

The Crystal and Molecular Structure of Adeninium Hemisulfate Hydrate, $C_5H_5N_5 \cdot \frac{1}{2}H_2SO_4 \cdot H_2O$

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The crystal and molecular structure of the title compound has been determined from 2369 observed three-dimensional data measured by a single-crystal automated X-ray diffractometer. The unit cell is triclinic with $a = 7.844$ (5), $b = 11.663$ (8), $c = 9.565$ (7) Å, $\alpha = 96.85$ (6), $\beta = 80.83$ (6), $\gamma = 103.88$ (5)°, $V = 835.8$ (9) Å³, and contains four formula units. The space group is $P\bar{1}$. The crystal structure was solved by direct methods and refined by the least-squares method in the block-diagonal approximation. The final R value was 0.067. Both independent adenine bases are protonated on N(1). Hydrogen bonds existing between adenine bases form two modes of pairing; one of them [N(19)—H(19)···N(23), N(29)—H(29)···N(13)] is described for the first time.

Introduction

The determination of the crystal and molecular structure of adeninium hemisulfate hydrate forms part of a study aimed at the elucidation of the structures of components of nucleic acids and their derivatives. Single crystals of these compounds serve as models in the interpretation of optical measurements on polynucleotides, carried out at the Institute of Physics, Charles University, Praha. This communication represents a continuation of our previous studies concerned with the crystal and molecular structures of adeninium sulfate (Langer & Huml, 1978*a*) and adenine hydrobromide hemihydrate (Langer & Huml, 1978*b*). Preliminary crystal data for the title compound were published by Moravcová (1975).

Experimental

Crystals of adeninium hemisulfate hydrate used in this study were prepared by Zachová (1978) at the Institute of Physics, Charles University, Praha. The formula has been verified by means of elemental analysis. The crystals were colorless and showed a pronounced cleavability along the plane (101); accordingly, it was not possible to grind them into spheres.

Crystal data

Triclinic, $P\bar{1}$, $a = 7.844$ (5), $b = 11.663$ (8), $c = 9.565$ (7) Å, $\alpha = 96.85$ (6), $\beta = 80.83$ (6), $\gamma =$

103.88 (5)°, $V = 835.8$ (9) Å³, $C_5H_5N_5 \cdot \frac{1}{2}H_2SO_4 \cdot H_2O$, FW 202.20, $\mu(\text{Cu } K\alpha) = 22.15 \text{ cm}^{-1}$, $D_m = 1.602$, $D_x = 1.607 \text{ g cm}^{-3}$, $Z = 4$, $F(000) = 420$. The unit-cell parameters were determined using the Syntex P2₁ automated diffractometer by refining 15 general reflexions (graphite monochromator, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, room temperature, the crystal in a general position). The decision about the existence of a center of symmetry was reached on the basis of statistical tests (Karle, Dragonette & Brenner, 1965) for the normalized structure factors E and confirmed by the successful refinement of the structure.

Intensity measurement

The intensities were measured with the same diffractometer by the θ - 2θ scan method. The crystal employed was of irregular shape with dimensions 0.25 × 0.40 × 0.40 mm. The measurement was carried out with the crystal in a general position at room temperature. Intensities higher than 5×10^3 c.p.s. were corrected for coincidence of pulses (dead time = 2×10^{-6} s). Reflexions with intensities higher than 50×10^3 c.p.s. were measured again at a lower anode current. The right and left backgrounds were measured for half the time needed for the measurement of the diffraction peak. The scan interval for 2θ was 1° below $K\alpha_1$, and 1° above $K\alpha_2$, of the Cu $K\alpha$ doublet. For determining the individual scan velocities the intensity at the maximum of the diffraction peak was rapidly estimated; the scan velocity changed from a minimum of $1.1^\circ \text{ min}^{-1}$ to a maximum of $29.3^\circ \text{ min}^{-1}$ for 2θ . Three standard reflexions were measured after each 50

