

and C(17). In episteganol the H atom on C(7) is 2.43 Å from C(17) and 2.34 Å from C(18). There are, however, short contacts between H atoms attached to the ring and exocyclic H atoms.

The shortest H...H contacts are about 2.2 Å and the shortest C...C contacts are about 3.4 Å. It is possible that there is a very weak intermolecular hydrogen bond between O(3) and O(5), which are 2.94 Å apart, although this is not indicated by the bond lengths C(5)–O(3) (1.431 Å) and C(14)–O(6) (1.207 Å).

We thank the MRC for financial support and the SRC for the provision of the diffractometer. Fig. 1 was drawn using the program *PLUTO* written by Dr W. D. S. Motherwell. We are grateful to Dr R. F. Bryan for sending us details of his work prior to publication.

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The Crystal and Molecular Structure of Adeninium Sulphate, C₅H₅N₅·H₂SO₄

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The crystal and molecular structure of the title compound was determined from 1645 observed three-dimensional data measured by a single-crystal automated X-ray diffractometer. The unit cell is orthorhombic with $a = 11.664$ (1), $b = 13.685$ (2), $c = 11.023$ (2) Å, $V = 1759.4$ (5) Å³ and contains eight formula units. The space group is *Pbca*. The crystal structure was solved by the heavy-atom method and refined by the least-squares method in a block-diagonal approximation. The final *R* factor is 0.055. The adenine base is diprotonated on N(1) and N(7). The crystal-packing arrangement consists of seven negatively charged sulphate groups surrounding each positively charged base. There is no hydrogen bonding between the bases.

Introduction

The crystal structure of adeninium sulphate was determined as a part of a complex programme of study of the energy and information transfer in nucleic acids, carried out in cooperation with the Institute of Physics of the Charles University in Praha. Single crystals of the title compound serve as a good physical model for the explanation of the emission characteristics of polynucleotides.

Structures containing the adenine base have been reviewed in papers by Voet & Rich (1970) and Ringertz (1972). Data on adenine bases diprotonated on N(1) and N(7) are presented in papers by Kistenmacher & Shigematsu (1974) and Iwasaki (1974) for

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the same compound, and in a paper by Bryan & Tomita (1962). Protonation on O(1) and N(7) was observed by Prusiner & Sundaralingam (1972) in the N¹-oxide of adeninium sulphate. Preliminary crystal data on adeninium sulphate have been published by Moravcová (1975).

Experimental

Crystals of C₅H₅N₅·H₂SO₄, used in the structure determination, were prepared by Zachová (1973) at the Institute of Physics, Charles University, Praha. The molecular formula was confirmed by elemental chemical analysis. The crystals thus obtained were colourless.

Crystal data

$C_5H_5N_5 \cdot H_2SO_4$, orthorhombic, *Pbca*, $a = 11.664$ (1), $b = 13.685$ (2), $c = 11.023$ (2) Å, $V = 1759.4$ (5) Å³, $M_r = 233.16$, $\mu_{Cu} = 32.8$ cm⁻¹, $D_m = 1.739$, $D_x = 1.760$ g cm⁻³, $Z = 8$, $F(000) = 960$.

In the course of the determination of the space group 32 weak reflexions were observed which did not obey the law of systematic absences for the space group *Pbca* (for $0kl$: $k = 2n + 1$; for $h0l$: $l = 2n + 1$; for $hk0$: $h = 2n + 1$). The reflexions were caused by multiple scattering, as proved by the ψ scan method.

