Acta Cryst. (1984). C**40**, 880–882

Structure of 2′-Deoxyadenosine, $C_{10}H_{13}N_5O_3$

BY TOMOHIRO SATO

Shionogi Research Laboratories, Shionogi & Co. Ltd, Fukushima-ku, Osaka 553, *Japan*

(*Received* 16 *September* 1983; *accepted* 25 *January* 1984)

Abstract. $M_r = 251{\cdot}2$, monoclinic, $P2_1$, $a = 11{\cdot}298$ (2), $b = 10{\cdot}393$ (2), $c = 4{\cdot}819$ (1) Å, $\beta = 101{\cdot}51$ (2)°, $V = 554{\cdot}5$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}505$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7107$ Å, μ(Mo $K\alpha$) $= 0{\cdot}12$ mm^{-1}, $F(000) = 264$, room temperature, $R = 0{\cdot}035$ for 2241 observed reflections. The molecule has a C(3′)-*endo* (^3E) sugar associated with an *anti* glycosidic bond rotation [torsion angle O(4′)—C(1′)—N(9)—C(8)23·4 (2)°]. The conformation about the C(4′)—C(5′) bond is *gauche–trans* [torsion angle C(3′)—C(4′)—C(5′)—O(5′) 175·5 (1)°]. No appreciable base stacking is observed. All available H atoms participate in hydrogen bonds.

Introduction. The crystal structure of 2′-deoxyadenosine monohydrate has been reported (Watson, Sutor & Tollin, 1965). We have found another crystalline form of 2′-deoxyadenosine and subjected it to X-ray analysis. This study is part of a series of crystallographic investigations of nucleic acid constituents.

Experimental. Crystals grown from a methanol/carbon tetrachloride solution by vapor diffusion. Colorless prism, 0·3–0·5 mm in diameter. Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$. Lattice parameters refined by least-squares method (24 reflections, $30 < 2\theta < 39°$). $2\theta \leq 70°$ ($\sin\theta/\lambda \leq 0{\cdot}807$ Å^{-1}), ω scan ($2\theta \leq 30°$), ω—2θ scan ($2\theta > 30°$); h −18 to 17, k 0 to 16, l 0 to 7. Three standard reflections: no variation. 2549 independent reflections. No absorption correction. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located from difference Fourier map. Block-diagonal least-squares refinement. Anisotropic temperature factors for non-H atoms, isotropic for H atoms. $\sum w\Delta^2$ minimized, $\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$ for $|F_c| \geq 2\sigma(F_o)$, $w = 0$ for $|F_c| < 2\sigma(F_o)$ or $|\Delta| \geq 3\sigma(F_o)$, $\sigma(F_o) = [\sigma_1^2(F_o) + 0{\cdot}00089|F_o|^2]^{1/2}$, $\sigma_1(F_o)$ = the e.s.d. based on counting errors (Grant, Killean & Lawrence, 1969). $R = 0{\cdot}035$ for 2241 reflections ($w \neq 0$), $R_w = 0{\cdot}044$, $S = 1{\cdot}03$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are in Table 1.* Bond distances and angles are listed in Table 2. A perspective view of the molecule is shown in Fig. 1.

The deoxyribose ring adopts a typical C(3′)-*endo* (^3E) puckering, which is in significant contrast to the C(3′)-*exo* (E_3) pucker observed in 2′-deoxyadenosine monohydrate (Watson, Sutor & Tollin, 1965). The pseudorotation coordinates of the five-membered ring (Sato, 1983) are $\Pi = 36{\cdot}9$ (2) and $\Phi = 102{\cdot}2$ (2)°. C(3′)-*endo*-like sugars are found in A and Z forms of DNA (Arnott & Hukins, 1972; Wang, Quigley, Kolpak, Crawford, van Boom, van der Marel & Rich, 1979), but they are not the most common type of pucker in the crystal structures of 2′-deoxynucleosides and nucleotides so far observed (Olson & Sussman, 1982). The sugar is associated with an *anti* glycosidic bond rotation. This conformation involves a short sugar–base contact between O(4′) and C(8) [2·843 (2) Å]. The conformation about the C(4′)—C(5′) bond is *gauche–trans*: C(5′)—O(5′) is *gauche* to C(4′)—O(4′) and *trans* to C(4′)—C(3′). These conformations about the glycosidic and the C(4′)—C(5′) bonds are those commonly found in nucleosides and nucleotides.

