

phorsäure-phenylestern (Engelhardt & Jürgens, 1980). Schwache intermolekulare Wasserstoffbrücken verbinden die Moleküle untereinander: $S \cdots H(41)^I$ 2,76 (3) mit $S \cdots N(4)^I$ 3,598 (5) Å; $S \cdots H(21)^{II}$ 2,68(6) mit $S \cdots N(2)^{II}$ 3,469 (6) Å [(i) $-x, -y, 1 - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$].

Wir danken den Herren Kollegen des Instituts für Kristallographie der Freien Universität Berlin für ihre Unterstützung bei den Messungen und für die Überlassung einiger Rechenprogramme. Dem Fonds der Chemischen Industrie danken wir für finanzielle Unterstützung.

Literatur

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 CLEGG, W. (1980). *Acta Cryst.* **B36**, 2830–2832.
 CLEGG, W., NOLTEMEYER, M., SHELDRIK, G. M. & VATER, N. (1980). *Acta Cryst.* **B36**, 2461–2463.
 CLEGG, W., SHELDRIK, G. M. & VATER, N. (1980). *Acta Cryst.* **B36**, 3162–3164.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 ENGELHARDT, U. (1979). *Acta Cryst.* **B35**, 3116–3119.
 ENGELHARDT, U. & BÜNGER, T. (1978). *Inorg. Nucl. Chem. Lett.* **14**, 21–22.
 ENGELHARDT, U. & BÜNGER, T. (1979). *Z. Naturforsch. Teil B*, **34**, 1107–1111.
 ENGELHARDT, U., FRIEDRICH, B. & STROMBURG, B. (1982). *Acta Cryst.* **B38**, 753–758.
 ENGELHARDT, U. & JÜRGENS, G. D. (1980). *Acta Cryst.* **B36**, 3059–3063.
 ENGELHARDT, U. & METTER, H.-P. (1980). *Acta Cryst.* **B36**, 2086–2091.
 ENGELHARDT, U., METTER, H.-P. & STEGER, L. (1977). *Z. Anorg. Allg. Chem.* **434**, 263–270.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 GLIDEWELL, C. (1979). *Inorg. Chim. Acta*, **36**, 135–138.
 GLIDEWELL, C. & HOLDEN, H. D. (1981). *Acta Cryst.* **B37**, 754–756.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 HURSTHOUSE, H. M. A. & MALIK, K. M. A. (1979). *Acta Cryst.* **B35**, 522–524.
International Tables for X-ray Crystallography (1962). Bd. III. S. 213. Birmingham: Kynoch Press.
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–669.
 PAULING, L. (1973). *Die Natur der Chemischen Bindung*, 3. Aufl. Weinheim: Verlag Chemie.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. K., HECK, H. & FLACK, H. (1976). The XRAY system – version of March 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WANNAGAT, U., GIESEN, K. P. & FALIUS, H. H. (1973). *Monatsh. Chem.* **104**, 1444–1447.
 WANNAGAT, U., GIESEN, K. P. & RABET, F. (1971). *Z. Anorg. Allg. Chem.* **382**, 195–197.

Acta Cryst. (1982). **B38**, 1176–1180

X-ray Structural Study of 3',6'-O-(1,1,3,3-Tetraisopropyl-1,3-disiloxanediyl)-neplanocin A, a Derivative of a Novel Antitumor Antibiotic

BY MASATOSHI YAMAZAKI, KENSAKU HAMADA, YURIKO YAMAGATA, TAKAJI FUJIWARA AND KEN-ICHI TOMITA
Faculty of Pharmaceutical Sciences, Osaka University, 133-1 Yamadaoka, Suita, Osaka 565, Japan

KIYOSHI FUKUKAWA AND TOHRU UEDA

Faculty of Pharmaceutical Sciences, Hokkaido University, Kita 12-jo, Nishi-6, Kita-ku, Sapporo 060, Japan

