

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

	x	y	z	U
Si	1807 (1)	0	7500	37 (1)
N	0	-1537 (3)	7500	40 (1)
H	0	-2155 (39)	7500	36 (15)
C(1)	2869 (3)	-26 (3)	7822 (1)	46 (1)
C(2)	4585 (3)	1034 (4)	7807 (1)	67 (2)
C(3)	2571 (4)	-1634 (3)	7878 (1)	61 (2)
C(4)	2334 (4)	482 (4)	8069 (1)	65 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

The prime denotes a symmetry-generated atom.

Si-N	1.727 (2)	Si-C(1)	1.924 (3)
N-H	0.631 (40)	C(1)-C(2)	1.535 (4)
C(1)-C(3)	1.541 (5)	C(1)-C(4)	1.523 (5)
N-Si-N'	104.1 (2)	N-Si-C(1)	110.0 (1)
N-Si-C(1')	111.1 (1)	C(1)-Si-C(1')	110.3 (2)
Si-N-Si'	135.9 (2)	Si-N-H	112.1 (1)
Si-C(1)-C(2)	113.9 (2)	Si-C(1)-C(3)	110.5 (2)
Si-C(1)-C(4)	110.3 (3)	C(2)-C(1)-C(3)	108.0 (3)
C(2)-C(1)-C(4)	106.0 (3)	C(3)-C(1)-C(4)	108.0 (3)

strictly planar as a consequence of the crystallographic 32 (D_3) symmetry of the molecule. Almost planar rings have been observed in other cyclotrisilazanes in which the substituents on N are not bulky (Rozsondai, Hargittai, Golubinskii, Vilkov & Mastuykov, 1975; Clegg, Noltemeyer, Sheldrick & Vater, 1980). Bulky N substituents (Adamson & Daly, 1970), including N-X-N bridges between cyclotrisilazane rings (Clegg, Noltemeyer, Sheldrick & Vater, 1981; Clegg, 1983), lead to non-planar rings, which may also be produced by other constraints, such as fusion of the ring to a planar cyclodisilazane ring (Clegg, 1980; Clegg, Klingebiel, Sheldrick, Skoda & Vater, 1980). In such cases, the ring usually approximates to a boat conformation, but deviations from the ideal boat can be large (Clegg, 1983).

The Si-N bond length and the N-Si-N and Si-N-Si angles in $(\text{Bu}_2\text{SiNH})_3$ are similar to those in other cyclotrisilazanes.

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Structure of 2'-Deoxy-2'-fluoroadenosine (dAf): $\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_3\text{F}$

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Abstract. $M_r = 269.2$, monoclinic, $P2_1$, $a = 4.791$ (2), $b = 10.428$ (2), $c = 11.507$ (2) \AA , $\beta = 102.06$ (1) $^\circ$, $V = 562.3$ (1) \AA^3 , $Z = 2$, $D_m = 1.576$ (4), $D_x = 1.590$ Mg m^{-3} , graphite-monochromated $\text{Cu K}\alpha$, $\lambda = 1.54173$ \AA , $\mu(\text{Cu K}\alpha) = 1.15$ mm^{-1} , $F(000) = 280$, T

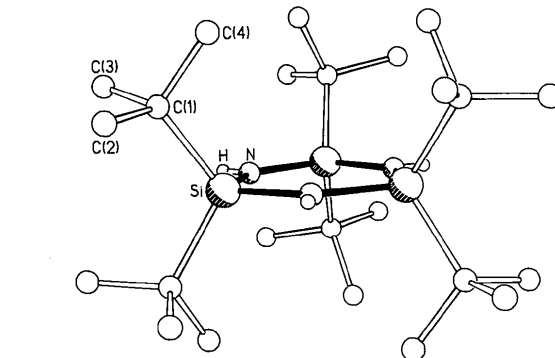


Fig. 1. The molecular structure, showing the atom-numbering scheme. *tert*-Butyl H atoms are omitted.

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Introduction. In order to understand the physico-chemical differences between DNA and RNA, physical properties of a series of nucleosides and nucleotides possessing different substituents (F, Cl, Br, I, or azido group) at the C(2') position have been studied (Ikehara & Miki, 1978; Uesugi, Takatsuka, Ikehara, Cheng, Kan & Ts'o, 1981; Guschlbauer & Jankowski, 1980). Some 2'-deoxy-2'-fluoronucleosides have been the subject of crystallographic studies (Hakoshima, Omori, Tomita, Miki & Ikehara, 1981; Suck, Saenger, Main, Germain & Declercq, 1974; Marck, Lesyng & Saenger, 1982). In particular, NMR studies indicate that 2'-deoxy-2'-fluoronucleosides have a novel sugar-ring conformation in solution: a strong preference for C(3')-endo type in equilibrium between C(3')-endo and C(2')-endo conformations. In this paper, the structure of 2'-deoxy-2'-fluoro-adenosine (dAfl) is described and the molecular conformation and packing are discussed in comparison with adenosine (Lai & Marsh, 1972).

