distances referred to as hydrogen bonds are fairly short (between 2·567 and 2·733 Å in mellite, between 2·64 and 2·68 Å in mellitic acid); accordingly the H-bonds are strong enough to justify the cohesion of mellite. All the oxygen atoms excepting $O_w(5)$ have three neighbouring atoms: 1 Al and 2 H for water oxygens, 1 C and 2 H for carboxyl oxygens. $O_w(5)$ is approximately tetrahedrally surrounded by four hydrogen atoms.

It is not unlikely that the observed tilts of the carboxyl groups with respect to the benzene ring are related, partly at least, to the hydrogen bonding system. If, for instance, the plane of the carboxyl groups were perpendicular to the benzene ring, the $O_w(4)$–$O(2^{ix})$ distance would be too long for a hydrogen bond; on the other side the $O_w(5)$–$O(1^{v})$ distance would be too short.

In conclusion, the structure of mellite can be regarded as composed of discrete $Al(H_2O)_6$ octahedra and $C_6(COO)_6$ radicals with strong hydrogen bonds between octahedra and metallic radicals, with the additional contribution of the 'free' water molecule.

References

Barth, F. W. & Ksanda, C. J. (1933). *Amer. Min.* **18**, 8–13.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Darlow, W. S. F. (1961). *Acta Cryst.* **14**, 159–166.

Duchamp, D. J. & Marsh, R. E. (1969). *Acta Cryst.* B**25**, 5–19.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jobbins, E. A., Sergeant, G. A. & Young, B. R. (1965). *Miner. Mag.* **35**, 542–544.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Kennard, O., Wampler, D. L., Coppola, J. C., Motherwell, W. D. S., Watson, D. G. & Larson, A. C. (1971). *Acta Cryst.* B**27**, 1116–1123.

Nowacki, W. & Jaggi, H. (1957). *Z. Kristallogr.* **109**, 272–283.

Okaya, Y. (1965). *Acta Cryst.* **19**, 879–882.

Palache, C., Berman, H. & Frondel, C. (1951). *Dana's System of Mineralogy*. Vol. II, pp. 1104–1105. New York: John Wiley.

Acta Cryst. (1973). B**29**, 31

The Crystal and Molecular Structure of Adenosine Hydrochloride

By Keiji Shikata,* Tatzuo Ueki and Toshio Mitsui

Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

(*Received* 13 *July* 1972; *accepted* 15 *September* 1972)

The crystal structure of adenosine hydrochloride ($C_{10}H_{13}N_5O_4.HCl$) has been determined using three-dimensional intensity data collected on a four-circle diffractometer. The crystal is monoclinic, space group $P2_1$. There are two molecules in the unit cell of dimensions $a=6\cdot647\pm0\cdot003$, $b=16\cdot739\pm0\cdot005$, $c=6\cdot397\pm0\cdot002$ Å and $\beta=114°54'\pm4'$. The structure was solved by the heavy-atom method and refined by the method of block-diagonal least squares. The final R value is 0·037 for 1895 observed reflexions including those of zero intensity. Adenosine is protonated at N(1) in the crystal. The purine ring is almost exactly planar. In comparison with the structure of the non-protonated adenosine molecule reported by Lai & Marsh [*Acta Cryst.* (1972). B**28**, 1982–1989] significant differences have been found in four bond lengths and three bond angles in the purine ring. The dihedral angle between the least-squares planes of the base and the ribose is 107·9° and the glycosidic torsional angle, φ_{CN}, is $-43°$. The ribose ring is in the C(2′)-*endo*-C(3′)-*exo* conformation, and the C(2′) atom is displaced by 0·60 Å from the least-squares plane of the remaining four ring atoms. The orientation of the C(5′)–O(5′) bond is *gauche* with respect to the bonds C(4′)–O(1′) and C(4′)–C(3′).

Introduction

Accurate information is desired on the structure of the adenosine molecule because of its importance in bioenergetics and genetics. In this connexion a considerable number of studies have been carried out on the non-protonated adenosine compounds, *viz.*, deoxyadenosine (Watson, Sutor & Tollin, 1965), 3′-*O*-acetyladenosine (Rao & Sundaralingam, 1970), 2′-amino-2′-deoxyadenosine (Rohrer & Sundaralingam, 1970) and adenosine (Lai & Marsh, 1972), and on protonated adenosine compounds, *viz.*, adenosine 5′-phosphate (Kraut & Jensen, 1963) and adenosine 3′-phosphate (Sundaralingam, 1966). The present paper provides accurate information on the structure of protonated adenosine molecule in the crystal of adenosine hydrochloride.

---

* Present address: Research and Development Centre, Maruzen Oil Company, Satte, Kita-katsushika, Saitama, Japan.

Experimental

Crystals of adenosine hydrochloride were obtained from aqueous ethanol solution by evaporation at 0 °C. They were colourless and parallelepiped in shape. The crystal used for the X-ray measurements had the dimensions $0·12 \times 0·27 \times 0·29$ mm and was mounted on a goniometer head with its *b* axis parallel to the spindle axis. The space group was determined from oscillation and Weissenberg photographs. The systematic absence of 0*k*0 reflexions with *k* odd suggests that the space group is either $P2_1$ or $P2_1/m$, and the former was adopted since the molecule is optically active. The unit-cell dimensions were measured on a diffractometer.

Crystal data

Adenosine hydrochloride $C_{10}H_{13}N_5O_4.HCl$
Monoclinic
Space group $P2_1$
$a=6·647\pm0·003$, $b=16·739\pm0·005$,
$c=6·397\pm0·002$Å, $\beta=114°54'\pm4'$;
$Z=2$
$D_m=1·559$ g cm^{-3}
$D_x=1·562$
λ(Mo $K\alpha$)$=0·71069$ Å.

Intensities were measured on a Rigaku automatic four-circle diffractometer with the ω–2θ scanning method, using Zr-filtered Mo $K\alpha$ radiation and a scintillation counter connected to a pulse-height analyser. Nickel foil attenuators were used to maintain measurements within the linear region of the scintillation counter. 1895 independent reflexions corresponding to $\sin\theta/\lambda\le0·699$ Å^{-1} were measured. All these reflexions, including those of zero intensity, were used for the least-squares calculations. In view of the small linear absorption coefficient ($\mu=3·25$ cm^{-1} for Mo $K\alpha$ radiation), no absorption correction was made. The extinction effect was found to be neglegible at the final stage of the refinement.