AND TAKAO HIRANO

Research Laboratories, Toyo Jozo Co., Ltd, Ohito, Shizuoka 410-23, Japan

(Received 29 July 1981; accepted 1 October 1981)

Abstract

The structure of the title compound, $C_{23}H_{39}N_5O_4Si_2$, $M_r = 505.54$, was determined by X-ray analysis using 5046 independent diffractometer data and refined to a final R of 0.055 including all H atoms. The crystal

belongs to the monoclinic space group $P2_1$, with $a = 8.953(1)$, $b = 34.638(4)$, $c = 8.957(1)$ Å, $\beta = 94.41(1)^\circ$, $V = 2769.5(7)$ Å³, $Z = 4$, and two independent molecules in the asymmetric unit; $D_x = 1.213$, $D_m = 1.215$ Mg m⁻³. The conformations of the two molecules are quite similar, and no significant

differences are found in bond distances and angles. Both the sugar C(2') atoms are displaced by 0.3 Å toward the base N(9), *i.e.* C(2')-*endo* puckering, and the torsion angles χ_{CN} are 34.4 (7)° and 33.0 (7)° for (I) and (II), respectively (*anti* conformation).

Introduction

Neplanocin A (Fig. 1) is a newly isolated antitumor antibiotic from *Ampullarilla regularis* A 11079, and its chemical structure has been recently determined as (–)-9-[*trans*-2,*trans*-3-dihydroxy-4-(hydroxymethyl)-4-cyclopentenyl]adenine (Hayashi, Yaginuma, Muto & Tsujino, 1980). Some of the most interesting structural features are that it contains adenine, a common nucleic acid base, and an unsaturated cyclopentene ring instead of the furanose found in adenosine and other common nucleosides, and that it exhibits marked antitumor activity. The modification of neplanocin A at the 2' position is expected to provide many active analogs, but a systematic approach to the synthesis of such compounds requires the protection of both the 3' and 6' hydroxyl groups of neplanocin A. As 1,3-dichloro-1,1,3,3-tetraisopropylidisiloxane is used for the simultaneous protection of the 3'- and 5'-hydroxyl groups of adenosine and other ribonucleosides (Markiewicz, 1979), we have applied the same procedure to neplanocin A to see whether the protection occurs at the 3' and 6' positions or at the 2' and 3' positions. This paper describes the X-ray structural study of the product, 3',6'-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-diyl)neplanocin A (Fukukawa, Ueda & Hirano, 1981), hereafter referred to as siloxane neplanocin A (Fig. 1).

Experimental

Transparent prismatic crystals of siloxane neplanocin A were obtained at room temperature from their ethanol solution. A crystal with dimensions 0.10 × 0.11 × 0.15 mm was mounted on a Rigaku four-circle diffractometer; Cu $K\alpha$ radiation and a graphite

monochromator were used. The unit-cell dimensions were determined by least-squares analysis of the angular positions of 25 relatively strong reflections. The systematic absence of $0k0$ reflections with k odd suggested that the space group was either $P2_1$ or $P2_1/m$, and the former was adopted since the molecule is optically active. The density, measured by flotation using a benzene-carbon tetrachloride mixture, revealed that the crystal contained two independent molecules in the asymmetric unit. X-ray intensities were measured with the ω - 2θ continuous scanning mode, with a scan speed 2° min⁻¹ and scan width calculated as $(0.70 + 0.15 \tan \theta)^\circ$. Stationary background counts of 10 s were taken at both limits of each scan. Three standard reflections measured after every 50 reflections showed a 3% gradual decrease in intensity during the course of the data collection. The intensities were collected for a total of 5040 unique reflections measured up to the limit $2\theta = 135^\circ$. Lorentz-polarization corrections were applied, but neither an absorption nor an extinction correction was made.