The bond distances in the adenine base are in good agreement with the 'standard' values derived for the neutral form by Taylor & Kennard (1982) to within 0·005 Å, except for C(4)—C(5) which is 0·011 Å longer than the 'standard' value. The purine ring is slightly buckled, as in other purine nucleosides and nucleotides [see Aoki (1976), for a typical example]. Relative to the mean plane through the imidazole ring which is essentially planar (within 0·002 Å), atoms N(1), C(2) and C(6) are displaced by 0·044, 0·020 and 0·019 Å, respectively, on the same side of the plane.

Some of the structural quantities involved in the sugar ring are known to be dependent on the sugar puckering (Westhof & Sundaralingam, 1980). Therefore, the bond distances and angles of the sugar moiety were

---

* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39164 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/050880-03$01.50

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{\rm eq}=\tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
N(1)	0·1955 (1)	0·9263	0·8850 (3)	2·60 (3)
C(2)	0·2868 (1)	0·9066 (1)	0·7494 (4)	2·71 (3)
N(3)	0·3105 (1)	0·8021 (1)	0·6098 (3)	2·29 (2)
C(4)	0·2278 (1)	0·7095 (1)	0·6174 (2)	1·71 (2)
C(5)	0·1299 (1)	0·7149 (1)	0·7528 (3)	1·78 (2)
C(6)	0·1148 (1)	0·8309 (1)	0·8946 (3)	1·98 (2)
N(7)	0·0647 (1)	0·6010 (1)	0·7141 (3)	2·38 (2)
C(8)	0·1237 (1)	0·5307 (1)	0·5598 (3)	2·42 (3)
N(9)	0·2226 (1)	0·5904 (1)	0·4933 (2)	1·85 (2)
N(6)	0·0259 (1)	0·8518 (1)	1·0358 (3)	2·74 (3)
O(4′)	0·2672 (1)	0·4300 (1)	0·1884 (2)	2·11 (2)
C(1′)	0·3160 (1)	0·5375 (1)	0·3512 (3)	1·91 (2)
C(2′)	0·4247 (1)	0·4899 (2)	0·5666 (3)	2·55 (3)
C(3′)	0·3956 (1)	0·3480 (1)	0·5957 (3)	2·17 (2)
C(4′)	0·3320 (1)	0·3144 (1)	0·2930 (2)	1·85 (2)
O(3′)	0·4959 (1)	0·2689 (1)	0·7039 (3)	3·18 (3)
C(5′)	0·2444 (1)	0·2043 (1)	0·2696 (3)	2·57 (3)
O(5′)	0·1845 (1)	0·1889 (1)	−0·0177 (2)	2·80 (2)

Table 2. *Molecular dimensions*

Bond distances (Å)			
N(1)–C(2)	1·342 (2)	C(8)–N(9)	1·371 (2)
N(1)–C(6)	1·354 (2)	N(9)–C(1′)	1·474 (2)
C(2)–N(3)	1·333 (2)	O(4′)–C(1′)	1·412 (2)
N(3)–C(4)	1·347 (2)	O(4′)–C(4′)	1·444 (2)
C(4)–C(5)	1·393 (2)	C(1′)–C(2′)	1·524 (3)
C(4)–N(9)	1·371 (2)	C(2′)–C(3′)	1·524 (3)
C(5)–C(6)	1·413 (2)	C(3′)–C(4′)	1·532 (2)
C(5)–N(7)	1·387 (2)	C(3′)–O(3′)	1·413 (2)
C(6)–N(6)	1·339 (2)	C(4′)–C(5′)	1·502 (2)
N(7)–C(8)	1·315 (2)	C(5′)–O(5′)	1·424 (2)
Bond angles (°)			
C(2)–N(1)–C(6)	119·5 (1)	C(4)–N(9)–C(1′)	124·5 (1)
N(1)–C(2)–N(3)	128·4 (2)	C(8)–N(9)–C(1′)	129·2 (1)
C(2)–N(3)–C(4)	111·0 (1)	C(1′)–O(4′)–C(4′)	110·5 (1)
N(3)–C(4)–C(5)	127·2 (1)	N(9)–C(1′)–O(4′)	108·5 (1)
N(3)–C(4)–N(9)	127·1 (1)	N(9)–C(1′)–C(2′)	111·0 (1)
C(5)–C(4)–N(9)	105·8 (1)	O(4′)–C(1′)–C(2′)	107·1 (1)
C(4)–C(5)–C(6)	116·4 (1)	C(1′)–C(2′)–C(3′)	102·6 (1)
C(4)–C(5)–N(7)	110·7 (1)	C(2′)–C(3′)–C(4′)	101·6 (1)
C(6)–C(5)–N(7)	132·9 (1)	C(2′)–C(3′)–O(3′)	115·2 (1)
N(1)–C(6)–C(5)	117·5 (1)	C(4′)–C(3′)–O(3′)	114·1 (1)
N(1)–C(6)–N(6)	118·5 (1)	O(4′)–C(4′)–C(3′)	104·6 (1)
C(5)–C(6)–N(6)	124·0 (1)	O(4′)–C(4′)–C(5′)	109·1 (1)
C(5)–N(7)–C(8)	103·6 (1)	C(3′)–C(4′)–C(5′)	114·9 (1)
N(7)–C(8)–N(9)	114·2 (1)	C(4′)–C(5′)–O(5′)	109·7 (1)
C(4)–N(9)–C(8)	105·8 (1)		

