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The Crystal and Molecular Structure of Adenine Hydrobromide Hemihydrate, $C_5H_5N_5.HBr.\frac{1}{2}H_2O$

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The crystal and molecular structure of the title compound has been determined from 972 observed three-dimensional data measured by a single-crystal automated X-ray diffractometer. The unit cell is monoclinic with $a = 9{\cdot}018$ (2), $b = 4{\cdot}845$ (2), $c = 19{\cdot}693$ (5) Å, $\beta = 112{\cdot}87$ (2)°, $V = 792{\cdot}9$ (3) Å^3 and contains four formula units. The space group is $P2/c$. The refinement of parameters has been carried out by the least-squares method in block-diagonal approximation. The final R value was 0·025. The adenine base is protonated at the N(1) site. The bond lengths and valence angles within the adenine cation are in good accord with the isomorphous structure of adenine hydrochloride hemihydrate and with other monoprotonated adenine bases.

Introduction

The crystal and molecular structure of adenine hydrobromide hemihydrate has been determined as part of a study of nucleic acids and their components. It is the aim of this programme to elucidate the transfer of energy and information in nucleic acids. Single crystals of the title compound represent a model suitable for the interpretation of optical measurements on polynucleotides, carried out at the Institute of Physics, Charles University, Praha.

Thematically, the present work is a continuation of the study of adenine derivatives (Langer & Huml, 1978). From the beginning of the study it has been assumed that the crystal and molecular structure of the title compound is similar to that of adenine hydrochloride hemihydrate, which was studied with two-dimensional data by Broomhead (1948) and Cochran (1951), and recently with three-dimensional data of considerably higher precision by Kistenmacher & Shigematsu (1974). Preliminary crystal data for the title compound were published by Moravcová (1975).

Experimental

Crystals of adenine hydrobromide hemihydrate used in this study were prepared by J. Zachová at the Institute of Physics, Charles University, Praha. The formula was verified by elemental analysis. The crystals were transparent, red-brown and very brittle.

Crystal data

$C_5H_5N_5.HBr.\frac{1}{2}H_2O$, monoclinic, $P2/c$, a = 9·018 (2), b = 4·845 (2), c = 19·693 (5) Å, β = 112·87 (2)°, V = 792·9 (3) Å^3, $F(000)$ = 444, FW 225·07, $\mu_{\rm Cu} = 74\cdot93$ cm^{-1}, $D_m = 1\cdot909$, $D_x = 1\cdot886$ g cm^{-3}, $Z = 4$.

The dimensions of the unit cell have been determined by refining 14 general reflexions (graphite monochromator, Cu $K\bar{\alpha}$ radiation, λ = 1·5418 Å, room temperature, the crystal in a general position). 14 reflexions that did not obey the law of systematic absences common to space groups $P2/c$ and Pc (for $h0l$: $l = 2n + 1$) were a result of multiple scattering, as confirmed by the ψ scan. The space group $P2/c$ was considered because of the assumed similarity with adenine hydrochloride hemihydrate.

Intensity measurement

Intensities were measured with an automated Syntex $P2_1$ diffractometer by the θ–2θ scan method. The crystal employed was 0·1 × 0·06 × 0·055 mm. Measurement was carried out according to a method described elsewhere (Langer & Huml, 1978). The whole measurement was corrected for the fluctuation of three standard reflexions (after each 50 reflexions) by means of the program *INTER* (Langer, 1973). 1177 independent reflexions were measured below $2\theta = 120°$ (hkl and $\bar{h}kl$), of which 972 were observed. A reflexion was considered as unobserved if $I_{\rm obs} < 1\cdot96\sigma(I)$, where $\sigma(I)$ was calculated from the counting statistics. Intensities and their e.s.d.'s were corrected for the Lorentz–polarization factor by means of the relation $\mathrm{Lp} = (1 + \cos^2 2\theta_M \cos^2 2\theta)/[\sin 2\theta(1 + \cos^2 2\theta_M)]$; $2\theta_M$ is the monochromator diffraction angle (=26·568°) for Cu $K\alpha$ radiation. No correction for absorption was made.

