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Structure of 8-Azaadenosine Hydrochloride

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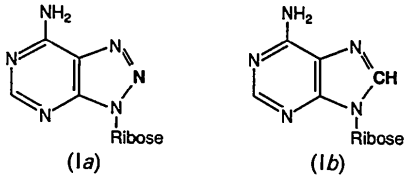
Abstract. $C_9H_{13}N_6O_4^+.Cl^-$, $M_r = 304{\cdot}70$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}801$ (3), $b = 21{\cdot}105$ (6), $c = 5{\cdot}944$ (3) Å, $V = 1229{\cdot}5$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}65$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 30{\cdot}4$ cm^{-1}, $F(000) = 632$, $T = 297$ K, $R = 0{\cdot}031$ for 1076 observed reflections. The protonated nucleoside assumes a high-*anti* glycosyl conformation ($\chi = 90{\cdot}5°$), C(3′)-*endo*-envelope ribose puckering ($P = 14{\cdot}4°$) and a *gauche–gauche* conformation around the exocyclic C(4′)—C(5′) bond.

Introduction. 8-Azaadenosine (I*a*) is a synthetic nucleoside possessing significant carcinostatic properties (Kajander, Kubota, Carrera, Montgomery & Carson, 1986; Crabtree, Dexter, Spremulli, Campbell, Chu, Quevedo, Calabresi & Parks, 1982). It is isoelectric with adenosine (I*b*) with an N atom replacing the CH group on the adenine base next to the glycosyl bond.



(I*a*) (I*b*)

In (I*b*), because of the CH group, there is a significant barrier to rotation around the glycosyl bond, but this is absent in (I*a*). There are two preferred glycosyl conformations for purine nucleosides: *syn*, in which the bulk of the base is located on top of the sugar, and *anti*, in which it is rotated away from the sugar. 8-Azapurine nucleosides seem to prefer a *syn* or a near-*syn* (high-*anti*) conformation, the latter having the glycosyl torsion angle [N(8)—N(9)—C(1′)—O(4′)] $\simeq 100 \pm 30°$ (Prusiner, Brennan & Sundaralingam, 1973; Singh & Hodgson, 1974*a*, 1977*a*; Abola, Sims, Abraham, Lewis & Townsend, 1974; Koyama, Umezawa & Iitaka, 1974; Sprang, Scheller, Rohrer & Sundaralingam, 1978; Birnbaum, Brisson, Krawczyk & Townsend, 1985). 6-Azapyrimidine nucleosides, which also lack an H atom next to the glycosyl bond, seem to prefer the high-*anti* conformation exclusively (Singh & Hodgson 1974*b*,*c*; Schwalbe & Saenger, 1973; Banerjee & Saenger, 1978; Graves, Hodgson, Katz, Wise & Townsend, 1978; Graves & Hodgson, 1981). The natural antibiotic formycin A, which has a C—C glycosyl bond and is an 8-azapurine nucleoside, has a glycosyl torsion angle of 109·5° (Prusiner *et al.*, 1973) which is a high-*anti* conformation but, when protonated, it goes over to the classical *syn* conformation with a χ of 210·7° (Koyama *et al.*, 1974). Formycin B which has a normal *anti* glycosyl conformation with a χ of 40° (Singh & Hodgson, 1975; Koyama, Nakamura, Umezawa & Iitaka 1976) also goes over to *syn* when protonated (Singh & Hodgson, 1977*b*). It was, therefore, of interest to see if 8-azaadenosine with a χ of 103·6° (Singh & Hodgson, 1977*a*) would go over to the *syn* conformation when protonated. As the following results show it does not do so and retains its high-*anti* conformation.

Experimental. 8-Azaadenosine was a gift from Dr J. A. Montgomery of the Southern Research Institute, Birmingham, Alabama, USA. Needle-shaped crystals of its hydrochloride were grown by dissolving a small amount of the nucleoside in 1*M* hydrochloric acid and evaporating slowly at room temperature. A crystal of dimensions 0·386 × 0·117 × 0·105 mm was used for all measurements. Preliminary cell constants and space group were determined with the aid of Weissenberg and precession photographs. The final cell constants and the intensity data were collected by using nickel-filtered Cu $K\alpha$ radiation on a Picker four-circle automatic diffractometer equipped with a pulse-height analyzer. For the cell constants, 12 reflections with 2θ values between 29 and 60° were centered accurately and their setting angles refined. The intensities were collected at a take-off angle of 1·9° by the $\theta/2\theta$ scan technique at 0·5° min^{-1} over a range $\pm 0{\cdot}8°$ from the $K\alpha_1/K\alpha_2$ peak positions and with a stationary background count of 40 s at each scan limit. Three reflections, measured as standards after every 100 reflections, showed random intensity