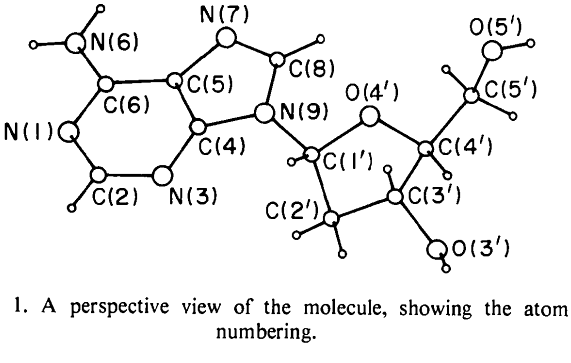

Fig. 1. A perspective view of the molecule, showing the atom numbering.

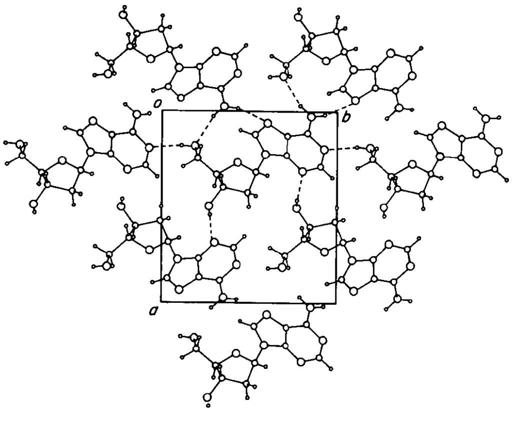

Fig. 2. A projection of the structure viewed along the c axis. Hydrogen bonds are shown as broken lines.

compared with those found in the well refined structure of 2′-deoxycytidine hydrochloride (Subramanian & Hunt, 1970) in which the sugar is puckered in a C(2′)-*exo*–C(3′)-*endo* ($^3T_2$) form similar to the present one. It shows that the bond angles of both structures are generally in good agreement (within 1·3°). In particular, the differences in the endocyclic bond angles are as low as 0·7°. On the other hand, the agreement in the bond distances is not so good: for example, deviations of up to 0·016 Å are observed in the endocyclic bonds. It seems unlikely that these differences arise simply from a small change in the sugar puckering.

The packing and hydrogen-bonding scheme in the crystal are shown in Fig. 2. No appreciable base stacking is observed in the structure. All available H atoms participate in hydrogen bonds, *i.e.* N(6)–H(1)···N(7) 3·115 (2), N(6)–H(2)···O(5′) 2·905 (2), O(3′)–H···N(3) 2·917 (2), and O(5′)–H···N(1) 2·776 (2) Å. There are no other notable short intermolecular contacts.

References

Aoki, K. (1976). *Acta Cryst.* B**32**, 1454–1459.

Arnott, S. & Hukins, D. W. L. (1972). *Biochem. Biophys. Res. Commun.* **47**, 1504–1509.

Grant, D. F., Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* B**25**, 374–376.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–75. Birmingham: Kynoch Press.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Olson, W. K. & Sussman, J. L. (1982). *J. Am. Chem. Soc.* **104**, 270–278.

Sato, T. (1983). *Nucleic Acids Res.* **11**, 4933–4938.

Subramanian, E. & Hunt, D. J. (1970). *Acta Cryst.* B**26**, 303–311.

Taylor, R. & Kennard, O. (1982). *J. Mol. Struct.* **78**, 1–28.
Wang, A. H.-J., Quigley, G. J., Kolpak, F. J., Crawford, J. L., van Boom, J. H., van der Marel, G. & Rich, A. (1979). *Nature (London)*, **282**, 680–686.
Watson, D. G., Sutor, D. J. & Tollin, P. (1965). *Acta Cryst.* **19**, 111–124.
Westhof, E. & Sundaralingam, M. (1980). *J. Am. Chem. Soc.* **102**, 1493–1500.