Intensity measurement

The intensities were measured with an automatic Syntex $P2_1$ diffractometer [$\lambda(\text{Cu } K\alpha) = 1.5418$ Å, graphite monochromator], using the θ - 2θ method. The crystal was ground to a sphere, 0.75 mm in diameter, and placed on the goniometric head in a general position. The whole measurement took place at room temperature. Intensities higher than 5 kcps were corrected for pulse coincidence (dead time = 5×10^{-6} s). Reflexions having intensity higher than 50 kcps were remeasured with a lower anode current. The right and left backgrounds of the reflexion were measured for half the time of the diffraction-peak measurement. The measurement interval was 1° below $K\alpha_1$ to 1° above $K\alpha_2$ of the Cu $K\alpha$ doublet. The individual rates of measurement were determined by a short measurement at each Bragg peak; the rate varied from 0.5° min⁻¹ to 29.3° min⁻¹. Three standard reflexions were measured after every 30 reflexions. Their intensities did not exhibit any unusual fluctuation or decay during the measurement (160 h). The measurements were reduced to the same scale by means of standard reflexions with the program *INTER* (Langer, 1973). In the range up to $2\theta = 140^\circ$, 1649 independent reflexions were measured, 1644 of which were regarded as observed. A reflexion was considered unobserved if $I_{\text{obs}} < 1.96\sigma(I)$, where $\sigma(I)$ was calculated from the counting statistics. The intensities and their estimated standard deviations were corrected for the Lorentz-polarization factor with the expression $L_p = (1 + \cos^2 2\theta_m \cos^2 2\theta) / [\sin 2\theta(1 + \cos^2 2\theta_m)]$ ($2\theta_m$ is the diffraction angle of the monochromator, 26.568°), and also corrected for absorption by a sphere (*International Tables for X-ray Crystallography*, 1959).

Structure determination and refinement

The phase problem was solved by the heavy-atom method. The position of the S atom was determined from the Patterson function sharpened by the L_p factor. The subsequent Fourier map showed the whole sulphate group and four atoms of the adenine moiety. In the next step the positions of all the non-hydrogen atoms were determined.

Table 1. *Positional parameters of the non-hydrogen atoms with e.s.d.'s ($\times 10^5$)*

	<i>x</i>	<i>y</i>	<i>z</i>
S	14124 (4)	13265 (3)	21374 (4)
O(1)	14351 (13)	9208 (12)	9182 (12)
O(2)	2236 (13)	13701 (10)	25974 (14)
O(3)	19086 (13)	23123 (11)	21445 (13)
O(4)	21014 (14)	6997 (12)	29702 (11)
C(2)	53964 (17)	41924 (14)	17740 (16)
C(4)	43623 (16)	34485 (13)	31593 (16)
C(5)	50820 (16)	37050 (11)	40902 (16)
C(6)	60740 (16)	42570 (12)	38322 (16)
C(8)	36807 (15)	28488 (14)	48463 (20)
N(1)	61645 (14)	44835 (12)	26305 (15)
N(3)	44879 (18)	36703 (12)	19646 (15)
N(6)	68508 (15)	45462 (13)	45972 (14)
N(7)	46419 (13)	33089 (12)	51443 (12)
N(9)	34789 (13)	29240 (13)	36586 (16)

Table 2. *Positional parameters of the hydrogen atoms with e.s.d.'s ($\times 10^3$)*

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	673 (2)	488 (2)	245 (2)
H(2)	560 (2)	438 (1)	103 (2)
H(7)	485 (3)	342 (2)	575 (2)
H(8)	312 (2)	261 (2)	550 (2)
H(9)	273 (3)	263 (3)	307 (2)
H(61)	758 (2)	496 (2)	439 (2)
H(62)	683 (2)	446 (2)	527 (2)

The structure was refined by the least-squares method in a block-diagonal approximation (9×9 matrix in the case of non-hydrogen atoms with anisotropic thermal vibrations and 4×4 matrix for H atoms refined with an isotropic temperature factor); the function minimized was $\sum w(|F_o| - |F_c|)^2$. The scattering factors for non-hydrogen atoms were taken from Cromer & Waber (1965). The correction for the anomalous scattering by the S atom was from Cromer & Liberman (1970). The scattering factors of the H atoms were taken as a spherical approximation of the bonded atom (Stewart, Davidson & Simpson, 1965). Unobserved reflexions were excluded from the refinement. The program used was *NRC-10* (Ahmed, Hall, Pippy & Huber, 1966) with the weighting scheme $w = 1/[\sigma_F^2 + (0.015F_o)^2]$. When the conventional R factor ($\sum ||F_o| - |F_c|| / \sum |F_o|$) had decreased to 0.061 the difference map for reflexions with $\sin \theta/\lambda < 0.4$ showed all the H atoms in the expected positions. At the end of the refinement, a correction for secondary extinction for the 15 strongest reflexions was included, using the formula $I_c/I_o = 1 + (g/\mu)I_c$ (Pinnock, Taylor & Lipson, 1956) with the coefficient $g/\mu = 1.13 \times 10^{-5}$. The process of refinement was complete when all parameter shifts dropped below $\frac{1}{3}$ of the respective e.s.d.'s. The final R factor is 0.055. There were ten observed

reflexions per refined parameter. The resulting positional parameters* of all the non-hydrogen atoms are in Table 1, and those for the H atoms in Table 2.

