	0.5530 (8)	0.2001 (6)	0.2249 (2)	4.1 (3)
N(1)	0.4219 (8)	0.2149 (6)	0.1560 (2)	2.1 (3)
N(3)	0.4604 (9)	0.3976 (6)	0.2059 (3)	3.0 (3)
N(4)	0.3543 (8)	0.5917 (7)	0.1873 (2)	3.3 (4)
Si(3')	-0.0468 (3)	-0.1336 (2)	0.1512 (1)	2.7 (1)
Si(5')	-0.0461 (3)	0.0474 (2)	0.0581 (1)	2.4 (1)
C(7)	-0.0764 (12)	-0.1193 (10)	0.2516 (3)	5.3 (6)
C(8)	-0.1225 (9)	-0.0478 (9)	0.2045 (3)	3.4 (5)
C(9)	-0.0746 (11)	0.0935 (10)	0.2095 (3)	4.9 (6)
C(10)	-0.2760 (13)	-0.3172 (11)	0.1516 (5)	8.7 (9)
C(11)	-0.1133 (11)	-0.3025 (9)	0.1470 (4)	4.4 (6)
C(12)	-0.0537 (13)	-0.3707 (9)	0.1054 (4)	6.4 (6)
C(13)	-0.2977 (10)	-0.0758 (8)	0.0135 (3)	3.7 (5)
C(14)	-0.1437 (10)	-0.0137 (7)	0.0023 (3)	3.1 (4)
C(15)	-0.0507 (12)	-0.1061 (8)	-0.0282 (3)	3.9 (5)
C(16)	-0.2540 (11)	0.2456 (8)	0.0855 (4)	4.5 (5)
C(17)	-0.0901 (9)	0.2232 (8)	0.0719 (3)	3.1 (5)
C(18)	-0.0505 (13)	0.3101 (8)	0.0312 (3)	4.4 (5)

Discussion. The intramolecular bond distances and valency angles are given in Fig. 1. A number of relevant torsion angles are given in Table 2. The overall shape of the molecule is depicted in Fig. 2.

The furanoside ring is nearly a perfect C(3') envelope. With the notation of Altona & Sundaralingam (1972), the angle of pseudorotation $P =$

* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36105 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected torsion angles ($^\circ$)*

The e.s.d.'s are given in parentheses.

		Conformation
τ_0	C(4')—O(1')—C(1')—C(2')	0.6 (7) $^\circ$
τ_1	O(1')—C(1')—C(2')—C(3')	-27.3 (7)
τ_2	C(1')—C(2')—C(3')—C(4')	42.8 (7)
τ_3	C(2')—C(3')—C(4')—O(1')	-43.1 (7)
τ_4	C(3')—C(4')—O(1')—C(1')	26.6 (7)
χ	O(1')—C(1')—N(1)—C(6)	21.4 (10)
	O(1')—C(1')—N(1)—C(2)	-161.0 (7)
	C(2')—C(1')—N(1)—C(2)	78.0 (9)
	C(3')—C(2')—C(1')—N(1)	94.0 (7)
	C(4')—O(1')—C(1')—N(1)	-125.0 (7)
	C(4')—C(3')—O(3')—Si(3')	-111.5 (6)
	C(3')—O(3')—Si(3')—O(Si)	41.7 (6)
	O(3')—Si(3')—O(Si)—Si(5')	-16.4 (10)
	Si(3')—O(Si)—Si(5')—O(5')	17.1 (10)
	O(Si)—Si(5')—O(5')—C(5')	41.7 (6)
	Si(5')—O(5')—C(5')—C(4')	-103.1 (6)
	O(5')—C(5')—C(4')—C(3')	46.3 (9)
	C(5')—C(4')—C(3')—O(3')	72.2 (8)

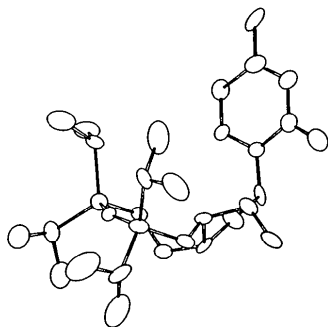


Fig. 2. ORTEP projection (Johnson, 1965) of the molecule; thermal ellipsoids are drawn at the 50% probability level.