Structure determination and refinement

The coordinates of the chloride ion were deduced from a three-dimensional Patterson function. A Fourier synthesis based on the coordinates of the chloride ion revealed positions of all the non-hydrogen atoms. Block-diagonal least-squares refinements were made

Table 1. *Positional parameters with the estimated standard deviations for the non-hydrogen atoms*

Positional parameters are in fractions of the unit cell axes and the e.s.d.'s in parentheses

	x	*y*	*z*
Cl	−0·1128 (7)	−0·0001 (9)	−0·2243 (8)
N(1)	−0·6519 (26)	0·0654 (27)	−0·1333 (29)
C(2)	−0·6622 (32)	0·1039 (33)	−0·3248 (35)
N(3)	−0·5100 (25)	0·1521 (26)	−0·3314 (26)
C(4)	−0·3405 (27)	0·1612 (27)	−0·1206 (28)
C(5)	−0·3191 (28)	0·1267 (30)	0·0846 (28)
C(6)	−0·4836 (29)	0·0735 (29)	0·0784 (30)
N(6)	−0·4838 (31)	0·0324 (30)	0·2553 (30)
N(7)	−0·1236 (28)	0·1490 (28)	0·2642 (27)
C(8)	−0·0313 (35)	0·1966 (34)	0·1679 (33)
N(9)	−0·1543 (25)	0·2060 (24)	−0·0665 (25)
C(1′)	−0·0978 (28)	0·2538 (28)	−0·2252 (29)
O(1′)	0·1293 (22)	0·2403 (21)	−0·1692 (26)
C(2′)	−0·1191 (28)	0·3436 (29)	−0·1963 (29)
O(2′)	−0·3373 (21)	0·3736 (23)	−0·3085 (22)
C(3′)	0·0464 (31)	0·3762 (30)	−0·2833 (31)
O(3′)	−0·0532 (25)	0·3727 (29)	−0·5292 (24)
C(4′)	0·2341 (31)	0·3146 (31)	−0·1876 (33)
C(5′)	0·4240 (31)	0·3340 (34)	0·0404 (34)
O(5′)	0·3634 (23)	0·3429 (25)	0·2283 (23)

Table 2. *Anisotropic thermal parameters* ($\times 10^5$) *for the non-hydrogen atoms*

The parameters are of the form:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right].$$

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	1725 (15)	211 (2)	2332 (18)	20 (11)	−1902 (27)	43 (12)
N(1)	1309 (57)	236 (9)	2242 (75)	160 (38)	−1121 (110)	86 (44)
C(2)	1475 (72)	258 (11)	2020 (86)	12 (45)	−372 (129)	226 (49)
N(3)	1402 (56)	245 (9)	1688 (65)	19 (38)	−675 (100)	163 (40)
C(4)	1366 (59)	149 (8)	1615 (68)	−22 (37)	−1172 (106)	−32 (39)
C(5)	1464 (62)	169 (8)	1612 (68)	108 (41)	−1015 (108)	12 (43)
C(6)	1468 (64)	178 (8)	1803 (73)	−21 (40)	−1438 (117)	−45 (42)
N(6)	2392 (83)	281 (10)	2013 (76)	510 (49)	−1856 (133)	52 (46)
N(7)	1968 (68)	276 (10)	1575 (65)	513 (44)	−632 (110)	46 (42)
C(8)	1864 (79)	276 (11)	1719 (80)	423 (50)	−434 (128)	126 (51)
N(9)	1499 (59)	181 (7)	1450 (60)	196 (34)	−952 (97)	18 (35)
C(1′)	1382 (63)	187 (8)	1612 (70)	151 (39)	−1598 (111)	−26 (41)
O(1′)	1562 (52)	185 (7)	3047 (75)	−14 (31)	−2533 (106)	−79 (37)
C(2′)	1290 (61)	186 (8)	1574 (70)	86 (39)	−1152 (111)	19 (42)
O(2′)	1410 (49)	260 (7)	1818 (55)	−196 (33)	−1244 (88)	−5 (35)
C(3′)	1613 (69)	213 (9)	1760 (74)	264 (43)	−1518 (119)	89 (46)
O(3′)	2281 (68)	437 (11)	1700 (61)	551 (48)	−1675 (110)	350 (44)
C(4′)	1475 (67)	246 (10)	1985 (80)	181 (43)	−1958 (126)	−114 (47)
C(5′)	1413 (69)	281 (11)	2095 (86)	−30 (48)	−1490 (129)	−125 (52)
O(5′)	1881 (57)	287 (8)	1914 (61)	−376 (38)	−1328 (99)	−34 (39)

Table 3. *Positional parameters with e.s.d.'s and the isotropic thermal parameters for the hydrogen atoms*

Positional parameters are in fractions of the unit cell axes and the e.s.d.'s in Å × 10^3. The thermal parameters are in $Å^2$.

	x	y	z	B
H(1)	−0·599 (41)	−0·005 (51)	0·237 (42)	1·8
H(2)	−0·379 (50)	0·041 (52)	0·393 (53)	3·0
H(3)	−0·767 (37)	0·044 (36)	−0·164 (38)	0·5
H(4)	−0·794 (36)	0·094 (36)	−0·450 (38)	0·7
H(5)	0·114 (54)	0·225 (54)	0·226 (56)	4·3
H(6)	−0·199 (34)	0·235 (34)	−0·379 (35)	0·1
H(7)	−0·054 (33)	0·356 (35)	−0·026 (34)	0·1
H(8)	−0·387 (36)	0·366 (38)	−0·448 (37)	0·6
H(9)	0·000 (37)	0·399 (34)	−0·572 (35)	0·3
H(10)	0·104 (39)	0·432 (39)	−0·245 (39)	1·1
H(11)	0·288 (35)	0·309 (35)	−0·292 (36)	0·2
H(12)	0·541 (42)	0·292 (42)	0·080 (40)	1·4
H(13)	0·501 (46)	0·374 (43)	0·021 (43)	1·2
H(14)	0·290 (44)	0·381 (43)	0·206 (44)	2·0

with isotropic temperature factors of the form $\exp(-B\sin^2\theta/\lambda^2)$, resulting in a discrepancy index R of 0·082. Further least-squares refinement was made with anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$, resulting in R=0·056. A three-dimensional difference Fourier synthesis was calculated at this stage and all the hydrogen atoms were located. Least-squares refinement was then made having assigned isotropic temperature factors to the hydrogen atoms. The real and imaginary parts of the anomalous dispersion for the chloride ion, $\Delta f'$=0·15, $\Delta f''$=0·19 (Dauben & Templeton, 1955), were taken into account at the final stage of the refinement, but no significant variation was found in the atomic parameters or in the R value.