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fluctuations of ±1·6%. A total of 1291 reflections, including the standards, were collected up to a 2θ limit of 126° (h 0–11, k 0–24, l 0–6); 1026 reflections with intensities greater than $3\sigma(I)$ were used in the structure refinement. Data were corrected for background and Lorentz and polarization effects by the method of Corfield, Doedens & Ibers (1967). $\sigma(I)$ were derived from counting statistics with an additional term p(I) ($p = 0{\cdot}005$) included to downweight the strong reflections. No absorption corrections were made.

The structure was solved by direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the full-matrix least-squares procedure (Busing, Martin & Levy, 1962) to an R of 0·031 and a wR of 0·040. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o/\sigma^2(|F_o|)^2$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The non-H atoms were refined with anisotropic thermal vibration parameters. H atoms were located from a difference Fourier synthesis and refined with isotropic thermal vibration parameters. No parameter shift in the final cycle of refinement was greater than 0·5 times its e.s.d. A final difference Fourier map was featureless with a maximum and minimum $\Delta\rho$ of ±0·15 e Å^{-3}.

The fractional atomic coordinates are given in Table 1 and the bond distances, bond angles, torsion angles, and distances and angles associated with possible hydrogen bonds are given in Table 2.* A drawing of the protonated nucleoside along with the numbering system is presented in Fig. 1 and a crystal-packing diagram is shown in Fig. 2.

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

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
Cl	0·81627 (9)	0·09771 (4)	0·4262 (2)	0·041 (1)
N(1)	0·5076 (3)	0·5246 (1)	0·2950 (6)	0·036 (1)
C(2)	0·5976 (4)	0·5177 (2)	0·4679 (7)	0·037 (1)
N(3)	0·6747 (3)	0·4685 (1)	0·5045 (5)	0·040 (1)
C(4)	0·6557 (3)	0·4235 (1)	0·3444 (6)	0·024 (1)
C(5)	0·5681 (3)	0·4259 (2)	0·1639 (6)	0·027 (1)
C(6)	0·4839 (3)	0·4801 (1)	0·1348 (6)	0·028 (1)
N(6)	0·3944 (3)	0·4892 (2)	−0·0242 (6)	0·040 (1)
N(7)	0·5795 (3)	0·3709 (1)	0·0442 (6)	0·037 (1)
N(8)	0·6722 (3)	0·3360 (1)	0·1424 (5)	0·037 (1)
N(9)	0·7182 (3)	0·3673 (1)	0·3270 (5)	0·029 (1)
C(1′)	0·8321 (4)	0·3441 (2)	0·4648 (6)	0·026 (1)
C(2′)	0·8468 (4)	0·2726 (2)	0·4618 (6)	0·027 (1)
O(2′)	0·8912 (3)	0·2539 (1)	0·6797 (5)	0·039 (1)
C(3′)	0·9604 (3)	0·2613 (2)	0·2901 (6)	0·027 (1)
O(3′)	1·0429 (3)	0·2083 (1)	0·3477 (5)	0·032 (1)
C(4′)	1·0471 (4)	0·3208 (1)	0·3064 (6)	0·026 (1)
O(4′)	0·9536 (2)	0·3705 (1)	0·3765 (4)	0·030 (1)
C(5′)	1·1191 (4)	0·3396 (2)	0·0945 (7)	0·036 (1)
O(5′)	1·0278 (3)	0·3519 (1)	−0·0872 (5)	0·042 (1)