Experimental. Colorless prismatic pillar crystals from *n*-butanol solution by slow evaporation at room temperature. D_m by flotation method using benzene tetrachloride/ethylene dibromide mixture. Cell dimensions: least squares on 25 reflections, $38 < \theta < 68^\circ$. Systematic absences $0k0$ for $k = 2n + 1$ indicate space group $P2_1$. Crystal $0.1 \times 0.1 \times 0.2$ mm. Rigaku-Denki AFC-5 automated diffractometer, 2θ limit 120° ($h = 0$ to 5, $k = 0$ to 11, $l = -13$ to 12), $\theta - 2\theta$ scan technique. 1086 unique reflections measured, 1072 considered observed [$|F_o| > 2\sigma(F_o)$]. Three standard reflections (210, 040, 004) monitored every 61 reflections: intensity fluctuation less than 3 (1)%. Intensities corrected for Lorentz and polarization factors but not for absorption. Structure solved by the direct method using the program *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Positional and thermal parameters refined by full-matrix least-squares methods using the programs of *The Universal Crystallographic Computing System - Osaka* (1979); $\sum w(|F_o| - k|F_c|)^2$ minimized, $w = [\sigma^2(F_o) - 0.07572|F_o| + 0.01147|F_o|^2]^{-1}$. All H atoms located on difference Fourier map. Six intense low-angle reflections (110, 101, $10\bar{1}$, 111, 112, $11\bar{2}$) affected by secondary extinction and excluded. Final $R = 0.066$, $wR = 0.073$ for 1066 reflections, $S = 3.65$ for 221 parameters. Mean and max. Δ/σ values in final refinement cycle 0.338 and 0.688 for non-hydrogen atoms, and 1.140 and 2.03 for H atoms; mean value involving all atoms 1.133. Max. and min. peak heights on final $\Delta\rho$ map 0.40 and $-0.52 e \text{ \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations carried out on an ACOS 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. The final positional and thermal parameters are given in Table 1.* Bond lengths and angles for non-hydrogen atoms shown in Fig. 1 are in good agreement with those of adenosine (Lai & Marsh, 1972) and deoxyadenosine monohydrate (Watson, Sutor & Tollin, 1965).

The molecular structure of dAfl shown in Fig. 2 is very similar to that of adenosine. The glycosyl torsion angles of dAfl and adenosine, $15.7 (5)^\circ$ and 9.9° , are both in the *anti* conformation range. Further, the exocyclic torsion angles [C(3')-C(4')-C(5')-O(5')] of dAfl [$177.3 (3)^\circ$] and adenosine (177.0°) are both in the *gauche-trans* conformation range. The furanose ring of dAfl has a C(3')-endo pucker with $P = 8.8^\circ$ and $\tau_m = 35.7^\circ$ and that of adenosine also has a C(3')-endo pucker with $P = 7.2^\circ$ and $\tau_m = 36.0^\circ$ (Altona & Sundaralingam, 1972).

Not only the molecular structure but also the crystal structure is similar to that of adenosine. Both crystals are stabilized by an extensive hydrogen-bonding network in which all H atoms connected to O or N atoms are included. The only difference between the networks of the two crystals is that dAfl lacks a hydrogen bond between O(2') and O(3') of adenosine (2.749 Å), where a repulsive contact [2.968 (5) Å] between F and O(3') is found as shown in Fig. 3.

As discussed in a previous paper on 2'-deoxy-2'-fluoro-inosine (Hakoshima, Omori, Tomita, Miki & Ikehara, 1981), furanose rings of nucleosides and nucleotides in crystals generally fall into two broad

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38980 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-H atoms with *e.s.d.*'s in parentheses

	x	y	z	$B_{eq}(\text{\AA}^2)$
N(1)	1031 (6)	-491	8132 (2)	2.50 (8)
C(2)	2350 (9)	-311 (4)	7222 (3)	2.91 (11)
N(3)	3788 (6)	709 (3)	6980 (2)	2.29 (8)
C(4)	3761 (6)	1637 (3)	7796 (3)	1.82 (8)
C(5)	2455 (7)	1612 (3)	8753 (3)	1.98 (9)
C(6)	1025 (6)	481 (3)	8916 (2)	1.93 (9)
N(6)	-371 (7)	300 (3)	9805 (2)	2.71 (10)
N(7)	2911 (7)	2754 (3)	9389 (2)	2.35 (8)
C(8)	4491 (8)	3427 (4)	8800 (3)	2.80 (12)
N(9)	5048 (6)	2817 (3)	7829 (2)	1.79 (8)
C(1')	6573 (7)	3301 (3)	6937 (3)	2.16 (9)
C(2')	4482 (10)	3684 (4)	5821 (3)	3.08 (11)
F	5811 (8)	3591 (2)	4871 (2)	5.12 (10)
C(3')	4023 (7)	5126 (3)	6006 (3)	2.45 (9)
O(3')	2964 (6)	5799 (3)	4954 (2)	3.61 (9)
C(4')	6972 (7)	5521 (3)	6660 (3)	1.94 (9)
O(4')	8126 (5)	4410 (2)	7360 (2)	2.37 (7)
C(5')	7049 (8)	6655 (3)	7496 (3)	2.81 (11)
O(5')	9929 (5)	6886 (3)	8092 (2)	3.10 (8)