The residual electron density on the final difference map did not exceed $\pm 0.40 \text{ e } \text{Å}^{-3}$, with the exception of a single minimum of $-1.09 \text{ e } \text{Å}^{-3}$ at the site of the S atom.

Structure description

The numbering scheme with bond distances, valency angles and their e.s.d.'s is given in Fig. 1. The thermal ellipsoids of 50% probability for non-hydrogen atoms in projection along the *b* axis (Šoler, 1973) are given in Fig. 2. The analysis of the thermal vibration of the adenine moiety and of the sulphate group was carried out in the TLS approximation to rigid-body motion (Schomaker & Trueblood, 1968). The correction of the bond distances for atomic libration was calculated by

* Lists of atomic thermal-motion parameters (anisotropic for the non-hydrogen atoms and isotropic for H) and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33115 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

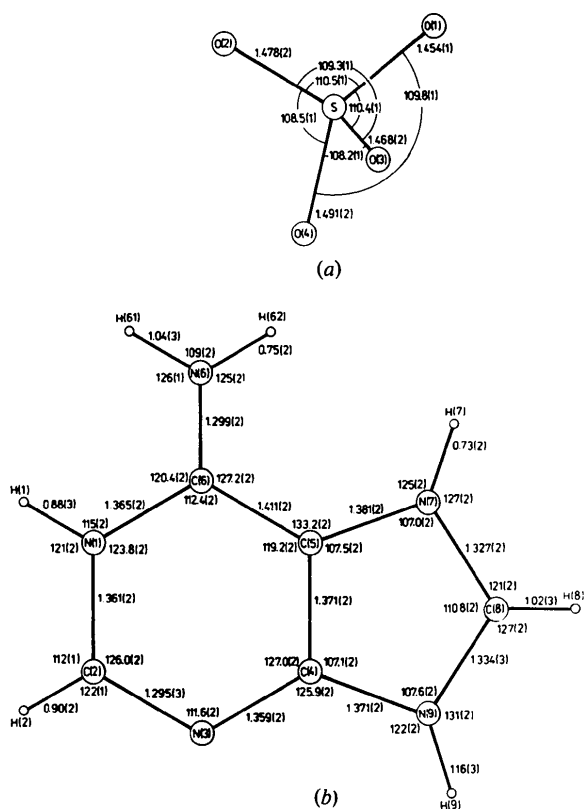


Fig. 1. Numbering scheme with bond distances, valency angles and their respective e.s.d.'s. (a) Sulphate group, (b) adenine base.

the Cruickshank (1956) method. The values of the tensors **T**, **L**, **S**, their eigenvalues and direction cosines are given in Table 3. The criteria for deciding if the rigid-body approximation is plausible were as follows:

$$\text{R.M.S.} = [\Sigma (U_{\text{obs}} - U_{\text{calc}})^2/n]^{1/2},$$

$$\text{E.S.D.} = [\Sigma (U_{\text{obs}} - U_{\text{calc}})^2/(n - s)]^{1/2},$$

$$(\text{R.M.S.})' = [\Sigma \sigma^2(U_{\text{obs}})/n]^{1/2}.$$

The values of the above criteria for the adenine base and for the sulphate group are also given in Table 3. These indicate that one may accept the rigid-body approximation. The bond distances for the adenine base corrected for libration differ by twice the value of the respective e.s.d. at most and have therefore been neglected. In the sulphate group changes in the bond distances are greater; they are summarized in Table 4. Further discussion is based on the uncorrected values.

