118 K may be ascribed to the anharmonicities which still remain at this temperature.

On lowering the temperature, an increase in the torsion angles of the C—Ph bond was observed. This is expected to be accompanied by the shortening of the ethylenic bond since its bond order is increased by the twisting of the C—Ph bond. But, in fact, a lengthening of the ethylenic bond was observed on lowering the temperature. This result may be explained by the assumption that on lowering temperature the shortening of the bond caused by the increase of the torsion angle of the C—Ph bond was outweighed by the lengthening due to the decrease of the above-mentioned anharmonicity.

The present study demonstrates that X-ray crystallographic data which apparently seem to be normal may not always give fully reliable geometry for a molecule and that the molecular structure may be changed without phase transition in a crystal on varying the temperature.

References

ALLINGER, N. L. (1982). QCPE Program No. *MMP2*. Quantum Chemistry Program Exchange, Indiana Univ., Bloomington, IN, USA.

ALLINGER, N. L. & FLANAGAN, H. L. (1983). *J. Comput. Chem.* **4**, 399.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

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.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

TIRADO-RIVES, J., FRONCZEK, F. R. & GANDOUR, R. D. (1985). *Acta Cryst.* C**41**, 1327–1329.

Acta Cryst. (1988). C**44**, 508–510

Structure of 3-Isoadenosine

BY SHIV KUMAR, SCOTT R. WILSON AND NELSON J. LEONARD*

School of Chemical Sciences, University of Illinois, 1209 *W. California St, Urbana,*
Illinois 61801-3731, *USA*

(*Received* 3 *August* 1987; *accepted* 4 *November* 1987)

Abstract. 3-β-D-Ribofuranosyladenine, $C_{10}H_{13}N_5O_4$, $M_r = 267{\cdot}25$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}470$ (4), $b = 16{\cdot}054$ (6), $c = 5{\cdot}141$ (2) Å, $V = 1111{\cdot}8$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}596$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}18$ cm^{-1}, $F(000) = 560$, $T = 298$ K, $R = 0{\cdot}043$, $wR = 0{\cdot}042$ for 1136 reflections. The tautomeric form present in the crystal is 6-NH_2. The adenine moiety is nearly planar and the torsional angle of the glycosidic linkage O(4′)—C(1′)—N(3)—C(4) is −161·5°. All N and O atoms except N(3) and O(4′) participate in a three-dimensional hydrogen-bonding system.

Introduction. 3-Isoadenosine (Leonard & Laursen, 1963, 1965) is an isomer of adenosine in which the D-ribofuranosyl moiety is attached to N(3) of adenine. Because of the close spatial relationship between these two compounds (Leonard, Cruickshank, Groziak, Clauson & Devadas, 1986), the determination of the structure of 3-isoadenosine is desired in order to furnish information concerning the preferred tautomeric form in the crystal, the orientation of the ribose ring, and the intermolecular hydrogen-bonding pattern, and to compare its structure with adenosine (Lai & Marsh, 1972) and other known N(3)-substituted adenines (Petersen & Furberg, 1975; Kistenmacher, Urmey & Rossi, 1977).

Experimental. The title compound was recrystallized from water as transparent, colorless acicular crystals of dimensions approximately 0·1 × 0·2 × 0·8 mm; D_m was not measured. The X-ray data were measured with a Syntex $P2_1$ automated four-circle diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation. The lattice parameters were refined using 15 reflections with 2θ values between 17·8 and 19·5°; 1448 unique reflections were measured ($+h$, $+k$, $+l$) to the limit of $2\theta < 54{\cdot}0°$ using the $\omega/2\theta$ scan technique, scan rate 2·0–15·0° min^{-1}, scan range 1·7° with a scan-to-background ratio of 0·25, 1136 reflections with $I > 2{\cdot}58\sigma(I)$, $\sigma(F_o^2)$ based on counting statistics plus the term $0{\cdot}02F_o^2$. Anomalous-dispersion, Lorentz, and polarization corrections were applied. Three standard intensities monitored per 100 reflections showed no

---

* To whom all correspondence should be addressed.