Acta Cryst. (1984). C**40**, 882–884

Structure of (3a*S*)-7-Chloro-4-(2-dimethylaminoethyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]benzothiadiazine 5,5-Dioxide, $C_{15}H_{22}ClN_3O_2S$

By Roberta Oberti

CNR Centro di Studio per la Cristallografia Strutturale, c/o Dipartimento di Scienze della Terra, Sezione Mineralogico Petrografica, Università, Via A. Bassi 4, 27100 *Pavia, Italy*

Maria Teresa Bernabei, Flavio Forni and Riccardo Cameroni

Istituto di Chimica Farmaceutica e Tossicologica dell'Università, Via S. Eufemia 19, 41100 *Modena, Italy*

and Ermanno Galli

Istituto di Mineralogia e Petrologia dell'Università, Via S. Eufemia 19, 41100 *Modena, Italy*

(*Received* 5 *December* 1983; *accepted* 3 *January* 1984)

Abstract. $M_r = 343\cdot9$, monoclinic, $P2_1/c$, $a = 10\cdot226\ (1)$, $b = 13\cdot155\ (1)$, $c = 12\cdot722\ (1)$ Å, $\beta = 100\cdot59(1)^\circ$, $V = 1682\cdot3\ (3)$ Å^3, $Z = 4$, $D_m = 1\cdot35\ (3)$, $D_x = 1\cdot358$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 3\cdot26$ mm^{-1}, $F(000) = 728$, room temperature, final $R = 0\cdot064$ for 1341 observed reflections. As in the 7-chloro-4-ethyl-2,3,3a,4-tetrahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]benzothiadiazine 5,5-dioxide [Oberti, Bernabei, Forni, Cameroni & Galli (1983). *Acta Cryst.* C**39**, 1278–1280] the thiadiazine and pyrrolidine rings exibit sofa and twist conformations with some conjugation between N(2), which is sp^2 hybridized, and the benzene ring. Only minor differences have been found on comparison of the structure of the title compound with that of the above mentioned compound.

Introduction. A series of 4-dimethylaminoethyl and 4-diethylaminoethyl derivatives of 2,3,3a,4-tetrahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]benzothiadiazine 5,5-dioxide substituted or unsubstituted in the benzene ring was prepared and subjected to preliminary investigation using the cardiovascular system of the anesthetized rat by Bernabei, Cameroni, Forni, Bellei & Baggio (1978). The introduction of a basic group in the alkyl chain gives compounds with a most pronounced hypotensive activity and a marked increase in differential pressure, sometimes accompanied by some bradycardiac activity. The X-ray crystal-structure determination of the title compound was undertaken in order to study the geometry of the tetrahydro-1*H*-pyrrolobenzothiadiazine system, the results of which should be useful in the interpretation of its biological properties.

Experimental. Transparent lath-shaped crystals (from 2-propanol), 0·6 × 0·3 × 0·2 mm; D_m by flotation; Philips PW 1100 four-circle diffractometer; accurate cell parameters from 25 high-angle reflections using the Philips *LAT* routine; ω–2θ scan mode, scan width = 1·2°, scan speed = 0·04° s^{-1}, each background time 5 s; 3 standard reflections monitored at 4 h intervals with max. intensity variation 4·6% (correction applied); 1740 unique reflections ($h = -10$ to 10, $k = 0$ to 13, $l = 0$ to 13, $2 \leq \theta \leq 50^\circ$), 399 of which [$I \leq 3\sigma(I)$] were considered unobserved; corrections for Lp and absorption (spherical shape, $r = 0\cdot025$ cm; max. and min. absorption corrections 1·440 and 0·751); direct methods (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), C(14) from ΔF synthesis; full-matrix refinement on F (*ORFLS*; Busing, Martin & Levy, 1962); coordinates of H atoms calculated by geometrical considerations (*XANADU*; Roberts & Sheldrick, 1975) and confirmed by ΔF synthesis; refined parameters: coordinates and anisotropic thermal parameters for non-H atoms, and alternately scale factor and secondary anisotropic extinction coefficient [final value = $2\cdot1\ (1) \times 10^{-4}$ following Coppens & Hamilton (1970)]; R(including zeros) = 0·064, R(omitting zeros) = 0·047, $R_w = 0\cdot048$, each reflection given a weight based on counting statistics; max. and min. heights in final difference Fourier map 0·27 and −0·26 e Å^{-3}; max. Δ/σ in the final refinement cycle

0108-2701/84/050882-03$01.50