Table 5 shows the deviations of the atoms from the weighted mean plane drawn through the six-atom ring (plane I), imidazole ring (plane II) and through the whole base with the exception of N(6) (plane III). For each plane a corresponding χ^2 value, showing the degree of non-planarity, is given. The dihedral angle between planes I and II is 0.6° .

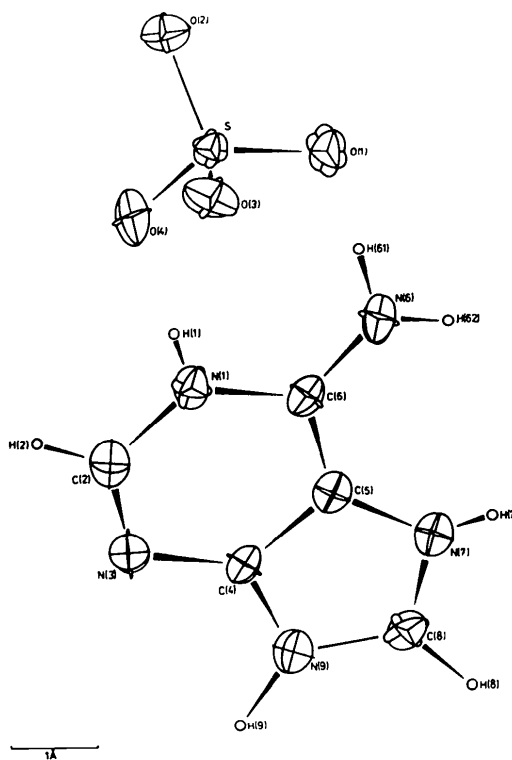


Fig. 2. Thermal ellipsoids at 50% probability for non-hydrogen atoms. Projection along the *b* axis. The H atoms are shown as small circles.

Table 3. *Rigid-body-motion parameters*

The tensors are referred to a Cartesian coordinate system defined by X parallel to \mathbf{a} , Y parallel to \mathbf{b} , Z parallel to \mathbf{c} . Origin is at the centre of mass. Estimated standard deviations are given in parentheses.

Base		\mathbf{S} ($\text{\AA} \text{ rad} \times 10^4$) trace (\mathbf{S}) = 0						
\mathbf{T} ($\text{\AA}^2 \times 10^4$)		\mathbf{L} ($\text{rad}^2 \times 10^4$)						
242(7)	36(8)	28(6)	43(4)	20(3)	-8(2)	6(5)	-4(2)	-1(4)
	201(10)	-12(7)		25(3)	-14(2)	-7(2)	-6(4)	5(2)
		208(7)			37(3)	-6(3)	-6(2)	0(17)

Eigenvalues of \mathbf{T} ($\text{\AA}^2 \times 10^4$)	Direction cosines ($\times 10^4$)		
269	8601	4031	3127
217	-30	-6117	7911
166	5101	-6796	-5272

Eigenvalues of \mathbf{L} ($\text{rad}^2 \times 10^4$)	Direction cosines ($\times 10^4$)		
63	6979	5277	-4842
32	5723	-48	8200
10	4304	-8494	-3055

Eigenvalues of \mathbf{S} ($\text{\AA} \text{ rad} \times 10^4$)	Direction cosines ($\times 10^4$)		
12	8150	-2857	-5042
0	-4170	3167	-8520
-12	4023	9050	1376

R.M.S. = 0.0014 \AA^2 , E.S.D. = 0.0017 \AA^2 , (R.M.S.)' = 0.0008 \AA^2 .

Sulphate group

Base		\mathbf{S} ($\text{\AA} \text{ rad} \times 10^4$) trace (\mathbf{S}) = 0						
\mathbf{T} ($\text{\AA}^2 \times 10^4$)		\mathbf{L} ($\text{rad}^2 \times 10^4$)						
240(9)	42(9)	-5(9)	112(10)	-34(12)	24(13)	-14(9)	-6(7)	-2(7)
	253(9)	-13(9)		61(11)	22(12)	-9(7)	-3(11)	13(6)
		191(9)			123(11)	50(7)	30(7)	17(12)

Eigenvalues of \mathbf{T} ($\text{\AA}^2 \times 10^4$)	Direction cosines ($\times 10^4$)		
291	6401	7574	-1287
205	7588	-5975	2592
188	1198	-2629	-9573