Structure analysis

The structure was solved by the direct method using the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All 68 expected non-hydrogen atoms were automatically located from the phase set with the highest combined figure of merit using 500 normalized structure factors ($E \geq 1.58$). The structure was refined by the block-diagonal least-squares method with anisotropic thermal parameters for all nonhydrogen atoms to an R of 0.078. A difference Fourier synthesis revealed the positions of all the H atoms except those of the methyl groups which were found by successive difference Fourier syntheses. The final refinement including all the H atoms with isotropic temperature factors converged to $R = 0.055$ for 4671 non-zero reflections. The weighting function used had the form $1/(\sigma^2|F_o| + 0.29765|F_o| - 0.00019|F_o|^2)$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are given in Table 1.* All the numerical computations were performed on an ACOS 700 computer of the Crystallographic Research Center, Institute for Protein Research, Osaka University, using the program *UNICS* (1979).

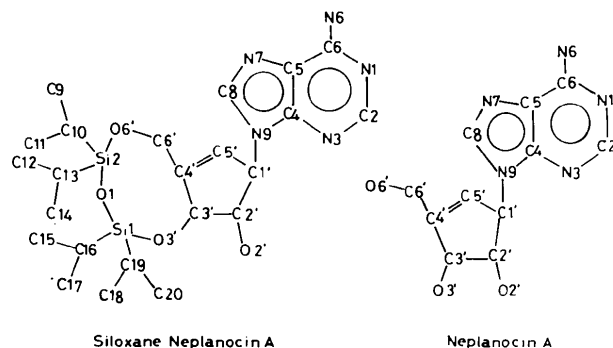


Fig. 1. Chemical structure and atomic numbering used in this work.

* Lists of structure factors, final positional parameters for H atoms and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36455 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters and equivalent isotropic thermal parameters (\AA^2) with their estimated standard deviations