Table 4. *Observed and calculated structure factors* (×10)

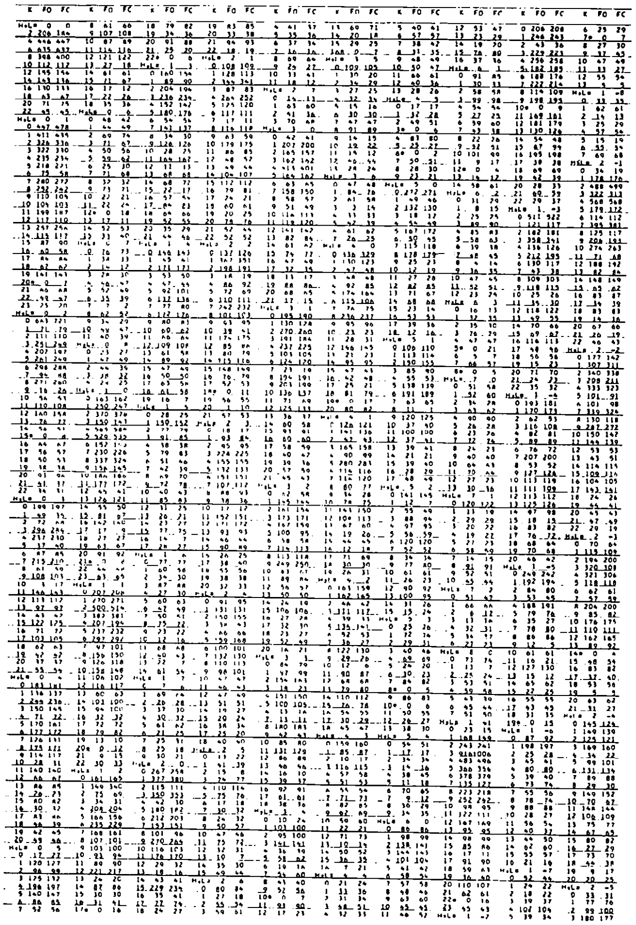
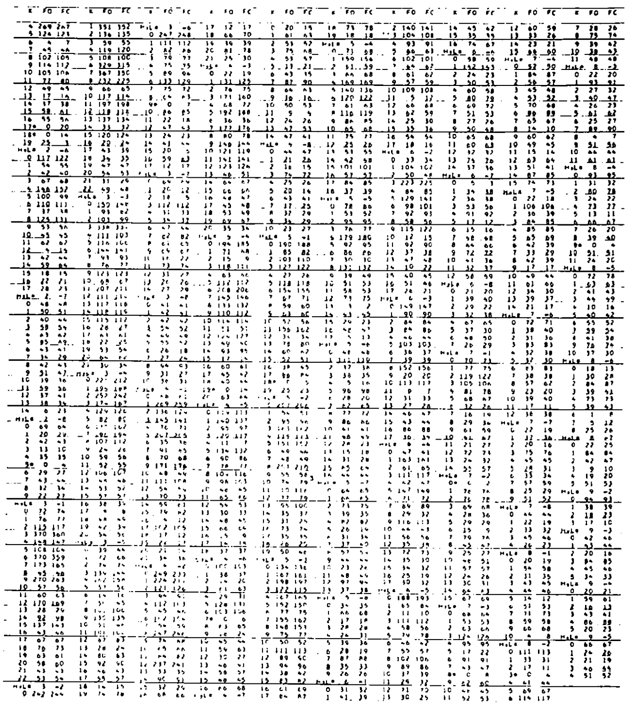


Table 4 (cont.)



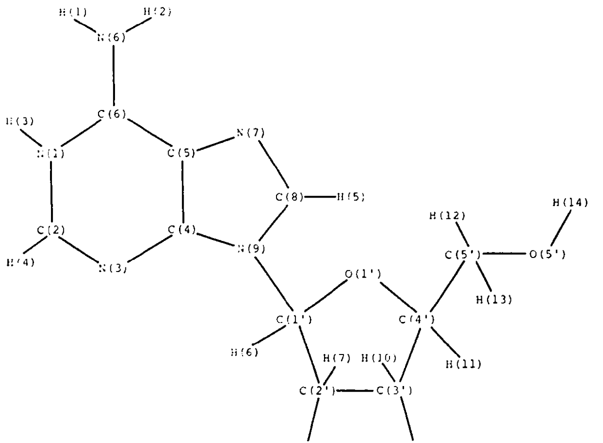


Fig. 1. Atomic numbering of the adenosine molecule, which is protonated at N(1) by H(3).

The final *R* value is 0·037 for the 1895 reflexions, including those of zero intensity. The positional and thermal parameters are listed in Tables 1, 2 and 3 with their estimated standard deviations. The numbering of the atom is illustrated in Fig. 1. The observed and calculated structure factors are listed in Table 4.

Table 5. *Bond distances and angles in adenosine hydrochloride compared with those in other adenosine compounds*

The numbers in parentheses are e.s.d.'s. The abbreviations are;

3′-AMP: adenosine 3′-phosphate,
5′-AMP: adenosine 5′-phosphate,
3′Acetyl-A: 3′-*O*-acetyladenosine.