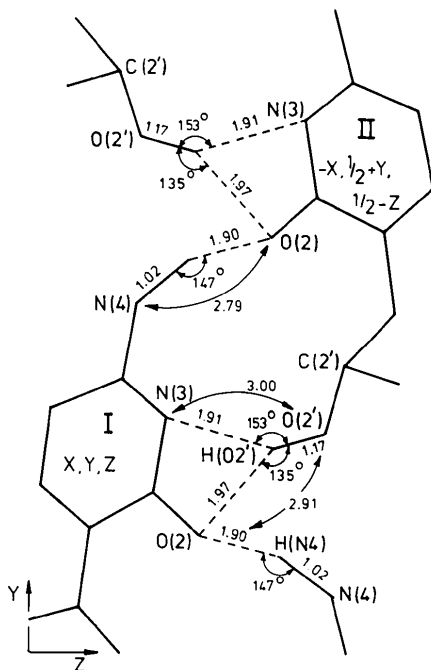


Fig. 3. Hydrophilic interactions between the molecules in a projection along [100]. Hydrogen bonds are shown as dashed lines. Note the 'bifurcation' from H(O2') to N(3) and O(2).

16.1° and the maximum puckering angle $\phi_{\max} = 46.3^\circ$, which is the largest value found until now, probably caused by the extra strain of the attached eight-membered ring. The conformation is C(3')-endo. The orientation of the cytosine base with respect to the five-membered ring is *anti* [$\chi = 21.4(10)^\circ$]. The eight-membered ring has an irregular shape with approximately six atoms in one plane and C(3') above and C(5') below this plane.

The bonds C(11)—C(10) and C(11)—C(12), and to a lesser degree C(18)—C(18), are too short. It was found that C(10), C(11) and C(12) have unrealistically large

U_{33} vibrational parameters. This might indicate disorder of the isopropyl group involving C(10), C(12) and H(11), or a riding motion of these atoms. The torsion angle α [H(1')—C(1')—C(2')—H(2')] is 95° , which is in agreement with the observed value for $J_{\text{H}(1'),\text{H}(2')}$, as derived from NMR.

Within an upper limit of 3.0 Å, each atom is surrounded by 14 neighbours at positions $x, \pm 1 + y, z$; $-x, \pm \frac{1}{2} + y, \frac{1}{2} - z$; $1 - x, \pm \frac{1}{2} + y, \frac{1}{2} - z$; $\pm 1 + x, y, z$; $\frac{1}{2} + x, \pm \frac{1}{2} - y, -z$; $-\frac{1}{2} + x, \pm \frac{1}{2} - y, z$; $1 + x, 1 + y, z$; $-1 + x, -1 + y, z$.

The stacking is governed by hydrogen bridges of the type N(4)—H...O(2), O(2')—H...N(3), O(2')—H...O(2) with lengths 2.79 (1), 3.00 (1) and 2.91 (1) Å, respectively. The molecule at position $-x, \frac{1}{2} + y, \frac{1}{2} - z$ (II, see Fig. 3) denotes H(O2') to either N(3) or O(2) of molecule I at x, y, z . The N(3)—H(O2') and O(2)—H(O2') distances being nearly equal (1.91 and 1.97 Å) and the corresponding angles N(3)—H(O2')—O(2') and O(2)—H(O2')—O(2') being 153 and 135° , one might consider the presence of a 'bifurcated' hydrogen bond (Kollman & Allen, 1969). Although the hydrogen atom H(O2') can only be located with low accuracy in Fourier difference maps, its position for a 'bifurcated' bond to O(2) and N(3) agrees with that predicted by the *ab initio* calculations of Newton, Jeffrey & Takagi (1979). In this way the molecules form antiparallel strands, separated by hydrophobic interactions in and about the net planes (002).

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