0108-2701/88/030508-03$03.00

significant intensity variation. The structure was solved using the direct-methods program *SHELX*86 (Sheldrick, 1985). The correct positions for all non-hydrogen atoms were deduced from an *E* map and were refined (*SHELX*76; Sheldrick, 1976) with anisotropic thermal coefficients in a process that minimized $\sum[w(|F_o| - |F_c|)^2]$, where $w = 1/[\sigma(F_o)]^2$. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974). H atoms were located by difference electron-density maps and were refined with a group isotropic thermal parameter; an empirical isotropic extinction parameter converged to $6{\cdot}15\,(7) \times 10^{-7}$. The final agreement factors for 1136 reflections were $R = 0{\cdot}043$ and $wR = 0{\cdot}042$ and goodness-of-fit $E = 1{\cdot}26$; max. $|\Delta/\sigma| < 0{\cdot}01$; range of residual electron density $= +0{\cdot}27 > \Delta\rho > -0{\cdot}27$ e Å^{-3}. Anomalous dispersion using molybdenum radiation would probably be insufficient to distinguish between enantiomers but it is known that the sugar moiety has the D configuration.

Discussion. An *ORTEP* view (Johnson, 1965) of the molecule of 3-isoadenosine, together with the standard adenosine atom numbering, is given in Fig. 1. The final atomic coordinates for the non-hydrogen atoms are given in Table 1, and selected bond lengths and bond angles are listed in Table 2.* As has been found for other N(3)-substituted adenines, 3-isoadenosine exists in the 6-NH_2 tautomeric form. Adenosine (Lai & Marsh, 1972) and other N(9)-substituted adenines also exist in 6-NH_2 form. The bond lengths and bond angles of the aglycone of 3-isoadenosine match those of other known N(3)-substituted adenines, namely 3-ethyladenine and tricanthine (3-Δ^2-isopentenyladenine) (Petersen & Furberg, 1975; Kistenmacher *et al.*, 1977). The N(3)—C(1′) bond length, 1·488 (5) Å, in 3-isoadenosine, is close to that in tricanthine (1·486 Å) (Kistenmacher *et al.*, 1977) and comparable to the N(9)—C(1′) bond length in adenosine (1·466 Å) (Lai & Marsh, 1972).

Table 1. *Final atomic parameters for non-*H *atoms with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

The equivalent isotropic *U* is defined as one-third the value of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
N(1)	0·3453 (2)	0·0656 (2)	−0·0682 (7)	0·028 (2)
N(3)	0·4768 (2)	0·1361 (2)	0·1469 (6)	0·023 (1)
N(6)	0·3712 (2)	−0·0223 (2)	−0·4167 (7)	0·033 (2)
N(7)	0·5952 (2)	0·0036 (2)	−0·3095 (6)	0·025 (1)
N(9)	0·6436 (2)	0·0976 (2)	0·0048 (6)	0·025 (1)
C(2)	0·3799 (3)	0·1175 (2)	0·1069 (8)	0·029 (2)
C(4)	0·5432 (2)	0·0934 (2)	−0·0050 (7)	0·021 (2)
C(5)	0·5120 (2)	0·0382 (2)	−0·1930 (8)	0·022 (2)
C(6)	0·4091 (2)	0·0255 (2)	−0·2331 (7)	0·024 (2)
C(8)	0·6683 (2)	0·0414 (2)	−0·1826 (8)	0·024 (2)
C(1′)	0·5135 (2)	0·1984 (2)	0·3384 (7)	0·023 (2)
C(2′)	0·5400 (2)	0·2811 (2)	0·2041 (8)	0·025 (2)
C(3′)	0·4431 (3)	0·3294 (2)	0·2418 (7)	0·024 (2)
C(4′)	0·4102 (2)	0·3015 (2)	0·5097 (7)	0·020 (2)
C(5′)	0·2999 (2)	0·3097 (3)	0·5501 (8)	0·027 (2)
O(2′)	0·6158 (2)	0·3237 (2)	0·3405 (7)	0·039 (2)
O(3′)	0·4550 (2)	0·4169 (2)	0·2324 (5)	0·032 (1)
O(4′)	0·4394 (2)	0·2144 (1)	0·5234 (5)	0·027 (1)
O(5′)	0·2690 (2)	0·2819 (2)	0·7997 (5)	0·030 (2)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and hydrogen-bond parameters*