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
N(1)(I)	0.4986 (4)	-0.6126 (1)	1.4937 (5)	4.00 (8)
C(2)(I)	0.5800 (5)	-0.6145 (1)	1.3766 (6)	4.2 (1)
N(3)(I)	0.7087 (4)	-0.5967 (1)	1.3544 (4)	3.61 (7)
C(4)(I)	0.7534 (5)	-0.5738 (1)	1.4702 (5)	3.09 (8)
C(5)(I)	0.6767 (5)	-0.5685 (1)	1.5983 (5)	3.30 (8)
C(6)(I)	0.5457 (5)	-0.5888 (1)	1.6097 (5)	3.44 (8)
N(6)(I)	0.4640 (4)	-0.5863 (1)	1.7299 (4)	4.18 (8)
N(7)(I)	0.7515 (4)	-0.5431 (1)	1.6986 (5)	4.38 (8)
C(8)(I)	0.8715 (6)	-0.5340 (1)	1.6274 (6)	4.4 (1)
N(9)(I)	0.8805 (4)	-0.5517 (1)	1.4915 (4)	3.71 (7)
C(1')(I)	1.0009 (5)	-0.5461 (1)	1.3903 (5)	3.38 (9)
C(2')(I)	0.9789 (5)	-0.5094 (1)	1.2955 (5)	3.34 (9)
O(2')(I)	0.9028 (3)	-0.5152 (1)	1.1519 (4)	4.39 (7)
C(3')(I)	1.1353 (5)	-0.4910 (1)	1.2940 (5)	3.00 (8)
O(3')(I)	1.2063 (3)	-0.4992 (1)	1.1592 (3)	3.28 (5)
C(4')(I)	1.2211 (4)	-0.5097 (1)	1.4253 (5)	3.31 (8)
C(5')(I)	1.1491 (5)	-0.5397 (1)	1.4783 (6)	3.8 (1)
C(6')(I)	1.3768 (5)	-0.4968 (1)	1.4782 (6)	4.0 (1)
O(6')(I)	1.3818 (3)	-0.4557 (1)	1.4924 (3)	4.10 (6)
S(11)(I)	1.3058 (1)	-0.46663 (4)	1.0759 (1)	2.92 (2)
O(1)(I)	1.3981 (3)	-0.4405 (1)	1.2011 (3)	3.56 (5)
S(12)(I)	1.4560 (1)	-0.42728 (4)	1.3703 (1)	3.45 (2)
C(9)(I)	1.7349 (8)	-0.4247 (3)	1.5416 (9)	9.9 (3)
C(10)(I)	1.6657 (6)	-0.4342 (2)	1.3882 (7)	5.4 (1)
C(11)(I)	1.7479 (7)	-0.4134 (2)	1.2702 (8)	6.8 (2)
C(12)(I)	1.439 (1)	-0.3471 (2)	1.317 (1)	10.9 (3)
C(13)(I)	1.3841 (7)	-0.3790 (1)	1.4143 (7)	5.6 (1)
C(14)(I)	1.2138 (9)	-0.3794 (2)	1.415 (1)	7.8 (2)
C(15)(I)	1.5466 (8)	-0.4700 (2)	0.8897 (9)	6.9 (2)
C(16)(I)	1.4386 (6)	-0.4956 (1)	0.9683 (6)	4.2 (1)
C(17)(I)	1.5232 (6)	-0.5249 (2)	1.0701 (7)	5.7 (1)
C(18)(I)	1.080 (1)	-0.4574 (2)	0.8408 (9)	8.6 (2)
C(19)(I)	1.1759 (6)	-0.4343 (1)	0.9616 (7)	5.2 (1)
C(20)(I)	1.251 (1)	-0.3994 (2)	0.893 (1)	8.8 (2)
N(1)(II)	0.9955 (4)	-0.0849 (1)	-0.0017 (4)	3.87 (8)
C(2)(II)	0.8780 (5)	-0.0833 (1)	0.0807 (6)	4.2 (1)
N(3)(II)	0.8546 (4)	-0.1012 (1)	0.2099 (4)	3.67 (7)
C(4)(II)	0.9723 (5)	-0.1238 (1)	0.2544 (5)	3.12 (7)
C(5)(II)	1.0978 (5)	-0.1293 (1)	0.1780 (5)	3.15 (7)
C(6)(II)	1.1094 (5)	-0.1083 (1)	0.0465 (5)	3.41 (8)
N(6)(II)	1.2291 (4)	-0.1110 (1)	-0.0341 (5)	4.20 (8)
N(7)(II)	1.1970 (4)	-0.1546 (1)	0.2515 (5)	4.36 (8)
C(8)(II)	1.1299 (6)	-0.1632 (1)	0.3721 (6)	4.47 (9)
N(9)(II)	0.9921 (4)	-0.1459 (1)	0.3802 (4)	3.42 (6)
C(1')(II)	0.8916 (5)	-0.1518 (1)	0.5003 (5)	3.42 (8)
C(2')(II)	0.7957 (5)	-0.1884 (1)	0.4786 (5)	3.41 (8)
O(2')(II)	0.6530 (4)	-0.1827 (1)	0.4024 (4)	4.61 (7)
C(3')(II)	0.7949 (5)	-0.2067 (1)	0.6370 (5)	2.97 (7)
O(3')(II)	0.6602 (3)	-0.1981 (1)	0.7065 (3)	3.35 (5)
C(4')(II)	0.9247 (5)	-0.1882 (1)	0.7215 (5)	3.28 (7)
C(5')(II)	0.9768 (5)	-0.1587 (1)	0.6500 (5)	3.63 (8)
C(6')(II)	0.9793 (5)	-0.2009 (1)	0.8761 (5)	3.80 (8)
O(6')(II)	0.9926 (3)	-0.2419 (1)	0.8815 (4)	4.02 (6)
S(11)(II)	0.5758 (1)	-0.23020 (4)	0.8056 (1)	2.97 (2)
O(1)(II)	0.7018 (3)	-0.2569 (1)	0.8978 (3)	3.65 (6)
S(12)(II)	0.8707 (1)	-0.26968 (4)	0.9555 (1)	3.44 (2)
C(9)(II)	0.7716 (8)	-0.2846 (2)	1.2463 (8)	6.7 (2)
C(10)(II)	0.8898 (6)	-0.2639 (1)	1.1642 (6)	5.0 (1)
C(11)(II)	1.0438 (8)	-0.2726 (3)	1.234 (1)	10.3 (3)
C(12)(II)	0.814 (1)	-0.3501 (2)	0.933 (1)	11.7 (3)
C(13)(II)	0.9160 (7)	-0.3188 (1)	0.8836 (8)	5.8 (1)
C(14)(II)	0.918 (1)	-0.3196 (2)	0.716 (1)	7.6 (2)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
C(15)(II)	0.3875 (8)	-0.2272 (2)	1.0427 (8)	7.0 (1)
C(16)(II)	0.4687 (5)	-0.2021 (1)	0.9381 (6)	4.0 (9)
C(17)(II)	0.5682 (7)	-0.1721 (2)	1.0233 (7)	5.7 (1)
C(18)(II)	0.3445 (9)	-0.2407 (2)	0.580 (1)	9.1 (2)
C(19)(II)	0.4613 (6)	-0.2630 (1)	0.6763 (7)	5.1 (1)
C(20)(II)	0.393 (1)	-0.2975 (2)	0.755 (1)	8.6 (2)