	Protonated			Non-protonated	
Bonds (Å)	Adenosine.HCl	3′-AMP*	5′-AMP†	Adenosine‡	3′-Acetyl-A§
N(1)–C(2)	1·361 (5)	1·349 (6)	1·368 (12)	1·340 (3)	1·335 (6)
C(2) –N(3)	1·308 (5)	1·306 (6)	1·312 (12)	1·330 (3)	1·337 (6)
N(3)–C(4)	1·353 (4)	1·353 (6)	1·341 (12)	1·349 (3)	1·339 (6)
C(4) –C(5)	1·384 (4)	1·381 (7)	1·403 (12)	1·381 (3)	1·378 (6)
C(5) –C(6)	1·397 (4)	1·401 (7)	1·448 (13)	1·415 (3)	1·418 (6)
N(1)–C(6)	1·353 (4)	1·363 (6)	1·362 (12)	1·351 (3)	1·340 (6)
C(6) –N(6)	1·325 (4)	1·319 (6)	1·312 (13)	1·332 (3)	1·336 (6)
C(5) –N(7)	1·375 (4)	1·384 (6)	1·364 (11)	1·385 (3)	1·406 (6)
N(7)–C(8)	1·307 (5)	1·312 (6)	1·328 (12)	1·308 (3)	1·314 (6)
C(8) –N(9)	1·382 (4)	1·368 (6)	1·398 (12)	1·362 (3)	1·367 (6)
C(4) –N(9)	1·362 (4)	1·355 (6)	1·377 (12)	1·374 (3)	1·380 (6)
N(9)–C(1′)	1·460 (4)	1·477 (6)	1·492 (12)	1·466 (3)	1·454 (5)
C(1′)–O(1′)	1·416 (4)	1·409 (5)	1·445 (11)	1·411 (3)	1·413 (5)
O(1′)–C(4′)	1·455 (4)	1·441 (5)	1·476 (11)	1·450 (3)	1·447 (5)
C(1′)–C(2′)	1·528 (4)	1·526 (7)	1·509 (13)	1·530 (3)	1·529 (6)
C(2′)–C(3′)	1·529 (4)	1·529 (7)	1·544 (12)	1·528 (3)	1·520 (6)
C(2′)–O(2′)	1·412 (4)	1·413 (5)	1·438 (11)	1·411 (3)	1·413 (5)
C(3′)–C(4′)	1·533 (5)	1·516 (7)	1·520 (12)	1·522 (3)	1·511 (6)
C(3′)–O(3′)	1·430 (4)	1·440 (5)	1·400 (11)	1·417 (3)	1·445 (5)
C(4′)–C(5′)	1·509 (5)	1·507 (7)	1·525 (13)	1·509 (3)	1·513 (7)
C(5′)–O(5′)	1·427 (4)	1·425 (5)	1·475 (12)	1·420 (3)	1·414 (6)
Angles (°)					
C(6) –N(1)–C(2)	124·2 (3)	123·3 (3)	122·8 (7)	119·3 (2)	118·9 (3)
N(1)–C(2) –N(3)	125·0 (3)	125·9 (3)	125·7 (8)	128·9 (2)	128·7 (3)
C(2) –N(3)–C(4)	111·6 (3)	111·6 (3)	112·3 (8)	110·4 (2)	111·4 (3)
N(3)–C(4) –C(5)	127·4 (3)	127·2 (3)	128·5 (8)	127·6 (2)	126·2 (3)
C(4) –C(5) –C(6)	118·2 (3)	118·2 (3)	115·6 (7)	116·4 (2)	117·1 (3)
C(5) –C(6) –N(1)	113·5 (3)	113·7 (3)	114·7 (8)	117·4 (2)	117·6 (3)
N(6)–C(6) –N(1)	120·4 (3)	120·2 (3)	121·5 (8)	118·1 (2)	118·5 (3)
N(6)–C(6) –C(5)	126·1 (3)	126·1 (3)	123·7 (8)	124·5 (2)	123·8 (3)
N(3)–C(4) –N(9)	127·0 (3)	127·3 (3)	127·4 (8)	126·7 (2)	—
C(6) –C(5) –N(7)	130·5 (3)	130·6 (3)	131·9 (8)	132·8 (2)	—
C(4) –C(5) –N(7)	111·3 (3)	111·2 (3)	112·3 (7)	110·8 (2)	110·7 (3)
C(5) –N(7)–C(8)	103·8 (3)	103·3 (3)	104·7 (7)	103·5 (2)	103·7 (3)
N(7)–C(8) –N(9)	113·6 (3)	113·4 (3)	111·8 (8)	114·3 (2)	113·5 (3)
C(8) –N(9)–C(4)	105·8 (3)	106·6 (3)	107·1 (7)	105·7 (2)	106·6 (3)
N(9)–C(4) –C(5)	105·6 (3)	105·4 (4)	104·1 (7)	105·7 (2)	105·5 (3)
C(4) –N(9)–C(1′)	126·7 (3)	125·2 (4)	123·8 (7)	124·3 (2)	127·6 (3)
C(8) –N(9)–C(1′)	127·6 (3)	128·0 (3)	128·6 (7)	130·0 (2)	125·6 (3)
N(9)–C(1′)–O(1′)	107·2 (3)	107·2 (3)	107·2 (7)	109·3 (2)	108·2 (3)
N(9)–C(1′)–C(2′)	113·0 (3)	113·5 (3)	112·6 (7)	111·6 (2)	114·2 (3)
O(1′)–C(1′)–C(2′)	105·6 (3)	108·6 (3)	106·7 (6)	107·3 (3)	105·3 (3)
C(1′)–C(2′)–C(3′)	101·0 (3)	100·6 (3)	101·7 (6)	101·4 (2)	101·2 (3)
O(2′)–C(2′)–C(3′)	115·5 (3)	111·7 (3)	110·0 (6)	107·9 (2)	117·6 (3)
C(1′)–C(2′)–O(2′)	114·6 (3)	106·1 (3)	107·0 (6)	109·5 (2)	108·5 (3)
C(2′)–C(3′)–C(4′)	101·8 (3)	103·7 (3)	99·9 (7)	102·7 (2)	103·7 (3)
C(2′)–C(3′)–O(3′)	105·9 (3)	112·4 (3)	115·4 (7)	114·8 (2)	110·5 (3)
O(3′)–C(3′)–C(4′)	111·4 (3)	112·2 (3)	115·5 (6)	114·3 (2)	107·6 (3)
C(3′)–C(4′)–C(5′)	116·7 (3)	114·3 (3)	119·1 (7)	114·6 (2)	114·4 (3)
C(3′)–C(4′)–O(1′)	105·7 (3)	103·1 (3)	104·0 (6)	104·7 (2)	106·7 (3)
C(5′)–C(4′)–O(1′)	109·9 (3)	109·4 (3)	107·9 (7)	107·9 (2)	107·9 (3)
C(4′)–O(1′)–C(1′)	109·8 (3)	110·1 (3)	108·3 (7)	110·5 (2)	108·9 (3)
C(4′)–C(5′)–O(5′)	114·7 (3)	110·7 (3)	107·6 (7)	109·4 (2)	111·6 (3)