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reflexions; during the total time of measurement (140 h) no unusual fluctuations of the standard reflexions were observed and they did not indicate any deterioration of the crystal with time. All intensity measurements were scaled to the same level with respect to the standard reflexions by means of the program *INTER* (Langer, 1973). 2480 independent reflexions were measured below $2\theta = 120^\circ$, of which 2369 were observed. A reflexion was considered as unobserved if $I < 1.96\sigma(I)$, where $\sigma(I)$ was calculated from the counting statistics. The intensities and their e.s.d.'s were corrected for Lorentz and polarization factors by means of the relation $L_p = (1 + \cos^2 2\theta_M \cos^2 2\theta) / [\sin 2\theta(1 + \cos^2 2\theta_M)]$, where $2\theta_M$ 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 direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971). The structure was refined by the least-squares method in the block-diagonal approximation (9×9 matrices for the non-hydrogen atoms with anisotropic temperature factors and 4×4 matrices for the H atoms with isotropic temperature factors); $\sum w_F(|F_o| - |F_c|)^2$ was the quantity minimized. Atomic scattering factors for the non-hydrogen atoms were taken from tables published by Cromer & Waber (1965); values tabulated by Cromer & Liberman (1970) were taken for the anomalous part of the scattering factor of the S atom; the atomic scattering factor for 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 $w_F = 1/[\sigma_F^2 + (0.015F_o)^2]$. The non-hydrogen atoms were refined anisotropically; when the conventional R factor ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) dropped to 0.087, a difference map was calculated with reflexions having $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$ and it showed all H atoms in the expected positions. At the end of the refinement procedure a correction for secondary extinction was applied to the six strongest reflexions according to the formula $I_c/I_o = 1 + (g/\mu)I_c$ (Pinnock, Taylor & Lipson, 1956) with $g/\mu = 6.5 \times 10^{-6}$. The process of refining non-hydrogen atoms anisotropically and H atoms isotropically was stopped when the changes in all parameters became less than $\frac{1}{10}$ of their respective e.s.d.'s.*

* Lists of atomic temperature parameters (anisotropic for the non-hydrogen atoms and isotropic for the H atoms) and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33440 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s for the non-hydrogen atoms (all parameters multiplied by 10^4)*

	x	y	z
S	1789 (1)	7614 (1)	4825 (1)
O(1)	1537 (3)	8825 (2)	5333 (3)
O(2)	1250 (4)	6870 (2)	6027 (3)
O(3)	3671 (3)	7686 (2)	4316 (3)
O(4)	702 (4)	7116 (2)	3700 (3)
N(11)	9556 (4)	-525 (2)	-2340 (3)
C(16)	8828 (4)	-1349 (3)	-1376 (3)
N(16)	9180 (4)	-2403 (2)	-1605 (3)
C(15)	7764 (4)	-927 (2)	-192 (3)
C(14)	7549 (4)	218 (3)	-119 (3)
N(13)	8280 (4)	1021 (2)	-1096 (3)
C(12)	9264 (4)	588 (3)	-2175 (3)
N(17)	6817 (4)	-1490 (2)	994 (3)
C(18)	6074 (4)	-664 (3)	1745 (3)
N(19)	6486 (4)	374 (2)	1130 (3)
N(21)	4648 (4)	4348 (2)	2944 (3)
C(26)	5617 (4)	5225 (3)	2084 (3)
N(26)	5481 (4)	6323 (2)	2379 (3)
C(25)	6694 (4)	4791 (3)	909 (3)
C(24)	6686 (4)	3603 (3)	744 (3)
N(23)	5749 (4)	2763 (2)	1621 (3)
C(22)	4778 (5)	3205 (3)	2695 (4)
N(27)	7770 (4)	5374 (2)	-208 (3)
C(28)	8377 (5)	4526 (3)	-1015 (4)
N(29)	7759 (4)	3441 (2)	-501 (3)
O(11)	7710 (3)	5291 (2)	4740 (3)
O(12)	3827 (4)	807 (2)	4017 (3)