Discussion. The site of protonation in 8-azaadenosine is N(1) similar to that in adenosine 3′-phosphate (Sundaralingam, 1966) and in formycin A hydrobromide (Koyama *et al.*, 1974). As pointed out by Rao & Sundaralingam (1970), the protonation at N(1) causes a large perturbation in the geometry of the segment bounded by N(6)—C(6)—N(1)—C(2)—N(3). Thus, comparing the structure of the protonated 8-azaadenosine (8-AZAH$^+$) with that of neutral 8-azaadenosine (8-AZA) (Singh & Hodgson, 1977*a*) we find that the two ring bonds to N(1), *i.e.* N(1)—C(2) and N(1)—C(6), have lengthened, as expected, by 0·024 and 0·021 Å, respectively, and the adjoining bonds, C(2)—N(3) and C(6)—N(6), have foreshortened by 0·021 and 0·020 Å, respectively. The changes in the endocyclic ring angles are also quite large, that at N(1) being increased by 4·9° (Singh, 1965) and those at C(2) and C(6) being decreased by 4·2 and 4·9°, respectively. A more surprising observation is a foreshortening of the N(8)—N(9) bond by 0·022 Å and a lengthening of the N(9)—C(1′) bond by 0·021 Å. Apparently, the protonation at N(1) perturbs the nature of electronic delocalization of the entire aglycon.

The bond distances in the ribose sugar are all within 3σ of the corresponding values for 8-AZA except for the exocyclic bonds C(2′)—O(2′) and C(3′)—O(3′), both of which are larger in 8-AZAH$^+$ (by 0·035 and 0·021 Å, respectively). These bonds were found to be abnormally short in 8-AZA. The bond angles, however, differ considerably from those observed in 8-AZA. The largest differences are in the endocyclic bond angles at O(4′), C(1′) and C(2′) with angles in 8-AZAH$^+$ being larger by 3·0, 2·9 and 3·5°, respectively. These differences are, no doubt, due to the different modes of puckering of the ribose sugar in the two molecules (Sundaralingam, 1973): C(3′)-*endo*-envelope (^3E) in 8-AZAH$^+$ [pseudorotation phase angle, $P = 14{\cdot}4°$, and the maximum amplitude $\tau_m = 2{\cdot}3°$ (Altona & Sundaralingam, 1972)] and C(2′)-*endo*–C(1′)-*exo* ($^2T_1$) in 8-AZA. The two different puckering modes, in turn, may be partly a result of an intramolecular hydrogen bond present in 8-AZAH$^+$ (Table 2) but not in 8-AZA between two adjacent —OH groups. The glycosyl torsion angle χ [O(4′)—C(1′)—N(9)—N(8)] is 90·6°, which is in the high-*anti* range commonly observed in *ortho*-azanucleosides (Singh & Hodgson, 1974*c*; Saenger, 1984). A lower value of χ in 8-AZAH$^+$ compared with that in 8-AZA (103·7°) is consistent with the observed pattern of lower χ values for C(3′)-*endo*

* Lists of structure-factor amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51969 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°), *selected torsion angles* (°) *and hydrogen-bonding parameters* (Å, °)

E.s.d.'s for bond angles are 0·3°.

N(1)—C(6)	1·357 (5)	N(9)—C(4)	1·339 (4)
N(1)—C(2)	1·362 (5)	N(9)—C(1′)	1·468 (5)
C(2)—N(3)	1·303 (5)	C(1′)—C(2′)	1·517 (5)
N(3)—C(4)	1·358 (4)	C(1′)—O(4′)	1·416 (4)
C(4)—C(5)	1·375 (5)	C(2′)—O(2′)	1·422 (5)
C(5)—C(6)	1·421 (5)	C(2′)—C(3′)	1·529 (5)
C(6)—N(6)	1·306 (5)	C(3′)—O(3′)	1·421 (4)
C(5)—N(7)	1·366 (4)	C(3′)—C(4′)	1·521 (5)
N(7)—N(8)	1·307 (4)	C(4′)—O(4′)	1·453 (4)
N(8)—N(9)	1·358 (4)	C(4′)—C(5′)	1·497 (6)
		C(5′)—O(5′)	1·427 (5)