* Sundaralingam (1966).
† Kraut & Jensen (1963).
‡ Lai & Marsh (1972).
§ Rao & Sundaralingam (1970).

The calculations were made using the NEAC-2200 computer with the block-diagonal least-squares program and the Fourier synthesis program written for this computer by Ashida (1967). The atomic scattering factors for Cl ion and neutral C, N, O, H atoms were taken from *International Tables for X-ray Crystallography* (1962).

Description of the structure

Intramolecular bond distances and angles

The intramolecular bond distances and angles for non-hydrogen atoms are given in Table 5 and in Fig. 2, and those involving hydrogen atoms are in Table 6. For comparison, bond distances and angles of other adenosine compounds also are given in Table 5. In the following, separate descriptions are given of the purine base, ribose ring and the bonding between them.

Table 6. *Bond distances and angles involving the hydrogen atoms, with e.s.d.'s in parentheses*

Bond length (Å)

N(6)–H(1)	0·96 (0·05)	N(6)–H(2)	0·89 (0·05)
N(1)–H(3)	0·78 (0·04)	C(2) –H(4)	0·93 (0·04)
C(8) –H(5)	1·01 (0·06)	C(1′)–H(6)	0·99 (0·04)
C(2′)–H(7)	1·01 (0·04)	O(2′)–H(8)	0·82 (0·04)
O(3′)–H(9)	0·73 (0·04)	C(3′)–H(10)	1·02 (0·04)
C(4′)–H(11)	0·90 (0·04)	C(5′)–H(12)	1·00 (0·04)
C(5′)–H(13)	0·90 (0·05)	O(5′)–H(14)	0·79 (0·05)

Bond angle (°)

C(6) –N(6)–H(1)	122 (3)	C(6) –N(6)—H(2)	120 (3)
H(1)–N(6)–H(2)	118 (5)	C(6)—N(1)–H(3)	127 (3)
C(2) –N(1)–H(3)	108 (3)	N(1)—C(2) –H(4)	112 (2)
N(3)–C(2) –H(4)	124 (2)	N(7)—C(8) –H(5)	133 (3)
N(9)–C(8) –H(5)	113 (3)	N(9)—C(1′)–H(6)	105 (2)
O(1′)–C(1′)–H(6)	114 (2)	C(2′) –C(1′)–H(6)	112 (2)
C(1′)–C(2′)–H(7)	108 (2)	O(2′)–C(2′)–H(7)	111 (2)
C(3′)–C(2′)–H(7)	106 (2)	C(2′) –O(2′)–H(8)	114 (3)
C(3′)–O(3′)–H(9)	106 (3)	O(3′)–C(3′)–H(10)	106 (2)
C(2′)–C(3′)–H(10)	120 (2)	C(4′) –C(3′)–H(10)	112 (2)
C(3′)–C(4′)–H(11)	107 (2)	O(1′)–C(4′)–H(11)	109 (2)
C(5′)–C(4′)–H(11)	128 (2)	C(4′) –C(5′)–H(12)	110 (2)
O(5′)–C(5′)–H(12)	109 (2)	H(13)–C(5′)–H(12)	99 (4)
C(4′)–C(5′)–H(13)	109 (3)	O(5′)–C(5′)–H(13)	115 (3)
C(5′)–O(5′)–H(14)	108 (3)		

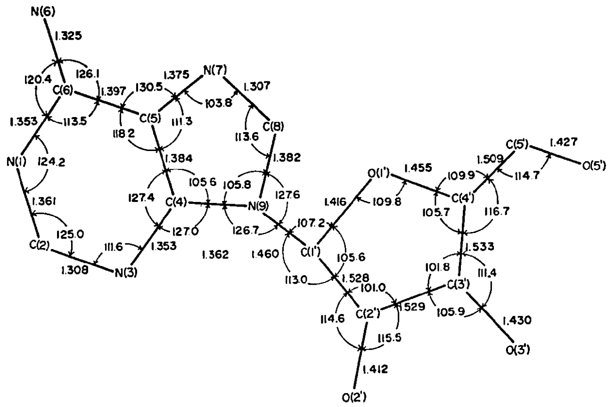


Fig. 2. Bond distances and angles in the molecule.

The purine base

As shown in Fig. 1, the adenosine molecule is protonated at N(1), as in the cases of adenosine 3′-phosphate (3′-AMP) and adenosine 5′-phosphate (5′-AMP). The bond distances and angles listed in Table 5 show that the protonated purine bases of these three compounds are quite similar in shape. Table 5 also gives the bond distances and angles of non-protonated adenosine bases and indicates that there are significant differences between the structures of the purine bases of adenosine hydrochloride and of neutral adenosine (Lai & Marsh, 1972), as has been pointed out for other compounds by Rao & Sundaralingam (1970). For instance, the N(1)–C(2) and C(8)–N(9) bond distances in the protonated base are longer than those in the neutral base, while the C(2)–N(3) and C(5)–C(6) distances are shorter. The bond angle at N(1) in the neutral base is 119·3°, while in the protonated base it is 124·2°. Significant differences are also observed in the angles at C(6) and C(2).