Eigenvalues of \mathbf{L} ($\text{rad}^2 \times 10^4$)	Direction cosines ($\times 10^4$)		
143	6641	-731	7441
120	5938	-5532	-5843
30	4544	8298	-3240

Eigenvalues of \mathbf{S} ($\text{\AA} \text{ rad} \times 10^4$)	Direction cosines ($\times 10^4$)		
36	2951	2167	9306
2	5137	-8571	365
-37	8056	4673	-3642

R.M.S. = 0.0007 \AA^2 , E.S.D. = 0.0012 \AA^2 , (R.M.S.)' = 0.0006 \AA^2 .

Table 4. *Bond distances in the sulphate group corrected for rigid-body motion*

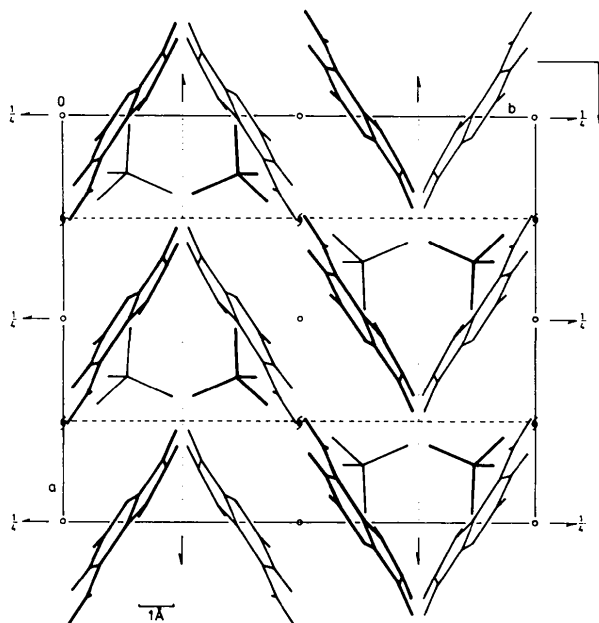
	Uncorrected	Corrected
S-O(1)	1.454 (1) \AA	1.465 \AA
S-O(2)	1.478 (2)	1.490
S-O(3)	1.468 (2)	1.483
S-O(4)	1.491 (2)	1.503

Table 5. *Weighted mean planes*

Deviations ($\text{\AA} \times 10^3$) marked with an asterisk indicate atoms defining the plane. Cartesian coordinate system: X parallel to \mathbf{a} , Y parallel to \mathbf{b} , Z parallel to \mathbf{c} .

Plane I	$0.5248X - 0.8389Y - 0.1441Z + 1.7870 = 0$		
Plane II	$0.5187X - 0.8411Y - 0.1536Z + 1.8747 = 0$		
Plane III	$0.5213X - 0.8405Y - 0.1475Z + 1.8286 = 0$		

	(I)	(II)	(III)
C(2)	-5 (2)*	13 (2)	-1 (2)*
C(4)	-3 (2)*	10 (2)*	1 (2)*
C(5)	-5 (2)*	-8 (2)*	-8 (2)*
C(6)	9 (2)*	0 (2)	2 (2)*
C(8)	0 (2)	2 (2)*	2 (2)*
N(1)	-5 (2)*	-2 (2)	-8 (2)*
N(3)	8 (2)*	32 (2)	16 (2)*
N(7)	13 (2)	3 (2)*	9 (2)*
N(9)	-21 (2)	-6 (2)*	-14 (2)*
N(6)	31 (2)	8 (2)	18 (2)
χ^2	80.1	68.7	239.2

Fig. 3. Projection of the crystal structure along the c axis.