Structure determination and refinement

The phase problem was solved by the heavy-atom method; the position of the bromide ion coincides with that of the chloride ion in adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974). The structure was refined (starting from the parameters of the hydrochloride) by the least-squares method in the block-diagonal approximation (9 × 9 matrix for the non-hydrogen atoms with anisotropic temperature factors and 4 × 4 matrix for the H atoms with isotropic temperature factors); $\sum w_F(|F_o| - |F_c|)^2$ was the function minimized. The O atom in the water molecule was fixed on the twofold axis. Atomic scattering factors for the non-hydrogen atoms were taken from Cromer & Waber (1965), and values from Cromer & Liberman (1970) were used for the anomalous part of the scattering factor of the bromide anion; the atomic scattering factor of H was taken as the spherical approximation of the bonded atom (Stewart, Davidson & Simpson, 1965). Unobserved reflexions were excluded from the refinement. The program *NRC*-10 (Ahmed, Hall, Pippy & Huber, 1966) was employed with the weighting scheme $w_F = 1/[\sigma_F^2 + (0\cdot015F_o)^2]$. No correction for secondary extinction was applied. The refinement was stopped when the shifts of all parameters were less than $\frac{1}{10}$ of their respective e.s.d.'s. The final R index ($R = \sum||F_o| - |F_c||/\sum |F_o|$) was

Table 1. *Positional parameters for the non-hydrogen atoms and their e.s.d.'s* (×10^5)

	x	y	z
Br	28532 (4)	18429 (9)	27561 (2)
O	0 (0)	73380 (74)	25000 (0)
N(1)	82367 (33)	40934 (62)	59668 (13)
N(3)	61038 (35)	25584 (57)	48803 (15)
N(7)	81666 (31)	79987 (61)	43619 (13)
N(9)	60675 (33)	51915 (66)	38240 (13)
N(10)	100530 (34)	76203 (59)	60391 (14)
C(2)	69341 (43)	24562 (71)	55926 (18)
C(4)	66732 (37)	45337 (72)	45511 (16)
C(5)	79643 (36)	62731 (64)	48783 (15)
C(6)	88168 (38)	60913 (66)	56464 (16)
C(8)	69917 (43)	72676 (76)	37423 (17)

Table 2. *Positional parameters for the hydrogen atoms and their e.s.d.'s* (×10^3)

	x	y	z
H(1)	866 (3)	397 (7)	642 (2)
H(2)	656 (4)	104 (7)	588 (2)
H(3)	524 (4)	452 (7)	347 (2)
H(4)	681 (4)	800 (7)	327 (2)
H(5)	1048 (4)	892 (8)	583 (2)
H(6)	1053 (4)	734 (6)	650 (2)
H(7)	64 (4)	828 (7)	246 (2)

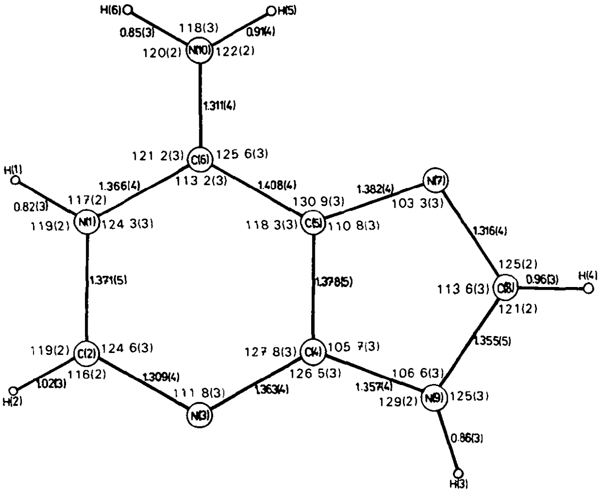

Fig. 1. Numbering scheme with bond distances (Å) and bond angles (°) and their e.s.d.'s. The water molecule lies on the twofold axis and the distance O–H(7) is 0·77 (4) Å; the valency angle at the O atom is 107 (5)°.

0·025.* Tables 1 and 2 summarize the final positional parameters for all non-hydrogen and H atoms respectively.

The residual electron density in the final difference map did not exceed ±0·40 e Å^{-3}.