The least-squares plane of the purine ring (plane 1 in Table 7) was calculated and the displacements of the atoms from the plane are listed in Table 7. Least-squares planes were also calculated for the five-membered and six-membered rings separately. The angle between them is 1·6°. The C(5) atom is displaced from plane 1 by 0·025 Å, which is the largest deviation among the ring atoms. Therefore, the purine ring is almost exactly planar. The plane of amino group of N(6), H(1) and H(2) is twisted through 7° from plane 1. The substituent atoms N(6) and C(1′) are displaced in the same direction from plane 1 by 0·073 and 0·054 Å respectively. The displacements of C(1′) observed in the related compounds are 0·21 Å in 5′-AMP and 0·08 Å in 3′-AMP.

Table 7. *Displacements* (*in* Å) *of atoms from the least-squares planes through the purine base and ribose ring*

Purine base		Ribose ring			
Atom	Plane 1	Atom	Plane 2	Plane 3	Plane 4
N(1)	0·013*	C(1′)	−0·117*	0·026*	0·000*
C(2)	−0·010*	C(2′)	0·230*	0·604	0·506
N(3)	−0·003*	C(3′)	−0·282*	−0·028*	−0·132
C(4)	−0·005*	C(4′)	0·101*	0·026*	0·000*
C(5)	−0·025*	O(1′)	0·108*	−0·018*	0·000*
C(6)	0·017*	C(5′)	1·416	1·216	1·207
N(7)	−0·010*	O(2′)	−0·301	0·361	0·206
C(8)	0·006*	O(3′)	−1·702	−1·376	−1·501
N(9)	0·019*	N(9)	0·751	0·873	0·882
N(6)	0·073				
C(1′)	0·054				

Plane 1: $0·6067X-0·7739Y-0·1824Z+3·1313=0·0$
Plane 2: $-0·0532X+0·1114Y+0·9924Z+0·7048=0·0$
Plane 3: $-0·2169X+0·2471Y+0·9444Z+0·2006=0·0$
Plane 4: $-0·1962X+0·2001Y+0·9599Z+0·3958=0·0$

Coordinates (X, Y, Z) are in Å referred to the orthogonal axes, a, b and c^*.

* Atoms involved in the calculation of the least-squares planes.

The ribose ring

The bond distances and angles in the ribose ring are listed in Table 5. The length of the bond C(4′)–O(1′) is 1·455 Å, which is significantly longer than 1·416 Å of C(1′)–O(1′). The average ring C–C single bond distance is 1·530 Å, which is close to the value 1·533 ± 0·003 Å of the normal single bond (Bartell, 1959). The exocyclic C(4′)–C(5′) bond distance of 1·509 Å is considerably less than the normal value. The angles N(9)–C(1′)–O(1′) of 107·2° and C(5′)–C(4′)–O(1′) of 109·9° are less than the angles N(9)–C(1′)–C(2′) of 113·0° and C(5′)–C(4′)–C(3′) of 116·7°. The C(2′)–O(2′) bond distance of 1·412 Å is significantly shorter than the C(3′)–O(3′) bond distance of 1·432 Å.

Least-squares planes 2, 3 and 4 were calculated using the atoms marked with an asterisk shown in Table 7. As shown in the table, the C(2′) atom is displaced by 0·604 Å from plane 3. The displacement of C(2′) or C(3′) is usually about 0·5 Å according to Spencer (1959). Table 7 shows that C(2′) and C(5′) are displaced to the same side of plane 3. Therefore, the conformation of the ribose ring is C(2′)-*endo* pucker. Plane 4 is the plane determined by the three atoms C(1′), C(4′) and O(1′). It can be seen that C(2′) is displaced to the same side of the plane as C(5′), but C(3′) is displaced to the opposite side. Therefore, the conformation of the ribose is of a C(2′)-*endo*–C(3′)-*exo* type.

The torsional angles about the exocyclic C(4′)–C(5′) bond denoted as φ_{OO} [O(1′)–C(4′)–C(5′)–O(5′)] and φ_{CO} [C(3′)–C(4′)–C(5′)–O(5′)] by Shefter & Trueblood (1965) are −60·9 and 59·3° respectively. Therefore, the conformation about C(4′)–C(5′) is *gauche–gauche*, as shown in Fig. 3. A similar *gauche–gauche* conformation was found in 5′-AMP, whereas *gauche–trans* conformations were observed in 3′-AMP and in deoxyadenosine. The torsional angles for H(8)–O(2′)–C(2′)–H(7) and H(9)–O(3′)–C(3′)–H(10) are 183·0 and −36·0° respectively. These H–O–C–H conformations are *trans–gauche*.

Bondings between the base and the ribose

As can be seen in Table 5, the length of the glycosidic bond N(9)–C(1′) is 1·460 Å which is smaller than the 1·477 Å of 3′-AMP, and the 1·492 Å of 5′-AMP. The dihedral angle between the least-squares planes of the ribose and purine units (Plane 1 and 2 in Table 7) is 107·9°. Haschemeyer & Rich (1967) define the torsional angle φ_{CN} as the dihedral angle between the least-squares plane of the purine base and the plane through N(9), C(1′) and O(1′). The value calculated for φ_{CN} is −43·0°. Therefore, adenosine is in *anti* conformation. Views of the conformation are shown in Figs. 4 and 5. The shortest intramolecular van der Waals contact is C(8)–H(5)···O(5′) with the H(5)···O(5′) distance of 2·56 Å. There therefore seems to be no intramolecular hydrogen bond in adenosine hydrochloride.

Crystal structure

The crystal structure viewed along the *c* axis is shown in Fig. 6. The arrangement of the molecules viewed along the *a* axis is shown in Fig. 7. All the hydrogen atoms bonded to oxygen and nitrogen atoms contribute to hydrogen bonding, and there are a number of short intermolecular contacts, as can be seen in Table 8.

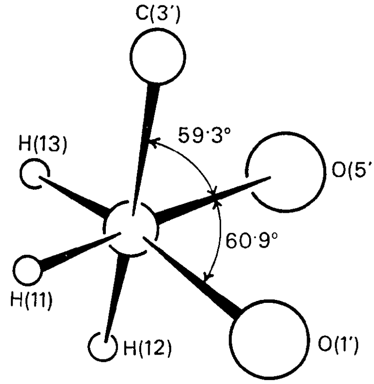


Fig. 3. Arrangement of the atoms around the C(4′)–C(5′) bond, viewed along C(4′)–C(5′).