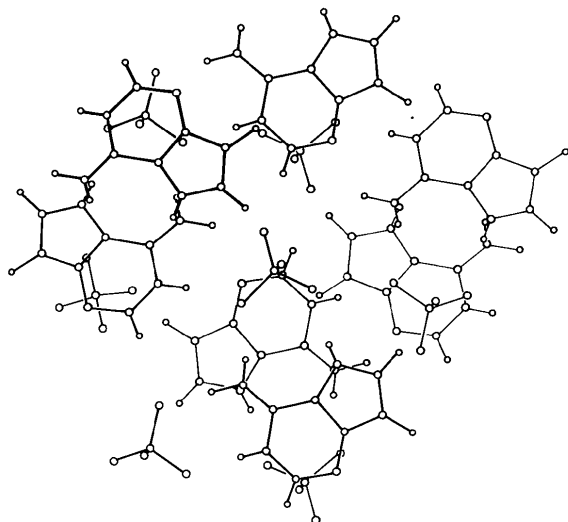


Fig. 4. The molecular packing viewed normal to the plane of the purine ring.

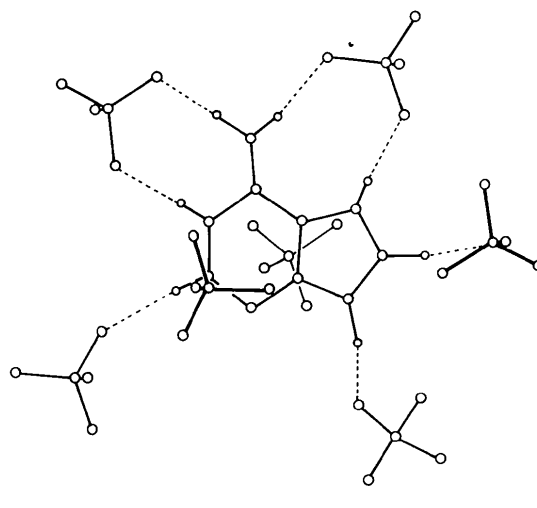


Fig. 5. A view normal to the plane of the purine ring showing the hydrogen-bonding scheme and adenine-sulphate group interaction.

The projection of the crystal structure along the *c* axis is shown in Fig. 3. It is obvious that the adenine bases form parallel layers. The projection of the crystal structure normal to plane III (Table 5) is shown in Fig. 4. Between the adenine base and the sulphate group there is an extensive field of hydrogen bonds, and each hydrogen atom of the adenine base, including the protonating ones, is included in these bonds (Table 6). There are no hydrogen bonds between the adenine bases.

Each adenine group is surrounded by seven sulphate groups and is hydrogen bonded to five adjacent sulphate groups; the remaining sulphate groups are above and below the base (Fig. 5). A similar arrangement can be seen for the *N*¹-oxide (Prusiner & Sundaralingam, 1972).

Table 6. Distances and angles in the hydrogen bonds *A*-H...*B*

<i>A</i> -H... <i>B</i>	<i>A</i> ... <i>B</i>	<i>B</i> ...H	∠ <i>A</i> -H... <i>B</i>
N(9)-H(9)...O(3 ^I)	2.616 (2) Å	1.46 (3) Å	170 (3)°
N(6)-H(61)...O(1 ^{II})	2.803 (2)	1.78 (3)	165 (2)
N(7)-H(7)...O(2 ^{III})	2.617 (2)	1.89 (2)	173 (3)
C(8)-H(8)...O(3 ^{IV})	3.277 (2)	2.30 (3)	159 (3)
N(6)-H(62)...O(4 ^{III})	2.718 (2)	1.98 (2)	169 (2)
N(1)-H(1)...O(4 ^{II})	2.702 (2)	1.83 (3)	179 (3)
C(2)-H(2)...O(1 ^V)	3.209 (2)	2.39 (2)	152 (3)

Symmetry code

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

Discussion

Comparing this structure with other structures of diprotonated adenine bases one finds good agreement among both the bond distances and the valency angles (Table 7). In comparison with the paper by Prusiner & Sundaralingam (1972) we find differences in the angles N(1)-C(2)-N(3), C(2)-N(3)-C(4), C(5)-C(6)-N(1), C(6)-N(1)-C(2) and N(1)-C(6)-N(6); these differences are most likely due to the presence of the O atom in the *N*¹-oxide. Important deviations can also be found between our results and those of Kistenmacher & Shigematsu (1974) for adenine dihydrochloride: namely, for the distances N(3)-C(4) and C(5)-C(6), and the angles N(1)-C(2)-N(3) and C(5)-N(7)-C(8). It is assumed that these deviations are due to different crystal packing modes. The same reason may be used to explain differences described by Iwasaki (1974) for the same compound, for the distance C(2)-N(3) and the angle N(1)-C(2)-N(3). Comparison with the structure of 9-methyladenine dihydrobromide (Bryan & Tomita, 1962) is difficult because of the e.s.d.'s for that compound.