Results and discussion

The bond distances and angles are shown in Figs. 2 and 3. There are no significant differences in bond distances and angles between the two independent molecules. A stereoview of the molecule (I) is shown in Fig. 4.

Adenine ring

C(5)–C(6), 1.378 (I) and 1.395 Å (II), is significantly shorter than in adenosine (Lai & Marsh, 1972), 1.415 Å. Significant differences are also found between the bond angles of the two molecules (I) and (II) and that of adenosine (AD): N(3)–C(4)–C(5) 125.3 (I), 125.7 (II) and 127.6° (AD); N(3)–C(4)–N(9) 129.2 (I), 128.3 (II) and 126.7° (AD); C(6)–C(5)–N(7) 130.1 (I), 130.4 (II) and 132.8° (AD); C(4)–N(9)–C(1') 128.7 (I), 129.5 (II) and 124.3° (AD); C(8)–N(9)–C(1') 125.7 (I), 125.4 (II) and 130.0° (AD). This may be due to the electronic state of the adenine ring being influenced by the substituent at N(9): either the cyclopentene ring in siloxane neplanocin A or the ribose ring in adenosine. The adenine ring is planar, as shown in Table 2, where the maximum deviation from the least-squares plane is 0.025 (6) Å at N(7) of molecule (II).

Cyclopentene ring

Bond lengths and angles in the cyclopentene ring are normal and the C(4')–C(5') double-bond distances are

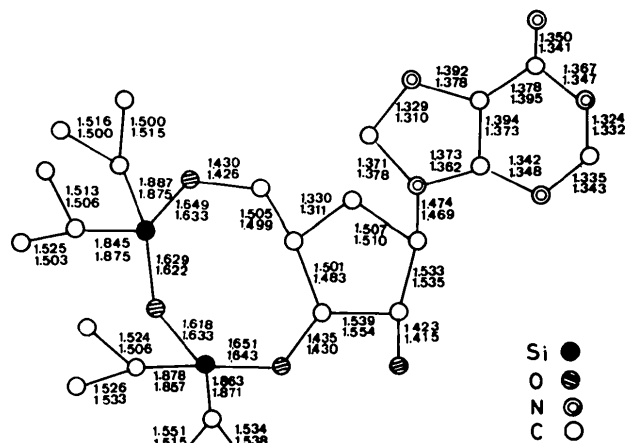


Fig. 2. Bond distances (\AA), where the upper and lower values are for molecules (I) and (II), respectively. The average standard deviation except for the isopropyl moiety (0.012 Å) is 0.007 Å.