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

	x	y	z
H(11)	1024 (5)	72 (4)	-320 (4)
H(12)	999 (5)	116 (4)	-299 (4)
H(161)	898 (4)	-278 (3)	-105 (3)
H(162)	963 (5)	-268 (3)	-242 (4)
H(18)	542 (5)	-76 (3)	272 (4)
H(19)	617 (7)	94 (4)	150 (5)
H(21)	396 (5)	457 (3)	379 (4)
H(22)	395 (5)	264 (3)	331 (4)
H(261)	617 (10)	705 (6)	176 (7)
H(262)	499 (5)	659 (3)	311 (4)
H(28)	930 (7)	459 (4)	-195 (5)
H(29)	781 (5)	283 (3)	-80 (4)
H(111)	881 (7)	578 (5)	440 (5)
H(112)	795 (7)	473 (4)	449 (5)
H(121)	470 (6)	115 (4)	453 (4)
H(122)	316 (8)	22 (6)	441 (6)

The final R index was 0.067. There were 7.7 observed reflexions per refined parameter. 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 including all observed reflexions did not exceed $\pm 0.40 \text{ e \AA}^{-3}$, with the exception of extremes of $+0.55$ and -0.69 e \AA^{-3} in the vicinity of the sulfate anion.

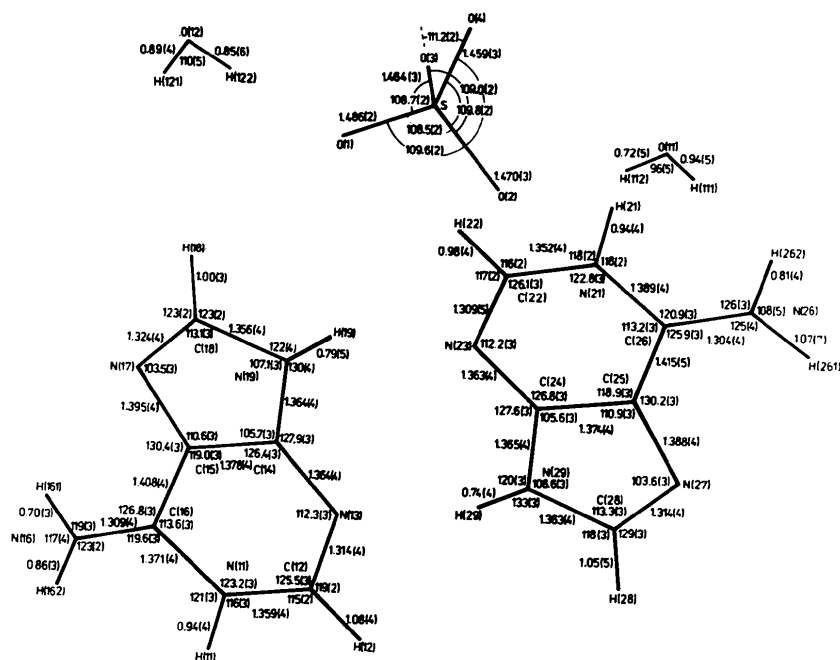


Fig. 1. Numbering scheme with bond distances (Å) and bond angles ($^{\circ}$). In parentheses are the respective e.s.d.'s. The two independent adenine bases are distinguished by the first figure of the atom number. The projection is along the a axis.