The protonation of the adenine base on the N(1) site is reflected in the change in bond angle. The angle C(2)-N(3)-C(4) at the unprotonated N(3) atom is 111.6 (2)°, while in the case of the protonated N(1) atom the angle, C(6)-N(1)-C(2), is 123.8 (2)°.

The protonation effect on the N(7) atom is as follows: the imidazole ring is an almost symmetrical resonance hybrid; the internal angles are very similar, and the distances N(7)-C(8) and C(8)-N(9) differ very little, in agreement with other studies of diprotonated adenine bases.

Table 7. *A comparison of the non-hydrogen-atom bond lengths and angles in diprotonated adenines*

	1	2	3	4	5
N(1)–C(2)	1.361 Å	1.355 Å	1.361 Å	1.368 Å	1.36 Å
C(2)–N(3)	1.295	1.312	1.302	1.320	1.35
N(3)–C(4)	1.359	1.344	1.348	1.347	1.37
C(4)–C(5)	1.371	1.382	1.377	1.378	1.40
C(5)–C(6)	1.411	1.408	1.400	1.398	1.38
C(6)–N(1)	1.365	1.365	1.358	1.360	1.39
C(5)–N(7)	1.381	1.382	1.377	1.375	1.37
N(7)–C(8)	1.327	1.333	1.320	1.325	1.33
C(8)–N(9)	1.334	1.336	1.335	1.333	1.35
N(9)–C(4)	1.371	1.373	1.372	1.370	1.37
C(6)–N(6)	1.299	1.310	1.307	1.316	1.30
N(1)–C(2)–N(3)	126.0°	122.9°	124.9°	124.2°	127°
C(2)–N(3)–C(4)	111.6	112.9	112.6	112.6	107
N(3)–C(4)–C(5)	127.0	126.9	126.4	126.7	129
C(4)–C(5)–C(6)	119.2	119.5	119.3	119.2	120
C(5)–C(6)–N(1)	112.4	110.8	112.9	113.3	111
C(6)–N(1)–C(2)	123.8	126.8	124.0	123.9	124
C(5)–N(7)–C(8)	107.0	107.5	108.3	107.6	109
N(7)–C(8)–N(9)	110.8	110.4	109.7	110.3	104
C(8)–N(9)–C(4)	107.6	107.9	108.5	108.0	116
N(9)–C(4)–C(5)	107.1	107.1	106.5	106.8	100
C(4)–C(5)–N(7)	107.5	107.1	107.1	107.3	111
N(1)–C(6)–N(6)	120.4	121.4	120.4	120.0	124
C(5)–C(6)–N(6)	127.2	127.7	126.7	126.8	124

Columns: (1) This study; e.s.d.'s: 0.002 Å for bond lengths, 0.2° for bond angles. (2) *N*¹-Oxide of adeninium sulphate (Prusiner & Sundaralingam, 1972); e.s.d.'s: 0.006 Å, 0.3°. (3) Adenine dihydrochloride (Kistenmacher & Shigematsu, 1974); e.s.d.'s: 0.003 Å, 0.2°. (4) Adenine dihydrochloride (Iwasaki, 1974); e.s.d.'s: 0.008 Å, 0.5°. (5) 9-Methyladenine dihydrobromide (Bryan & Tomita, 1962); e.s.d.'s: 0.1 Å, 6°.

Compared with the *N*¹-oxide (Prusiner & Sundaralingam, 1972), the compound studied in this work does not exhibit such large differences between the exocyclic angles of the imidazole ring, with the exception of the angles at N(9).

The dimensions of the sulphate group can be compared with the values published by other authors (e.g. Subramanian & Marsh, 1971; Prusiner & Sundaralingam, 1972). The S–O distances lie between 1.465 (2) and 1.503 (2) Å (after correction for thermal motion), while the O–S–O angles vary between 108.2 (1) and 111.5 (1)°, in agreement with the tetrahedral conformation. The S–O bond distances depend on the strength of the respective hydrogen bonds, from which it may be deduced that differences in the strengths of the hydrogen bonds may affect the geometry of the molecular fragments under consideration.