N(1)—C(2)	1·312 (5)	N(3)—C(1′)	1·488 (5)
C(2)—N(3)	1·354 (4)	C(1′)—C(2′)	1·538 (5)
N(3)—C(4)	1·371 (4)	C(2′)—O(2′)	1·415 (4)
C(4)—C(5)	1·378 (5)	C(2′)—C(3′)	1·531 (5)
C(5)—C(6)	1·416 (4)	C(3′)—O(3′)	1·414 (4)
C(6)—N(1)	1·368 (4)	C(3′)—C(4′)	1·515 (5)
C(6)—N(6)	1·320 (5)	C(4′)- O(4′)	1·453 (4)
C(5)—N(7)	1·387 (4)	C(4′)—C(5′)	1·506 (4)
N(7)—C(8)	1·327 (4)	C(5′)—O(5′)	1·421 (5)
C(8)—N(9)	1·362 (5)	C(1′)—O(4′)	1·403 (4)
N(9)—C(4)	1·355 (4)		

C(2)—N(1)—C(6)	120·0 (3)	N(3)—C(4)—N(9)	127·2 (3)
N(1)—C(2)—N(3)	125·9 (3)	N(7)—C(5)—C(6)	132·2 (3)
C(2)—N(3)—C(4)	115·6 (3)	C(2)—N(3)—C(1′)	124·7 (3)
N(3)—C(4)—C(5)	121·5 (3)	C(4)—N(3)—C(1′)	119·7 (3)
C(4)—C(5)—C(6)	119·5 (3)	C(1′)—C(2′)—C(3′)	100·5 (3)
C(5)—C(6)—N(1)	117·2 (3)	C(2′)—C(3′)—C(4′)	102·5 (3)
N(1)—C(6)—N(6)	118·3 (3)	C(3′)—C(4′)—O(4′)	104·5 (3)
N(6)—C(6)—C(5)	124·5 (3)	O(4′)—C(1′)—C(2′)	108·1 (3)
C(5)—N(7)—C(8)	101·8 (3)	C(4′)—O(4′)—C(1′)	109·6 (2)
N(7)—C(8)—N(9)	118·0 (3)	N(3)—C(1′)—O(4′)	109·6 (3)
N(9)—C(4)—C(5)	111·3 (3)	C(1′)—C(2′)—O(2′)	111·3 (3)
C(4)—C(5)—N(7)	108·3 (3)	C(2′)—C(3′)—O(3′)	113·8 (3)
C(4)—N(9)—C(8)	100·6 (3)		

N(6H)*A*···N(1)	2·21 (4)	N(6)*A*···N(1)	3·097 (4)
N(6H)*B*···O(3′)	2·22 (4)	N(6)*B*···O(3′)	3·012 (4)
H(2′)···O(5′)	1·97 (3)	O(2′)···O(5′)	2·766 (4)
H(3′)···N(7)	1·79 (4)	O(3′)···N(7)	2·669 (4)
H(5′)···N(9)	1·98 (4)	O(5′)···N(9)	2·757 (4)
N(6)—H(6)*A*···N(1)	163 (3)	O(2′)—H(2′)···O(5′)	167 (3)
N(6)—H(6)*B*···O(3′)	153 (3)	O(3′)—H(3′)···N(7)	158 (3)
		O(5′)—H(5′)···N(9)	170 (4)

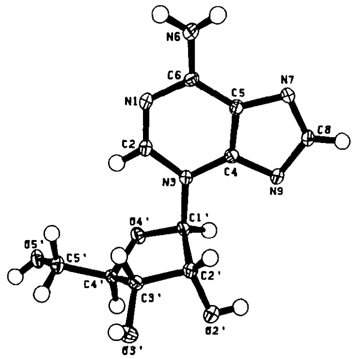

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the molecule with the atom numbering.

---

* Lists of structure factors, anisotropic thermal parameters, mean-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44513 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

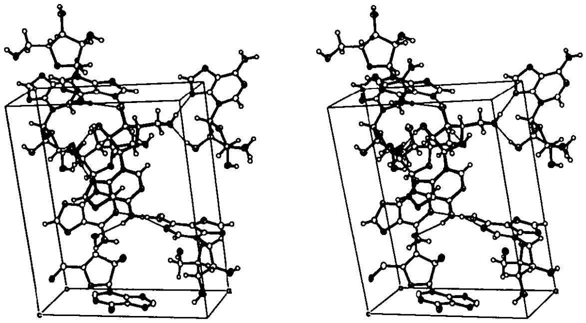

Fig. 2. Stereoscopic view of the unit cell with hydrogen bonding.