Description of the structure

The numbering scheme of the compound studied is presented in Fig. 1 together with the bond lengths, valence angles, and corresponding e.s.d.'s. The thermal ellipsoids of 50% probability for all non-hydrogen atoms in the projection along the a axis (Söler, 1973) are illustrated in Fig. 2. An analysis of the thermal vibrations of both independent adenine bases as well as the sulfate ion was carried out in the TLS approximation of rigid-body motion (Schomaker & Trueblood, 1968). Bond lengths were corrected for the librations of the molecules according to Cruickshank (1956). The tensors T , L , and S , and their eigenvalues and direction cosines with respect to an orthogonal coordinate system are listed in Table 3. The following criteria were used in deciding whether the rigid-body approximation was valid: $R.M.S. = [\sum (U_{obs} - U_{calc})^2/n]^{1/2}$; $E.S.D. = [\sum (U_{obs} - U_{calc})^2/(n - s)]^{1/2}$; $(R.M.S.)' = [\sum \sigma^2(U_{obs})/n]^{1/2}$. The corresponding values for both independent adenine bases (base 1 and base 2) and for the sulfate anion are also given in Table 3; it is clear that there are no objections against accepting the rigid-body-motion approximation for the thermal motions of these three groups. The bond lengths corrected for libration do not differ significantly from the uncorrected values for either independent adenine moiety – the deviations do not exceed the corresponding e.s.d.'s. However, more pronounced changes in bond lengths are observed within the sulfate group and these

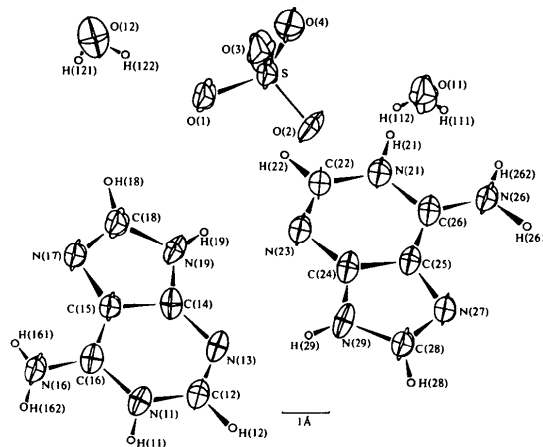


Fig. 2. Thermal ellipsoids drawn at the 50% probability level for the non-hydrogen atoms. Positions of H atoms are marked by a circle. The projection is along the a axis.

are given in Table 4. Nevertheless, only uncorrected values will be used in the following discussion.

Table 5 summarizes the deviations of atoms from the weighted mean planes through the six-membered rings (plane I for base 1 and plane IV for base 2), through the imidazole rings (plane II for base 1 and plane V for base 2 respectively), and finally through the whole adenine base (plane III for base 1 and plane VI for base 2 respectively) with the exception of atoms N(16) and

Table 3. *Rigid-body-motion parameters*

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

Adenine base 1

$T(\text{\AA}^2 \times 10^4)$			$L(\text{rad}^2 \times 10^4)$		
415 (13)	-11 (9)	30 (10)	24 (4)	-8 (3)	-21 (4)
	226 (9)	-41 (8)		31 (4)	-4 (3)
		438 (9)			50 (5)
$S(\text{rad } \text{\AA} \times 10^4)$					
[trace (S) = 0]					
	-11 (6)	6 (3)		-7 (3)	
	1 (3)	-4 (7)		17 (4)	
	8 (3)	-13 (5)		14 (22)	

Eigenvalues ($\text{\AA}^2 \times 10^4$) and direction cosines ($\times 10^4$) of T

465	5293	-1669	8319
396	8480	711	-5252
218	284	9834	1793

Eigenvalues ($\text{rad}^2 \times 10^4$) and direction cosines ($\times 10^4$) of L

62	-4973	233	8673
34	-3073	9300	-2017
8	-8114	-3665	-4553

Eigenvalues ($\text{rad } \text{\AA} \times 10^4$) and direction cosines ($\times 10^4$) of S

13	83	2071	9783
-6	-6791	7181	-1524
-7	-7352	-6613	1488

R.M.S. = 0.0018 \AA^2 , E.S.D. = 0.0022 \AA^2 , (R.M.S.)' = 0.0014 \AA^2

Adenine base 2

$T(\text{\AA}^2 \times 10^4)$			$L(\text{rad}^2 \times 10^4)$		
445 (12)	23 (8)	2 (9)	20 (3)	-1 (3)	-18 (3)
	230 (8)	-29 (7)		32 (4)	-1 (2)
		494 (8)			38 (4)
$S(\text{rad } \text{\AA} \times 10^4)$					
[trace (S) = 0]					
	13 (5)	1 (3)		-5 (3)	
	-6 (3)	-1 (6)		-13 (3)	
	-6 (3)	1 (4)		-12 (19)	