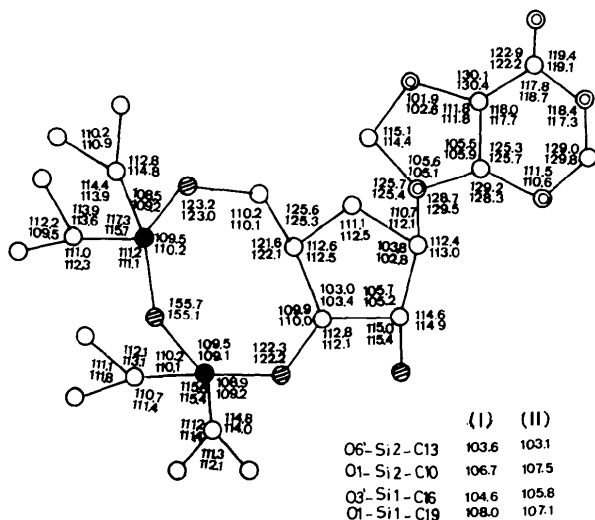


Fig. 3. Bond angles ($^{\circ}$), where the upper and lower values are for molecules (I) and (II), respectively. The average standard deviation is 0.5° .

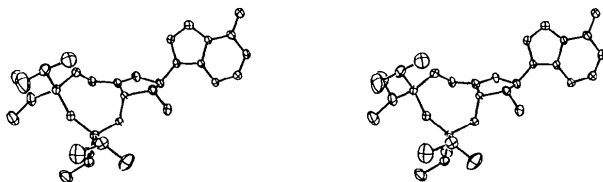


Fig. 4. Stereoscopic view of the molecular conformation of molecule (I).

Table 2. *Least-squares planes of the adenine ring in molecules (I) and (II)*

Atom displacements (\AA)					
(I)	(II)	(I)	(II)		
*N(1)	-0.019 (6)	-0.021 (6)	*N(7)	0.009 (6)	0.025 (6)
*C(2)	0.006 (7)	0.008 (7)	*C(8)	-0.004 (7)	-0.020 (7)
*N(3)	0.010 (6)	0.016 (6)	*N(9)	-0.022 (5)	-0.018 (5)
*C(4)	0.010 (5)	0.003 (5)	N(6)	-0.025 (7)	-0.030 (7)
*C(5)	0.016 (6)	0.023 (6)	C(1')	-0.022 (7)	-0.013 (7)
*C(6)	-0.006 (6)	-0.015 (6)			

Molecule (I):
 $-0.47426X + 0.76325Y - 0.43877Z + 23.65933 = 0$

Molecule (II):
 $0.40014X + 0.76358Y + 0.50679Z - 1.292810 = 0$

* Atoms used to calculate the best planes.

1.330 and 1.311 \AA for molecules (I) and (II), respectively. The puckering of the cyclopentene ring was evaluated from the calculation of the best plane through C(1'), C(4') and C(5'), as shown in Table 3.

The C(3') atoms of molecules (I) and (II) are on the best planes, whereas the C(2') atoms are displaced by 0.31 and 0.30 \AA toward N(9). Although there is no

Table 3. *Least-squares planes of the cyclopentene ring in molecules (I) and (II)*

Atom displacements (\AA)					
	(I)	(II)	(I)	(II)	
*C(1')	0.000 (8)	0.000 (7)	N(9)	-1.011 (9)	-0.996 (9)
C(2')	-0.31 (2)	-0.30 (2)	O(2')	0.33 (2)	0.34 (2)
C(3')	0.00 (2)	0.01 (2)	O(3')	1.29 (2)	1.30 (2)
*C(4')	0.000 (7)	0.000 (7)	C(6')	0.10 (1)	0.08 (1)
*C(5')	0.000 (8)	0.000 (8)			