C(2)—N(1)—C(6)	124·5	N(8)—N(9)—C(1′)	122·8
N(1)—C(2)—N(3)	125·9	N(9)—C(1′)—C(2′)	113·4
C(2)—N(3)—C(4)	111·2	N(9)—C(1′)—O(4′)	107·6
N(3)—C(4)—C(5)	127·3	C(2′)—C(1′)—O(4′)	107·9
N(3)—C(4)—C(9)	127·7	C(1′)—C(2′)—C(3′)	103·4
C(5)—C(4)—N(9)	105·0	C(1′)—C(2′)—O(2′)	107·1
C(4)—C(5)—C(6)	119·2	C(3′)—C(2′)—O(2′)	110·0
C(4)—C(5)—N(7)	108·9	C(2′)—C(3′)—C(4′)	103·6
C(6)—C(5)—N(7)	131·9	C(2′)—C(3′)—O(3′)	112·1
N(1)—C(6)—C(5)	111·8	C(4′)—C(3′)—O(3′)	108·5
N(1)—C(6)—N(6)	121·4	C(3′)—C(4′)—C(5′)	115·4
C(5)—C(6)—N(6)	126·7	C(3′)—C(4′)—O(4′)	105·2
C(5)—N(7)—N(8)	107·7	C(5′)—C(4′)—O(4′)	110·3
N(7)—N(8)—N(9)	108·5	C(4′)—O(4′)—C(1′)	110·7
C(4)—N(9)—N(8)	109·9	C(4′)—C(5′)—O(5′)	112·9
C(4)—N(9)—C(1′)	126·9		

N(7)—N(8)—N(9)—C(1′)	−174·2 (1)	O(4′)—C(1′)—C(2′)—C(3′) (τ_1)	−20·0 (2)
N(8)—N(9)—C(1′)—O(4′) (χ)	90·6 (2)	C(1′)—C(2′)—C(3′)—C(4′) (τ_2)	29·2 (2)
N(8)—N(9)—C(1′)—C(2′)	−28·7 (2)	C(2′)—C(3′)—C(4′)—O(4′) (τ_3)	−28·5 (2)
C(4)—N(9)—C(1′)—O(4′)	−81·3 (2)	C(3′)—C(4′)—O(4′)—C(1′) (τ_4)	16·8 (2)
C(4)—N(9)—C(1′)—C(2′)	159·5 (1)	C(1′)—C(2′)—C(3′)—O(3′)	145·9 (1)
N(9)—C(1′)—O(4′)—C(4′)	−120·5 (1)	O(3′)—C(3′)—C(4′)—O(4′)	−147·7 (2)
N(9)—C(1′)—C(2′)—C(3′)	99·1 (2)	O(3′)—C(3′)—C(4′)—C(5′)	90·5 (2)
N(9)—C(1′)—C(2′)—O(2′)	−144·7 (2)	C(3′)—C(4′)—C(5′)—O(5′)	60·1 (2)
C(4′)—O(4′)—C(1′)—C(2′) (τ_0)	2·2 (3)	O(4′)—C(4′)—C(5′)—O(5′)	−58·9 (2)

A—H···*B*	Symmetry of *B*	*A*—H	H···*B*	*A*···*B*	∠*AHB*
N(1)—H···O(5′)	1·5 − *x*, 1 − *y*, 0·5 + *z*	0·81	2·02	2·721	144
N(6)—H1···Cl	−0·5 + *x*, 0·5 − *y*, −*z*	0·93	2·19	3·107	171
N(6)—H2···Cl	1 − *x*, 0·5 + *y*, 0·5 − *z*	0·97	2·19	3·136	166
O(2′)—H···O(3′)	*x*, *y*, *z*	0·67	2·31	2·652	113
O(3′)—H···N(7)	0·5 + *x*, 0·5 − *y*, −*z*	0·75	2·27	2·890	141
O(5′)—H···O(2′)	*x*, *y*, −1 + *z*	0·82	2·06	2·827	156

sugars than for C(2′)-*endo* sugars (Altona & Sundaralingam, 1972). The conformation of C(5′)—O(5′) around the exocyclic bond, C(4′)—C(5′), is *gauche–gauche* with O(5′) sitting on top of the ribose ring. This conformation also differs from that observed in 8-AZA where it is *gauche–trans* with O(5′) rotated away from the ribose ring, *gauche* to the C(4′)—O(4′) bond and *trans* to the C(4′)—C(3′) bond. The dihedral angle between the mean planes of the base and the five-atom ribose ring is 78·1°. The heterocyclic base is planar, the maximum deviation of an atom being ±0·01 Å.