Eigenvalues ($\text{\AA}^2 \times 10^4$) and direction cosines ($\times 10^4$) of T

497	66	1076	-9942
447	9944	1045	170
225	1057	-9887	-1063

Eigenvalues ($\text{rad}^2 \times 10^4$) and direction cosines ($\times 10^4$) of L

49	-5247	-40	8513
32	-362	9991	-206
9	-8506	-341	-5247

Eigenvalues ($\text{rad } \text{\AA} \times 10^4$) and direction cosines ($\times 10^4$) of S

15	-9618	-1491	2272
0	2129	-9435	2628
-15	1742	2933	9381

R.M.S. = 0.0016 \AA^2 , E.S.D. = 0.0019 \AA^2 , (R.M.S.)' = 0.0015 \AA^2

Sulfate group

$T(\text{\AA}^2 \times 10^4)$			$L(\text{rad}^2 \times 10^4)$		
588 (10)	-17 (12)	149 (9)	81 (12)	-63 (18)	-60 (12)
	244 (11)	-43 (8)		216 (14)	45 (9)
		477 (13)			133 (17)
$S(\text{rad } \text{\AA} \times 10^4)$					
[trace (S) = 0]					
	12 (16)	-21 (9)		6 (7)	
	-39 (9)	41 (17)		-2 (6)	
	-22 (7)	22 (6)		-53 (15)	

Table 3 (cont.)

Eigenvalues ($\text{\AA}^2 \times 10^4$) and direction cosines ($\times 10^4$) of T

694	-8146	862	-5735
378	-5789	-1804	7952
236	-348	9799	1967

Eigenvalues ($\text{rad}^2 \times 10^4$) and direction cosines ($\times 10^4$) of L

272	4045	-8050	-4340
123	2793	5606	-7796
36	8708	1942	4516

Eigenvalues ($\text{rad } \text{\AA} \times 10^4$) and direction cosines ($\times 10^4$) of S

55	-3961	8996	1838
-7	-9158	-3998	-381
-48	385	-1835	9823

R.M.S. = 0.0008 \AA^2 , E.S.D. = 0.0015 \AA^2 , (R.M.S.)' = 0.0013 \AA^2

N(26). The value of χ^2 is given for each plane; some dihedral angles between planes are also listed. It is evident that the six-membered ring of adenine base 1 (plane I) and the imidazole ring of base 2 (plane V) can be considered planar. In all remaining instances the χ^2 value indicates a statistically significant nonplanarity.

A projection of the crystal structure along the c axis is shown in Fig. 3. It is evident that the adenine bases form parallel layers related by a center of symmetry. In the crystal structure there is a system of hydrogen bonds among the adenine bases, the sulfate anion, and the molecules of water, as given in Table 6. The hydrogen bonds found here between adenine bases represent two modes of base pairing: N(16)—H(161)···N(27ⁱⁱ), N(26)—H(261)···N(17^{iv}) and N(19)—H(19)···N(23), N(29)—H(29)···N(13); for the symmetry codes see Table 6. The first mode of pairing is similar to that in adenine hydrochloride (Kistenmacher & Shigematsu, 1974) or in adenine hydrobromide (Langer & Huml, 1978*b*), whereas the second mode (*cf.* Fig. 4) is, to the authors' knowledge, described here for the first time. The sulfate anion participates in hydrogen bonding to the maximum possible extent. The adenine base 1 is doubly hydrogen-bonded to a single sulfate group [*i.e.* by N(11)···O(1^l) and N(16)···O(2^l); see Table 6], as in adeninium sulfate (Langer & Huml, 1978*a*). This mode of hydrogen bonding is common in interactions between the base and a phosphate group (Sundaralingam, 1966).