Molecule (I):
 $0.49307X - 0.60705Y - 0.62320Z - 7.69138 = 0$

Molecule (II):
 $-0.66379X + 0.60756Y + 0.43617Z + 6.31585 = 0$

* Atoms used to calculate the best planes.

classification for the puckering of cyclopentene rings as exists for the furanose ring in nucleosides or nucleotides, we may apply the same approach to siloxane neplanocin A. Then, the puckering of the cyclopentene ring is C(2')-endo. Neplanocin A, without the siloxane ring between O(6') and O(3'), is shown in Fig. 1. In comparison with the C(2')-exo-C(3')-endo puckering of neplanocin A (Nakatsu, 1980), the C(2')-endo puckering of siloxane neplanocin A may be attributed to the planarity of the siloxane ring which may cause the 2' position of the latter to be situated at the more open side or in a more suitable position to be attacked by reagent than that of neplanocin A. Although the C(4')-C(6') lengths of 1.505 and 1.499 \AA for molecules (I) and (II) are comparable to those for C(1')-C(5'), the hydroxymethyl C(6') is displaced by 0.10 and 0.08 \AA from the cyclopentene plane in the opposite direction to C(2'), which may be due to the distortion caused by the siloxane-ring formation. The torsion angle χ_{CN} , C(8)-N(9)-C(1')-C(5'), is 34.4 and 33.0° for molecules (I) and (II), and therefore siloxane neplanocin A has the *anti* conformation as does neplanocin A (Nakatsu, 1980) ($\chi_{CN} = 61.3^{\circ}$). The dihedral angle between the cyclopentene and adenine best planes is 64.9 (5) and 65.2 (5) $^{\circ}$ for molecules (I) and (II) respectively.

Siloxane moiety

The Si-O distances of this compound seem the same as those of related compounds having the cyclic siloxane skeleton (Peyronel, 1954; Steinfink, Post & Fankuchen, 1955; Bokii, Zakharova & Struchkov, 1972; Hossain, Hursthouse & Malik, 1979), whereas the Si-C distances vary depending on the neighboring groups, for example methyl (1.90-1.95 \AA), isopropyl (1.85-1.89 \AA) and phenyl (1.84-1.86 \AA). The C-Si-C angles (115.4-117.3 $^{\circ}$) of siloxane neplanocin A having isopropyl as the neighboring group deviate significantly from the normal tetrahedral angle, compared with those having the methyl (102-110 $^{\circ}$) or

Table 4. *Least-squares planes about the siloxane moiety in molecules (I) and (II)*

Atom displacements (Å)

	(I)	(II)		(I)	(II)
*O(3')	-0.014 (4)	-0.014 (4)	C(4')	0.133 (7)	0.131 (7)
*Si(1)	0.018 (2)	0.022 (2)	C(3')	-0.780 (6)	-0.774 (6)
*O(1)	-0.005 (4)	-0.012 (4)	C(10)	1.579 (8)	1.551 (7)
*Si(2)	-0.012 (3)	-0.007 (2)	C(13)	-1.601 (8)	-1.615 (8)
*O(6')	0.013 (5)	0.011 (5)	C(16)	1.648 (7)	1.628 (7)
C(6')	0.891 (7)	0.885 (7)	C(19)	-1.511 (7)	-1.518 (7)

Molecule (I):

$$0.77311X - 0.63400Y - 0.01862Z - 18.51606 = 0$$

Molecule (II):

$$-0.07444X + 0.63521Y + 0.76875Z - 0.10177 = 0$$

* Atoms used to calculate the best planes.

phenyl groups (110.7–114.7°) as neighboring groups. This may reflect the inevitable repulsion between the two isopropyl groups.