The O atoms O(4ⁱⁱⁱ) and O(2ⁱⁱⁱ) of the sulphate group (cf. Table 6) form a pair of hydrogen bonds with N(6) and N(7) of the adenine base (Fig. 5). A similar mode of interaction was observed between phosphate and the protonated adenine base in nucleotides (Hecht &

Sundaralingam, 1972). A more frequent mode of interaction between base and phosphate is the formation of a pair of hydrogen bonds from the atoms N(6) and N(1) of the adenine base to the phosphate (Sundaralingam, 1966). In the structure studied here, the oxygen atoms O(1ⁱⁱ) and O(4ⁱⁱ) of the sulphate group are hydrogen bonded to these N atoms.

Theoretically, the purine bases must be planar. Deviations from planarity are usually small, owing to the packing forces (Voet & Rich, 1970). In some cases, however, the deviations from planarity are rather large, especially for the pyrimidine ring (Subramanian & Marsh, 1971). In our case (cf. Table 5), neither the adenine base, the pyrimidine nor the imidazole ring is planar, and consequently one cannot refer here to puckering of the base (cf. Table 5).

Although there are no hydrogen bonds between bases and the adenine base is surrounded by sulphate groups, there exists a different mode of interaction between bases, namely one normal to the parallel base layers. These forces are probably of the dipole-induced dipole type (Bugg, Thomas, Sundaralingam & Rao, 1971). This type of interaction may be relatively strong, because the distance between parallel base layers is small, 2.80 Å (calculated for plane III from Table 5), although the actual overlap of the adenine bases is slight (cf. Fig. 4).

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The Crystal Structure and Absolute Configuration of Lactucin

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The crystal structure and absolute configuration of lactucin, $C_{15}H_{16}O_5$, have been determined by single-crystal X-ray crystallographic techniques. Crystals of the sesquiterpenoid lactone isolated from *Lactuca virosa* are monoclinic, space group $P2_1$, with $a = 7.097$ (3), $b = 11.091$ (5), $c = 8.713$ (4) Å, $\beta = 110.40$ (3)° and $Z = 2$. The structure was solved by direct methods and refined to $R = 3.2\%$. Estimated standard deviations of the bond lengths not involving hydrogen are 0.002–0.004 Å. Anomalous scattering from oxygen was used to determine the absolute configuration.

Introduction

Lactucin is one of the bitter principles of *Lactuca virosa*. It was the first compound of a group of sesquiterpenoid lactones to be isolated having a carbonyl group at the C(2) position of the guaiane skeleton and a cross-conjugated system of double bonds. Until recently (Barton & Narayanan, 1958) it seemed as if lactucin was the only sesquiterpenoid lactone of this type possessing a 5β hydrogen atom. A new interpretation of ORD data, however (Bachelor & Ito, 1973), revised this to the 5α configuration, which we now confirm (Fig. 1).

Experimental

Whitish crystals obtained from an acetone solution were examined by standard X-ray crystallographic film techniques. They were found to be monoclinic. The optical activity together with the space-group ex-

tinctions ($0k0$ absent for $k = 2n + 1$) led to the space group $P2_1$. A summary of the most important crystallographic data is given in Table 1.

Intensity data were collected on an 'off-line' four-circle Siemens single-crystal diffractometer with a

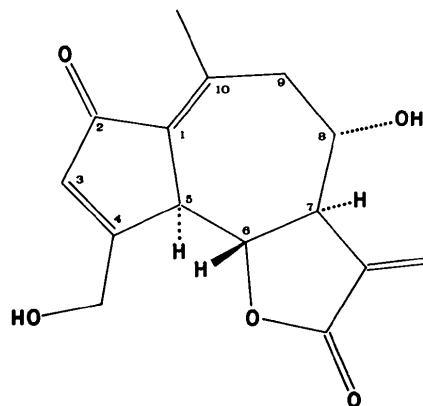


Fig. 1. Lactucin configuration.