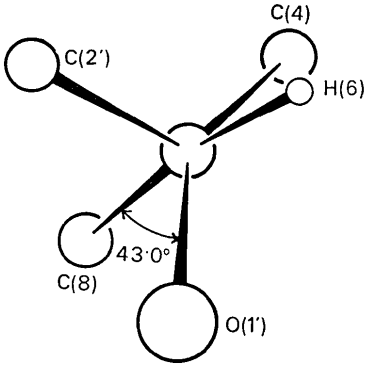


Fig. 4. Conformation about the glycosidic bond C(1′)–N(9), viewed along C(1′)–N(9).

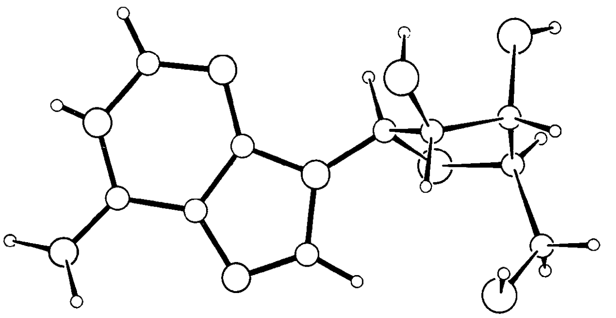


Fig. 5. Conformation of the molecule, viewed perpendicularly to the purine base.

The chloride ion participates in four hydrogen bonds, forming the three-dimensional hydrogen-bond network shown in Figs. 6 and 7. It is interesting to observe that the contact N(7)···H(4) of 2·36 Å is shorter than the van der Waals contact distance of 2·60 Å (Pauling, 1960).

The purine base near the origin lies approximately on the $(4\bar{8}\bar{1})$ plane. The bases do not overlap, as shown in Fig. 8, where short contacts between two molecules are also indicated. The shortest distance between the ribose and base is O(1′)···C(2) at 3·047 Å. This short contact also exists in 3′-AMP (3·143 Å).

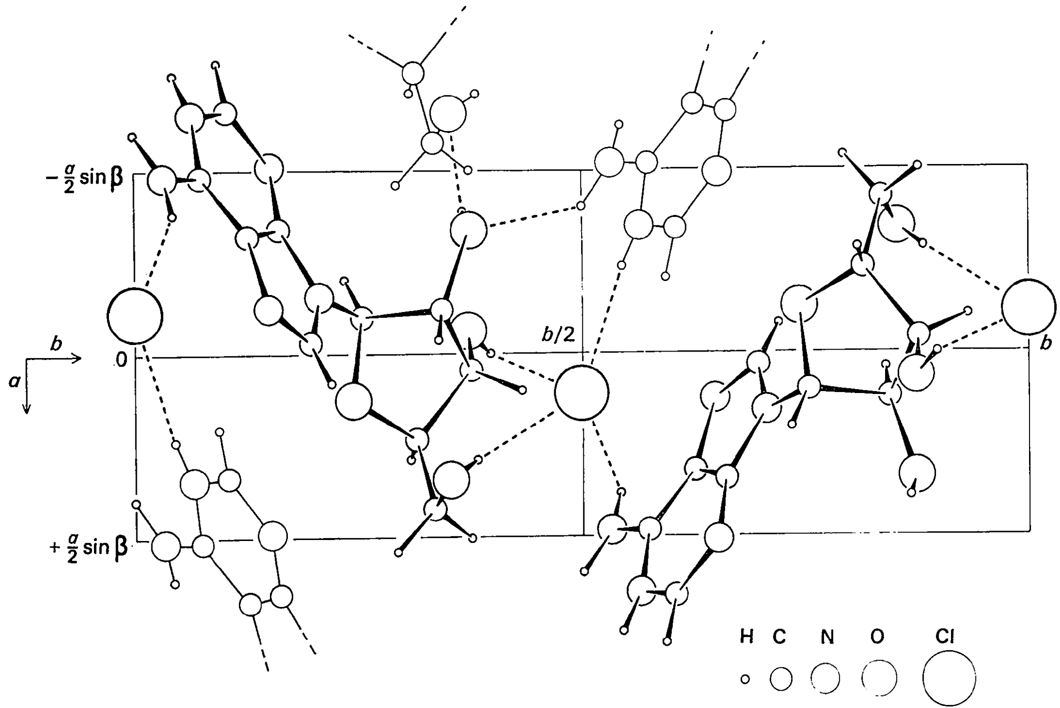


Fig. 6. Crystal structure viewed along the *c* axis. The hydrogen bonds are shown as broken lines.

Table 8. *Hydrogen bonds and short van der Waals contacts*

A···H–*D*	Symbol*	*A*···H	*A*···*D*	H–*D*	*A*–H–*D*
Hydrogen bonds					
Cl·····H(2)—N(6)	4	2·42 (6) Å	3·247 (3) Å	0·89 (5) Å	151°
Cl·····H(14)-O(5′)	2	2·33 (5)	3·105 (3)	0·79 (4)	167
Cl·····H(3)—N(1)	3	2·31 (4)	3·070 (3)	0·78 (4)	171
Cl·····H(9)—O(3′)	7	2·45 (4)	3·153 (3)	0·73 (4)	163
O(2′)···H(1)—N(6)	6	2·17 (6)	2·990 (4)	0·96 (5)	143
O(5′)···H(8)—O(2′)	5	2·07 (4)	2·835 (3)	0·82 (4)	155
Short van der Waals contacts					
O(5′)···H(5)—C(8)	1	2·56 (6)	3·490 (4)	1·01 (6)	152
O(2′)···H(11)-C(4′)	8	2·74 (4)	3·397 (4)	0·90 (4)	129
Cl·····H(7)—C(2′)	2	2·86 (3)	3·600 (3)	1·01 (4)	131
Cl·····H(10)-C(3′)	2	3·17 (4)	3·717 (3)	1·02 (4)	114
N(7)···H(4)—C(2)	5	2·36 (4)	3·176 (5)	0·93 (4)	145
C(8)···H(4)—C(2)	5	2·85 (4)	3·498 (5)	0·93 (4)	127
O(1′)·········C(2)	2		3·047 (4)		
O(1′)·········N(3)	2		3·331 (4)		
O(1′)·········N(1)	2		3·232 (4)		

* Symbols stand for the relative positions of donor group to the acceptor at (*x*, *y*, *z*) as follows.