Table 4. *Correction of bond lengths (Å) in the sulfate group for rigid-body motion (with the respective e.s.d.'s in parentheses)*

	Uncorrected	Corrected
S—O(1)	1.486 (2)	1.497
S—O(2)	1.470 (3)	1.487
S—O(3)	1.464 (3)	1.482
S—O(4)	1.459 (3)	1.478

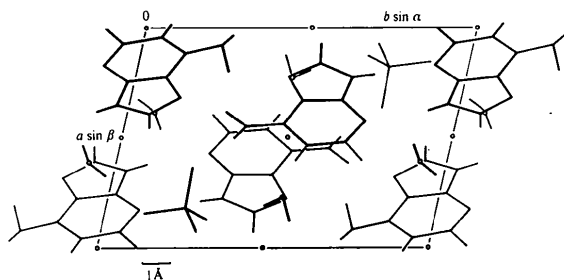


Fig. 3. Crystal structure of adeninium hemisulfate hydrate viewed along the c axis.

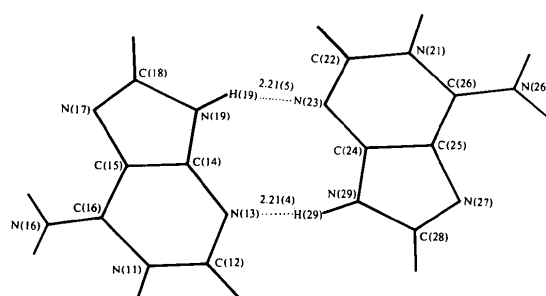


Fig. 4. Base-base hydrogen bonding – the second mode.

Table 5. *Weighted mean planes*

Equations are referred to a Cartesian coordinate system defined by: $X \parallel a$, Y in the ab plane, $Z \parallel c^*$. Deviations from planes ($\text{Å} \times 10^3$) marked with daggers indicate plane-defining atoms.

Plane

I	$-0.8294X - 0.2807Y - 0.4830Z + 4.8632 = 0$
II	$-0.8336X - 0.2754Y - 0.4788Z + 4.8934 = 0$
III	$-0.8314X - 0.2787Y - 0.4807Z + 4.8801 = 0$
IV	$-0.8277X - 0.1330Y - 0.5452Z + 4.5256 = 0$
V	$-0.8533X - 0.1292Y - 0.5051Z + 4.5808 = 0$
VI	$-0.8386X - 0.1337Y - 0.5281Z + 4.5318 = 0$

	Plane I	Plane II	Plane III
N(11)	-2 (3)†	-13 (3)	6 (3)†
C(16)	4 (3)†	-8 (3)	0 (3)†
N(16)	-7 (3)	-29 (3)	-14 (3)
C(15)	-2 (3)†	-4 (3)†	0 (3)†
C(14)	0 (3)†	6 (3)†	5 (3)†
N(13)	1 (3)†	8 (3)	6 (3)†
C(12)	0 (4)†	-2 (4)	1 (4)†
N(17)	0 (3)	0 (3)†	4 (3)†
C(18)	-7 (4)	4 (4)†	2 (4)†
N(19)	-20 (3)	-5 (3)†	-10 (3)†
χ^2	2.1	9.3	23.8
	Plane IV	Plane V	Plane VI
N(21)	10 (3)†	120 (3)	29 (3)†
C(26)	-8 (4)†	64 (4)	-8 (4)†
N(16)	-16 (3)	81 (3)	-8 (3)
C(25)	-4 (3)†	2 (4)†	-31 (3)†
C(24)	9 (4)†	-4 (4)†	-23 (4)†
N(23)	-2 (3)†	24 (3)	-15 (3)†
C(22)	-11 (4)†	75 (4)	1 (4)†
N(27)	47 (3)	1 (3)†	-4 (3)†
C(28)	92 (4)	-4 (4)†	22 (4)†
N(29)	82 (3)	4 (3)†	22 (3)†
χ^2	33.3	4.2	333.3

Some dihedral angles: $I \wedge II = 0.6^\circ$, $IV \wedge V = 2.8^\circ$, $III \wedge VI = 8.8^\circ$.