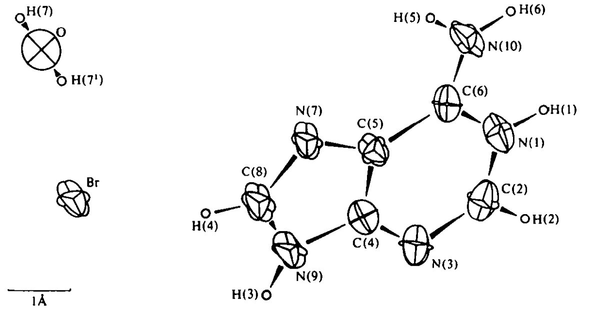

Fig. 2. Thermal ellipsoids drawn at the 50% probability level for the non-hydrogen atoms. Positions of the H atoms are marked by circles. The projection is along **b**.

Table 3. *Rigid-body-motion parameters of the adenine base*

The tensors are referred to a Cartesian coordinate system defined by $X \parallel \mathbf{a}$, Y in the ab plane, $Z \parallel \mathbf{c}^*$; the origin is at the centre of mass.

$$\mathbf{T} = \begin{pmatrix} 316\,(14) & 40\,(12) & 7\,(9) \\ & 299\,(13) & -5\,(9) \\ & & 244\,(9) \end{pmatrix} (\text{Å}^2 \times 10^4)$$

$$\mathbf{L} = \begin{pmatrix} 36\,(4) & 17\,(3) & -2\,(3) \\ & 39\,(4) & -7\,(3) \\ & & 42\,(7) \end{pmatrix} (\text{rad}^2 \times 10^4)$$

$$\mathbf{S} = \begin{pmatrix} -18\,(7) & 9\,(3) & -6\,(4) \\ 1\,(3) & 16\,(7) & 12\,(4) \\ 3\,(4) & -9\,(5) & 2\,(25) \end{pmatrix} (\text{Å rad} \times 10^4)$$

Eigenvalues of **T** (Å^2 × 10^4)	Direction cosines (× 10^4)		
348	7780	6278	223
269	5931	−7460	3030
242	2070	−2224	−9527

Eigenvalues of **L** (rad^2 × 10^4)	Direction cosines (× 10^4)		
57	5905	7063	−3905
40	3798	1829	9068
20	7120	−6837	−1599

Eigenvalues of **S** (Å rad × 10^4)	Direction cosines (× 10^4)		
14	−1375	−9549	−2620
5	−2723	−2182	9374
−18	−9523	2006	−2301

R.M.S. = 0·0020 Å^2, E.S.D. = 0·0025 Å^2, (R.M.S.)′ = 0·0013 Å^2.

Description of the structure

The numbering scheme is presented in Fig. 1 together with bond distances, bond angles and the corresponding e.s.d.'s. Thermal ellipsoids of 50% probability for all non-hydrogen atoms in a projection along **b** (Šoler, 1973) are shown in Fig. 2. Results of the thermal-motion analysis of the adenine base, carried out in the **TLS** approximation of the rigid-body motion (Schomaker & Trueblood, 1968), are presented in Table 3. The following criteria: R.M.S. = $[\sum (U_{\text{obs}} - U_{\text{calc}})^2/n]^{1/2}$, E.S.D. = $[\sum(U_{\text{obs}} - U_{\text{calc}})^2/(n-s)]^{1/2}$, (R.M.S.)′ = $[\sum \sigma^2(U_{\text{obs}})/n]^{1/2}$ show that the rigid-body-motion approximation is acceptable. Bond lengths corrected for the libration of atoms (Cruickshank, 1956) differ at most by the corresponding e.s.d.; accordingly, the changes in bond lengths were ignored.

In Table 4 are some weighted mean planes. χ^2 values show the significant nonplanarity of the six-membered ring, whereas the imidazole ring can be considered planar.

Table 4. *Weighted mean planes*

Equations are referred to a Cartesian coordinate system defined by $X \parallel \mathbf{a}$, Y in the ab plane, $Z \parallel \mathbf{c}^*$. Departures from the plane are in Å × 10^3. Daggers indicate the plane-defining atoms.