The adenine ring of the molecule is nearly planar (Fig. 1), but is slightly folded about the C(4)—C(5) vector with an interplanar angle of 2·5°. The torsion-angle values of N(1)—C(6)—N(6)—HN(6)*A* and N(1)—C(6)—N(6)—HN(6)*B*, 1 (3) and 171 (3)°, respectively, are indicative of the approximate coplanarity of the two amino H atoms at N(6) with the bicyclic ring. As in adenosine, the furanose ring is puckered with a C(3′) *endo* conformation.

A stereoview of the crystal packing arrangement is shown in Fig. 2. As with adenosine, all N and O atoms except N(3) and O(4′) [O(1′)] participate in a three-dimensional hydrogen-bonding scheme. In the crystal structure of adenosine the 6-amino group donates a hydrogen bond to both the N(7) and O(5′) atoms of a neighboring adenosine molecule. In tricanthine and 3-ethyladenine, this same amino group participates in a hydrogen-bonding scheme with two neighboring molecules. In tricanthine the N(1) atom of one neighbor and the N(7) atom of the other participate in this scheme, whereas in 3-ethyladenine it is the N(7) atom of one neighbor and the N(9) atom of the second neighbor that participate. 3-Isoadenosine represents yet another variation in the hydrogen-bonding pattern. The 6-amino-group H bonds with the N(1) atom of one neighbor and the O(3′) atom of the second neighboring molecule. The hydrogen-bond-related lengths and angles are provided in Table 2.

This work was supported by a grant from the National Institutes of Health (GM-34125).

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kistenmacher, T. J., Urmey, W. F. & Rossi, M. (1977). *J. Cryst. Mol. Struct.* 7, 219–227.

Lai, T. F. & Marsh, R. E. (1972). *Acta Cryst.* **B28**, 1982–1989.

Leonard, N. J., Cruickshank, K. A., Groziak, M. P., Clauson, G. L. & Devadas, B. (1986). *Ann. NY Acad. Sci.* **471**, 255–265 (and references cited therein).

Leonard, N. J. & Laursen, R. A. (1963). *J. Am. Chem. Soc.* **85**, 2026–2027.

Leonard, N. J. & Laursen, R. A. (1965). *Biochemistry*, **4**, 354–365.

Petersen, C. H. & Furberg, A. (1975). *Acta Chem. Scand. Ser. B*, **29**, 37–40.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELX86*. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Kruger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Acta Cryst. (1988). C**44**, 510–512

Structure of (4*SR*,6a*RS*)-4-[2-(2-Methyl-1,3-dioxolan-2-yl)ethyl]-4,5,6,6a-tetrahydro-5,5,6a-trimethyl-2(1*H*)-pentalenone

By Veerapaneni Nalini and Gautam R. Desiraju*

School of Chemistry, University of Hyderabad, PO Central University, Hyderabad 500 134, *India*

(*Received* 30 *March* 1987; *accepted* 28 *October* 1987)

Abstract. $C_{17}H_{26}O_3$, $M_r = 278{\cdot}21$, triclinic, $P\bar{1}$, $a = 7{\cdot}545\ (1)$, $b = 10{\cdot}465\ (2)$, $c = 10{\cdot}629\ (1)$ Å, $\alpha = 95{\cdot}41\ (1)$, $\beta = 103{\cdot}32\ (1)$, $\gamma = 104{\cdot}30\ (1)^\circ$, $V = 781{\cdot}1\ (2)$ Å^3, $Z = 2$, $F(000) = 304$, $D_x = 1{\cdot}18$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo}\ K\alpha) = 0{\cdot}74$ cm^{-1}, $T = 133$ K, $R = 0{\cdot}046$, $wR = 0{\cdot}053$ with 1659 independent non-zero reflections. The stereochemistry is 4*SR*, 6a*RS*, the two fused rings form a boat-like arrangement and the crystal structure is stabilized by distinctive directionally-specific C—H···O hydrogen bonds.

Introduction. In the course of the stereoselective synthesis of (±)-silphenene from isophorone (Rao & Nagarajan, unpublished results) the pentalenone (1)

---

* To whom all correspondence should be addressed.

0108-2701/88/030510-03$03.00