Discussion of the structure

In comparing the bond lengths and valence angles of both independent adenine bases (*cf.* Table 7) we find significant differences only in the bond $C(6)-N(1)$ and

in the valence angle $N(1)-C(6)-N(6)$. These discrepancies can be explained by the fact that the atoms $N(16)$ and $N(11)$ of adenine base 1 are in contact with the same sulfate anion [*i.e.* $O(1')$ and $O(2')$], whereas $N(26)$ and $N(21)$ of base 2 are in contact with a sulfate group and with a molecule of water respectively (*cf.* Table 6). A comparison of the structure under discussion with other adenine bases monoprotonated on $N(1)$ (*cf.* Table 7) shows good agreement both in bond lengths and in valence angles, with the following exceptions: the length of bond $N(1)-C(2)$ and the angles $N(1)-C(2)-N(3)$, $C(6)-N(1)-C(2)$, $N(3)-C(4)-C(5)$, and $C(5)-C(6)-N(6)$, in comparison with adenine hydrobromide hemihydrate (Langer & Huml, 1978*b*). These deviations can be explained by a different crystal packing of adenine hydrobromide hemihydrate, as the values found in the above study are in good accord with values found for adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974). Comparison with mean values published by Voet & Rich (1970) shows only a single significant difference in the above-mentioned distance $C(6)-N(1)$.

Because of the protonation of the adenine bases on $N(1)$, a change has been found in the pyrimidine ring internal angles at N atoms, in accordance with other studies (*e.g.* Langer & Huml, 1978*a,b*; Voet & Rich, 1970).

As was the case in adeninium sulfate N^1 -oxide (Prusiner & Sundaralingam, 1972) we find considerable departures from equality in the exocyclic angles of the imidazole rings.

The dimensions of the sulfate anion are comparable with those found in other sulfates (*e.g.* Langer & Huml, 1978*a*; Prusiner & Sundaralingam, 1972). The length of the $S-O$ bond lies within the interval 1.478 (3) to 1.497 (2) Å (corrected for thermal motion), while the angles $O-S-O$ range from $108.5(2)$ to $111.2(2)^\circ$, in accord with a tetrahedral conformation. The lengths of the $S-O$ bonds depend considerably on the strengths of the respective hydrogen bonds (*cf.* Table 6). The angles $H-O-H$ in the water molecules are in good agreement with quantum-mechanical calculations, but the $O-H$

Table 6. *Hydrogen bonds (A—H...B)*

A	H	B	A...B	B...H	∠A—H...B
N(26)	H(262)	O(3)	2.742 (4) Å	1.98 (4) Å	156 (4)°
N(29)	H(29)	N(13)	2.924 (4)	2.21 (4)	162 (4)
N(19)	H(19)	N(23)	2.948 (4)	2.21 (5)	156 (5)
N(11)	H(11)	O(1 ^I)	2.646 (4)	1.71 (4)	174 (4)
O(12)	H(122)	O(1 ^{II})	2.853 (4)	2.01 (6)	179 (6)
N(16)	H(162)	O(2 ^I)	2.742 (4)	1.90 (4)	163 (4)
O(11)	H(112)	O(2 ^{II})	2.812 (4)	2.09 (5)	174 (5)
O(12)	H(121)	O(3 ^{III})	2.856 (4)	1.99 (4)	163 (4)
O(11)	H(111)	O(4 ^V)	2.898 (4)	1.98 (5)	164 (5)
N(26)	H(261)	N(17 ^{IV})	2.905 (4)	1.86 (7)	163 (6)
N(21)	H(21)	O(11 ^{III})	2.711 (4)	1.78 (4)	167 (3)
N(16)	H(161)	N(27 ^{II})	2.952 (4)	2.32 (3)	150 (3)

Symmetry code: (i) $1 + x, y - 1, z - 1$; (ii) $x, y - 1, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, 1 + y, z$; (v) $1 + x, y, z$.