Plane (I) $0{\cdot}7242X - 0{\cdot}6742Y - 0{\cdot}1449Z + 0{\cdot}8394 = 0$
Plane (II) $0{\cdot}7225X - 0{\cdot}6729Y - 0{\cdot}1586Z + 0{\cdot}9564 = 0$
Plane (III) $0{\cdot}7238X - 0{\cdot}6735Y - 0{\cdot}1499Z + 0{\cdot}8870 = 0$

	(I)	(II)	(III)
N(1)	5 (3)†	−28 (3)	0 (3)†
N(3)	2 (3)†	−4 (3)	6 (3)†
N(7)	−5 (3)	2 (3)†	5 (3)†
N(9)	−19 (3)	2 (3)†	−5 (3)†
N(10)	−20 (3)	−56 (2)	−25 (3)
C(2)	−5 (4)†	−29 (4)	−7 (4)†
C(4)	−3 (4)†	0 (4)†	5 (4)†
C(5)	5 (3)†	−1 (3)†	10 (3)†
C(6)	−7 (3)†	−32 (3)	−9 (3)†
C(8)	−27 (4)	−4 (4)†	−11 (4)†
χ^2	11·4	2·1	38·3

Dihedral angle (I) ∧ (II) = 0·9°.

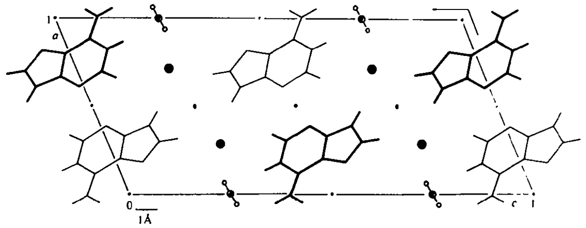

Fig. 3. The crystal structure of adenine hydrobromide hemihydrate viewed along **b**.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33297 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Hydrogen bonds and some close contacts*

A	H	*B*	*A*···*B*	*B*···H	∠*A*−H···*B*
N(1)	H(1)	O^{ii}	2·897 (3) Å	2·10 (3) Å	164 (3)°
N(9)	H(3)	Br	3·274 (3)	2·44 (4)	164 (3)
N(10)	H(5)	N(7^{iii})	2·948 (4)	2·06 (4)	165 (3)
N(10)	H(6)	Br^{iv}	3·353 (3)	2·58 (3)	152 (3)
O	H(7)	Br^{v}	3·260 (2)	2·53 (4)	160 (4)
C(2)	H(2)	Br^{vi}	3·803 (3)	2·89 (3)	149 (2)
C(8)	H(4)	Br^{vii}	3·736 (4)	2·84 (3)	156 (3)

Symmetry code

(i) $-x, y, \frac{1}{2}-z$
(ii) $1-x, 1-y, 1-z$
(iii) $2-x, 2-y, 1-z$
(iv) $1+x, 1-y, \frac{1}{2}+z$
(v) $-x, 1+y, \frac{1}{2}-z$
(vi) $1-x, -y, 1-z$
(vii) $1-x, 1+y, \frac{1}{2}-z$

A projection of the crystal structure along **b** is shown in Fig. 3. The lengths and angles of the hydrogen bonds are in Table 5, together with the two C—H···Br short contacts.

Discussion of the structure

The structure of the title compound is in good accord with that of adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974), the only exception being the distance C(2)—N(3): 1·309 (4) Å in the hydrobromide, 1·289 (4) Å in the hydrochloride. However, the mean value of this length given by Voet & Rich (1970) is 1·309 (4) Å and the value 1·310 (8) Å is given by Ringertz (1972).

As a result of the protonation of the adenine base at the N(1) site, a change has been found in the pyrimidine ring internal angles at the N atoms, in agreement with other work (*e.g.* Langer & Huml, 1978; Voet & Rich, 1970).

In addition to the interaction of adenine bases through hydrogen bonding, an interaction perpendicular to the layers of bases is possible (Voet & Rich, 1970), which is probably of the dipole–induced dipole type (Bugg, Thomas, Sundaralingam & Rao, 1971). The perpendicular distance between the planes through the adenine bases is 3·30 Å (calculated for plane III in Table 4).

The authors are indebted to Professor V. Prosser for bringing this problem to their attention and for his continued interest in their work during the structure determination, and also to Dr J. Zachová who prepared the crystals.

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