conformational categories, i.e. C(3')-endo and C(2')-endo types. In fact, the number of ribonucleosides which appeared to have the C(3')-endo type pucker is nearly equal to that of ribonucleosides having the C(2')-endo type pucker. However, all of the 2'-fluoronucleosides, including the present dAfl, 2'-deoxy-2'-fluorinosine (Hakoshima, Omori, Tomita, Miki & Ikehara, 1981), 2'-deoxy-2'-fluorocytidine and 2'-deoxy-2'-fluorouridine (Marck, Lesying & Saenger,

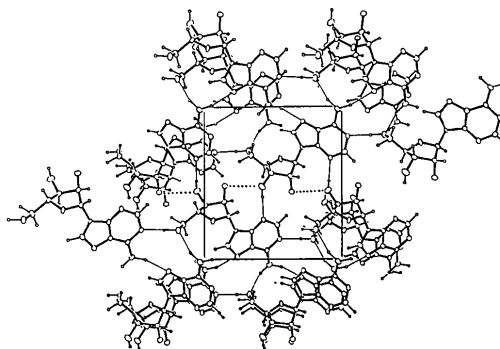


Fig. 3. The *a*-axis projection showing the packing of the molecules. Dotted lines show repulsive contacts between F and O(3').

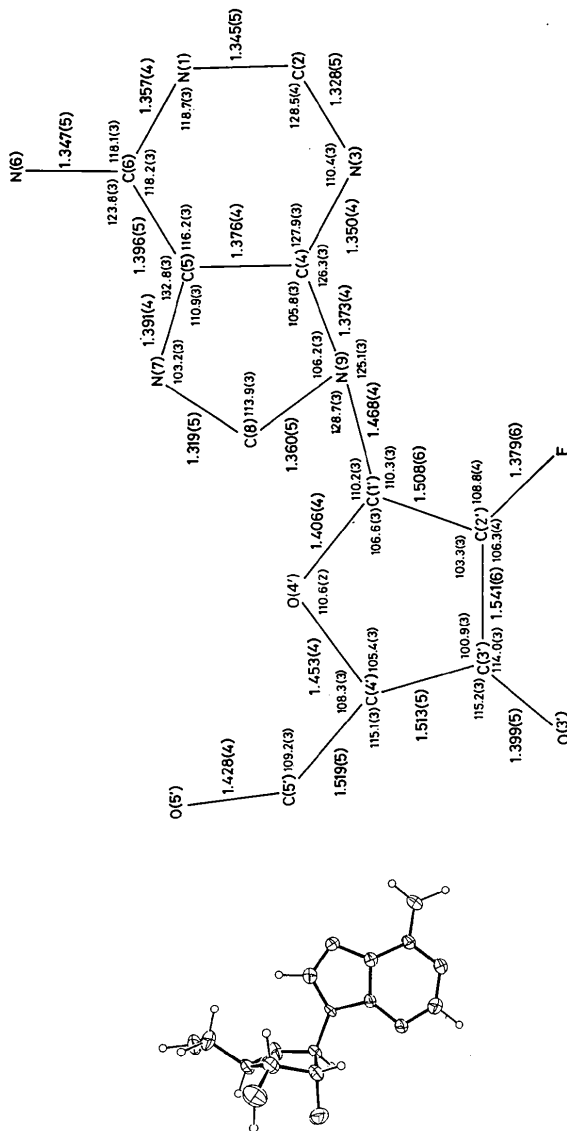


Fig. 1. Bond lengths (Å) and bond angles (°).

Fig. 2. Thermal-ellipsoid drawing of the molecule.

1982) and 2'-deoxy-2'-fluoroguanosine (Hakoshima, Fujiwara, Tomita, Imura & Ikehara, 1984), have the C(3')-endo type pucker. This fact supports NMR studies showing that all 2'-fluoronucleosides strongly prefer the C(3')-endo type pucker in solution (Uesugi, Miki, Ikehara, Iwahashi & Kyogoku, 1979; Guschlbauer & Jankowski, 1980).

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