Table 7. *A comparison of heavy-atom bond lengths (Å) and angles (°) in some adenines monoprotonated on N(1)*

	1	2	3	4	5
N(1)—C(2)	1.359	1.352	1.371	1.374	1.358 (13)
C(2)—N(3)	1.314	1.309	1.309	1.289	1.309 (4)
N(3)—C(4)	1.364	1.363	1.363	1.358	1.347 (8)
C(4)—C(5)	1.378	1.374	1.378	1.377	1.392 (16)
C(5)—C(6)	1.408	1.415	1.408	1.403	1.424 (33)
C(6)—N(1)	1.371	1.389	1.366	1.360	1.362 (1)
C(5)—N(7)	1.395	1.388	1.382	1.377	1.374 (14)
N(7)—C(8)	1.324	1.314	1.316	1.320	1.320 (11)
C(8)—N(9)	1.356	1.363	1.355	1.351	1.383 (21)
N(9)—C(4)	1.364	1.365	1.357	1.360	1.366 (16)
C(6)—N(6)	1.309	1.304	1.311	1.311	1.315 (5)
N(1)—C(2)—N(3)	125.5	126.1	124.6	125.1	125.8 (1)
C(2)—N(3)—C(4)	112.3	112.2	111.8	112.0	111.9 (5)
N(3)—C(4)—C(5)	126.4	126.8	127.8	127.8	127.8 (9)
C(4)—C(5)—C(6)	119.0	118.9	118.3	117.7	116.9 (18)
C(5)—C(6)—N(1)	113.6	113.2	113.2	113.8	114.2 (7)
C(6)—N(1)—C(2)	123.2	122.8	124.3	123.5	123.0 (4)
C(5)—N(7)—C(8)	103.5	103.6	103.3	103.1	104.0 (10)
N(7)—C(8)—N(9)	113.1	113.3	113.6	113.6	112.6 (11)
C(8)—N(9)—C(4)	107.1	106.6	106.6	106.8	106.8 (4)
N(9)—C(4)—C(5)	105.7	105.6	105.7	105.2	104.7 (9)
C(4)—C(5)—N(7)	110.6	110.9	110.8	111.3	111.7 (8)
N(1)—C(6)—N(6)	119.6	120.9	121.2	120.8	120.8 (9)
C(5)—C(6)—N(6)	126.8	125.9	125.6	125.5	124.9 (17)

(1) This study, adenine base 1; e.s.d.'s: 0.004 Å for bond lengths, 0.3° for bond angles. (2) This study, adenine base 2; e.s.d.'s as for (1). (3) Adenine hydrobromide hemihydrate (Langer & Huml, 1978b); e.s.d.'s as for (1). (4) Adenine hydrochloride hemihydrate (Kistenmacher & Shigematsu, 1974); e.s.d.'s: 0.004 Å for bond lengths, 0.2° for bond angles. (5) Mean values for monoprotonated adenine (Voet & Rich, 1970).

bonds seem to be somewhat shorter, particularly the bond O(11)—H(112), which was found to be 0.72 (5) Å.

In addition to the interaction of adenine bases through hydrogen bonding there exists another mode of base-base interaction, perpendicular to the parallel layers of bases related by a center of symmetry. This

force probably has the character of a dipole-induced-dipole interaction (Bugg, Thomas, Sundaralingam & Rao, 1971) and seems to be quite common in compounds of this type (Voet & Rich, 1970). The perpendicular distance between adenine bases 1 is 2.34 Å and that between bases 2 is 2.62 Å (calculated for planes III and VI in Table 5). However, as a result of the small overlap of bases a considerable cleavability has been shown to exist along the plane (101), whose dihedral angles with planes III and VI are 6.5 and 4.5° respectively.

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