As shown in Table 4, O(3')–Si(1)–O(1)–Si(2)–O(6') forms a plane with a maximum deviation of 0.02 Å for molecules (I) and (II), which makes a dihedral angle with the cyclopentene ring of 141.0 (4) or 140.4 (4)° for molecules (I) and (II) respectively. Such a planar conformation of the siloxane ring is thought to be unstable because of the strains in the Si–O–Si and Si–O–C bonds, and the siloxane ring may be rather easily removed by reagent, for example 1 *M* tetra-*n*-butylammonium fluoride, 0.2 *M* HCl, or 0.2 *M* NaOH (Markiewicz, 1979).

Crystal structure

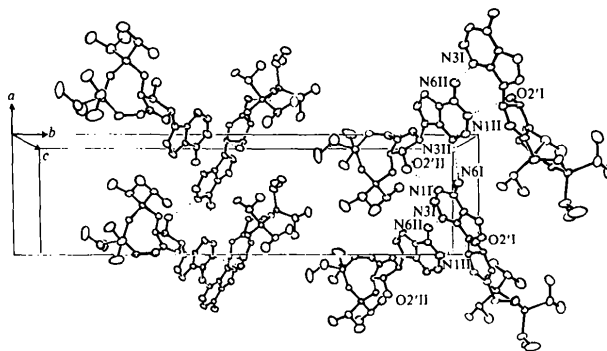
The crystal structure viewed down the *c* axis is shown in Fig. 5, and the hydrogen bonds are also listed in Table 5. One of the two independent molecules in the

Table 5. *Hydrogen-bond distances (Å) and angles (°) in the crystal of siloxane neplanocin A*

D–H	A	Trans- lation for A	D...A	D–H	H...A	∠D–H...A
N(6)I–H(N6)2I*	N(3)II	1, –1, 2	2.988 (7)	1.21 (6)	2.13 (6)	124 (4)
O(2')I–H(O2')	N(1)II	2, –1, 1	2.942 (6)	0.98 (6)	2.02 (7)	157 (5)
N(6)II–H(N6)2II	N(3)I	2, 0, 1	3.005 (7)	0.87 (7)	2.19 (7)	155 (6)
O(2')II–H(O2')II	N(1)I	1, 0, 2	2.966 (6)	1.09 (7)	1.92 (7)	162 (5)

Symmetry code for the acceptor atoms is $-x, y + \frac{1}{2}, -z$.

* I and II denote molecules (I) and (II) respectively.

Fig. 5. The structure viewed down the *c* axis. Hydrogen bonds are indicated by dotted lines.

asymmetric unit is connected by hydrogen bonds to another two molecules related by the *c* translation: N(1) (I)···H–O(2') (II), N(6) (I)–H···N(3) (II), O(2') (I)–H···N(1) (II) and N(3) (I)···N(6) (II). These four hydrogen bonds form a sheet structure parallel to the *ac* plane.

References

- BOKII, N. G., ZAKHAROVA, G. N. & STRUCHKOV, YU. T. (1972). *Zh. Strukt. Khim.* **13**, 291–297.
- FUKUKAWA, K., UEDA, T. & HIRANO, T. (1981). *Chem. Pharm. Bull.* **29**, 597–600.
- HAYASHI, M., YAGINUMA, S., MUTO, N. & TSUJINO, M. (1980). *Nucleic Acids Res. Symp. Ser.* No. 8, s65.
- HOSSAIN, M. A., HURSTHOUSE, M. B. & MALIK, K. M. A. (1979). *Acta Cryst.* **B35**, 522–524.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LAI, T. F. & MARSH, R. E. (1972). *Acta Cryst.* **B28**, 1982–1989.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MARKIEWICZ, W. T. (1979). *J. Chem. Res. (S)*, pp. 24–25; (M), pp. 0181–0197.
- NAKATSU, K. (1980). Private communication.
- PEYRONEL, G. (1954). *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* **16**, 231–236.
- STEINFINK, H., POST, B. & FANKUCHEN, I. (1955). *Acta Cryst.* **8**, 420–424.
- UNICS (1979). *The Universal Crystallographic Computing System*. The Computation Center, Osaka Univ.