The hydrogen-bonding distances and angles are given in Table 2. All except C—H hydrogens are involved in hydrogen bonding. One of the hydrogen bonds, O(2′)—H···O(3′), however, is an intramolecular bent hydrogen bond between two —OH groups on adjacent C atoms, a rather unusual occurrence in

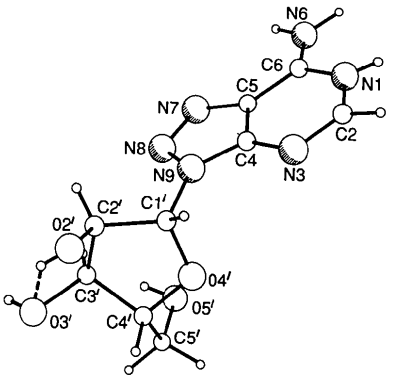

Fig. 1. Protonated 8-azaadenosine in an arbitrary orientation showing the atom-numbering scheme. H atoms are not labelled. The dashed line indicates a possible intramolecular hydrogen bond.

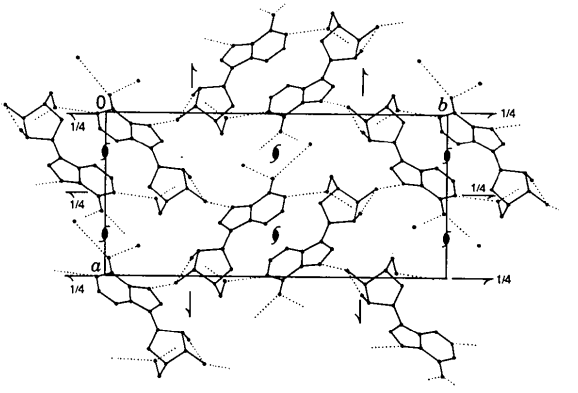

Fig. 2. Crystal-packing diagram projected down the *c* axis. Hydrogen bonds are shown as dotted lines.

a nucleoside structure. There are no interbase hydrogen bonds. The crystal packing shown in Fig. 2 gives rise to alternate hydrophobic and hydrophilic channels running parallel to the *a* axis, the former consisting of the base moieties around $b = 0$ and $\frac{1}{2}$ and the latter consisting of the sugar moieties around $b = \frac{1}{4}$ and $\frac{3}{4}$.

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Structure of Dicyano-15-norcobyrinic Acid Heptamethyl Ester

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Abstract. $[Co(C_{51}H_{71}N_4O_{14})(CN)_2]$, $M_r = 1075{\cdot}09$, orthorhombic, $P2_12_12_1$, $a = 15{\cdot}595\ (2)$, $b = 18{\cdot}672\ (4)$, $c = 19{\cdot}023\ (5)$ Å, $V = 5539\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}289$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 3{\cdot}086$ mm^{-1}, $F(000) = 2280$, $T = 293$ K, $R = 0{\cdot}078$ for 3172 observed reflections [$F > 4\sigma(F)$] and 462 parameters. The molecular structure of the title complex closely resembles that of the parent cobyrinic acid heptamethyl ester. The corrin ring system is not planar, with a maximum deviation of 0·50 (3) Å [for C(11)] from the least-squares plane through the ring atoms, and the dihedral angles between the pyrrole rings lie in the range 7·5 (3)–15·0 (3)°. The replacement of the methyl group on C(19) in the parent complex by an H atom in the title complex has little effect on the local geometry. The side chains show some disorder.

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Introduction. Cobyrinic acid (1), which is a late biosynthetic precursor (Battersby & McDonald, 1982; Leeper, 1985, 1987) of vitamin B_{12}, is heavily C-methylated around the periphery of its macrocycle. The C-methyl groups coordinated to C(9) and C(19) [corresponding to C(5), C(15), respectively, on normal corrin numbering] stand apart from the rest by being sited on the chromophoric conjugated system. Analogues of the natural structure lacking one or both of these methyl groups have recently been prepared (Lewis, Nussberger, Kräutler & Eschenmoser, 1983; Nussbaumer & Arigoni, 1983) by chemical transformations of cobyrinic acid heptamethyl ester, cobester (2). These analogues are 15-norcobester (3), 5-norcobester (4) and 5,15-bisnorcobester (5). In relation to biosynthetic studies, the preparation of 15-norcobester (3) was repeated, and suitable crystals obtained for X-ray analysis. The structure was determined in order to analyse the