1.	x,	y,	z	5.	$1+x$,	$-y$,	$1+z$
2.	$-x$,	$-\frac{1}{2}-y$,	$-z$	6.	$-1-x$,	$\frac{1}{2}-y$,	$-z$
3.	$1+x$,	$-y$,	z	7.	$-x$,	$-\frac{1}{2}-y$,	$1-z$
4.	x,	$-y$,	$-1+z$	8.	$-1+x$,	$-y$,	z.

The e.s.d.'s of the bond distances given in parentheses refer to the last figure.

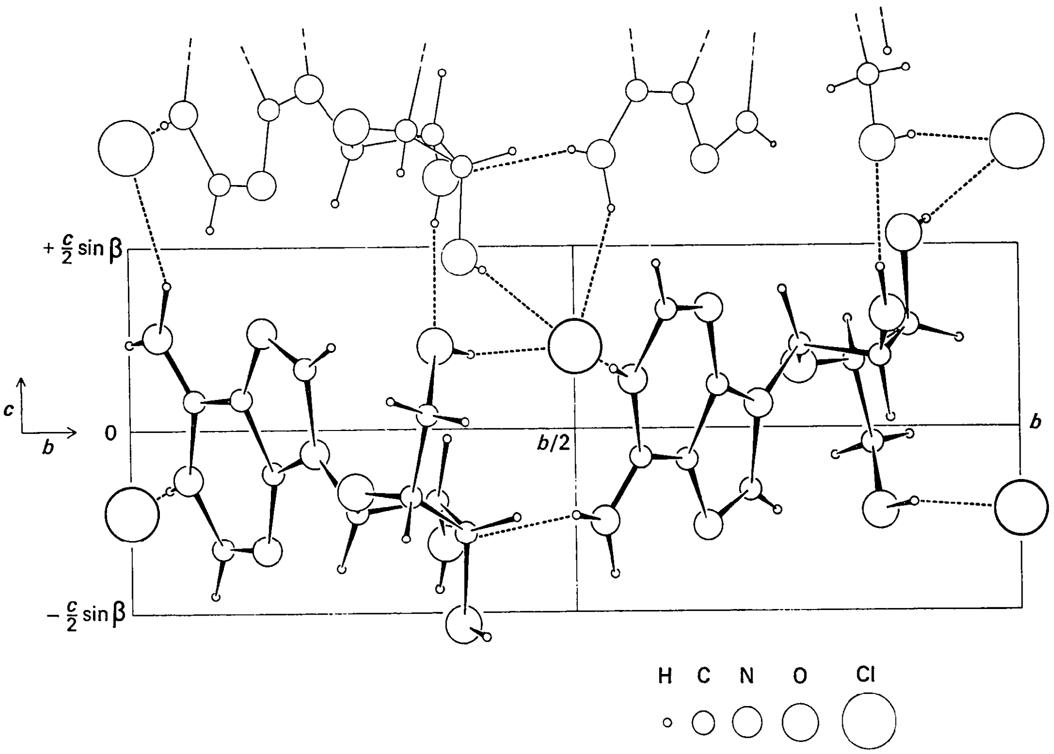


Fig. 7. Crystal structure viewed along the *a* axis. The hydrogen bonds are shown as broken lines.

The authors wish to express their thanks to Dr Nobuo Tanaka for his advice in the structure analysis, and to Dr Tamaichi Ashida of Institute for Protein Research for his help in the computer programing. They are indebted to Dr T. F. Lai for providing the data for the non-protonated adenosine molecule prior to publication. Thanks are due to the Computing Centre of Osaka University for making available to the authors the NEAC-2200 computer facilities.

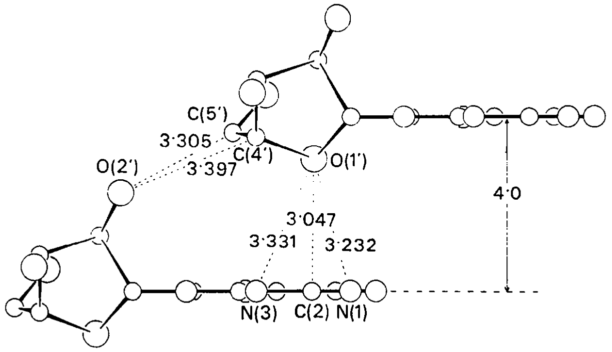


Fig. 8. Arrangement of molecules viewed approximately along the direction of the bond N(9)–C(8). The dashed lines show short intermolecular contacts and the numbers are the atomic distances in Å.

References

ASHIDA, T. (1967). *The Universal Crystallographic Computing System* I, pp. 65–75. Edited by T. SAKURAI. Tokyo: Japan Crystallographic Association.

BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3497–3498.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841–842.

HASCHEMEYER, A. E. V. & RICH, A. (1967). *J. Mol. Biol.* **27**, 369–384.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KRAUT, J. & JENSEN, L. H. (1963). *Acta Cryst.* **16**, 79–88.

LAI, T. F. & MARSH, R. E. (1972). *Acta Cryst.* B**28**, 1982–1989.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd Ed. pp. 257–264. Ithaca: Cornell Univ. Press.

RAO, S. T. & SUNDARALINGAM, M. (1970). *J. Amer. Chem. Soc.* **92**, 4963–4970.

ROHRER, D. C. & SUNDARALINGAM, M. (1970). *J. Amer. Chem. Soc.* **92**, 4956–4962.

SHEFTER, E. & TRUEBLOOD, K. N. (1965). Unpublished results.

SPENCER, M. (1959). *Acta Cryst.* **12**, 59–65.

SUNDARALINGAM, M. (1966). *Acta Cryst.* **21**, 495–506.

WATSON, D. G., SUTOR, D. J. & TOLLIN, P. (1965). *Acta Cryst.* **19**, 111–124.