

Table 3. *Hydrogen-bond lengths* (Å)

$A-H\cdots B$	$A\cdots B$	$H\cdots B$
$N(A)-H\cdots O(1B)$	2.811 (9)	1.753 (9)
$N(A)-H\cdots O(2A')$	2.885 (11)	1.887 (11)
$N(A)-H\cdots O(1B'')$	2.789 (9)	1.721 (9)
$N(B)-H\cdots O(1A)$	2.764 (9)	1.689 (9)
$N(B)-H\cdots O(1A''')$	2.952 (9)	2.104 (9)*
$N(B)-H\cdots O(2A''')$	3.070 (10)	2.027 (10)*
$N(B)-H\cdots O(2B)$	2.842 (11)	1.765 (11)

Symmetry code: (i) $x, -1+y, z$; (ii) $1-x, -\frac{1}{2}+y, 2-z$; (iii) $1-x, -\frac{1}{2}+y, 1-z$.

* Bifurcated hydrogen bond.

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Structure of 9-{2-[(4-Imidazolyl)methylthio]ethyl}adenine

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Abstract. $C_{11}H_{13}N_7S$, $M_r = 275.33$, monoclinic, $P2_1/c$, $a = 15.495$ (1), $b = 8.345$ (1), $c = 9.926$ (1) Å, $\beta = 97.205$ (5)°, $V = 1273.4$ (2) Å³, $Z = 4$, $D_m = 1.44$, $D_x = 1.436$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54184$ Å, $\mu = 21.9$ cm⁻¹, $F(000) = 576$, room temperature, $R = 0.069$ for 1496 reflexions. The adenine moieties are arranged so as to form ribbons along the twofold screw axes through $N(6)H\cdots N(7)$ and $N(6)H\cdots N(1)$ hydrogen bonds. The imidazolyl groups are connected to each other along the c axis by $N(1')H\cdots N(3')$ hydrogen bonds. There are no direct interactions between the neutral imidazolyl group and the adenine moiety. This is in contrast with the stacking interactions between the protonated imidazolyl group and the adenine moiety in the crystal of 3-(9-adeninyl)propionhistamide hydrochloride (9-{2-[(4-imidazolyl)methylthio]ethyl}adenine hydrochloride).

Introduction. As a model of the interaction between histidine and adenine, we have determined the structure of 3-(9-adeninyl)propionhistamide hydrochloride by X-ray analysis and found that the imidazolium group stacks with the adenine moiety in the crystal

(Takenaka, Takimoto & Sasada, 1984). Changes in UV and NMR spectra on mixing histamine and adenine derivatives are different between acidic and neutral solutions (Takenaka, Takimoto & Sasada, 1984). In order to reveal the structural basis of the difference, we have determined the crystal structure of the title compound in which the imidazolyl group is not protonated.

Experimental. The title compound was synthesized by one of the authors (MO, unpublished work). Prism-like crystals from ethanol solution; D_m by flotation in a mixture of cyclohexane and carbon tetrachloride; crystal size $0.48 \times 0.15 \times 0.01$ mm; Rigaku four-circle diffractometer; graphite-monochromated $Cu K\alpha$ radiation; unit-cell dimensions determined by least squares with 34 high-angle reflexions; intensities measured for $5^\circ < 2\theta < 125^\circ$; $h = 18\sim 18$, $k = 0\sim 10$, $l = 0\sim 12$; ω -scan mode; scan rate 4° min^{-1} ; scan width 2° ; five reference reflexions monitored every 50 reflexions, no significant intensity deterioration; corrections for Lorentz, polarization and absorption; 2028 independent reflexions, 485 reflexions with no net

Table 1. Fractional coordinates and equivalent isotropic temperature factors

$B_{eq} = 8\pi^2(U_1 + U_2 + U_3)/3$, where U_1 , U_2 and U_3 are the principal components of the mean-square displacement matrix U . Values in parentheses are e.s.d.'s and those in angle brackets give the anisotropy defined by $[\sum(B_{eq} - 8\pi^2U_i)^2/3]^{1/2}$; these refer to the last decimal places.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
N(1)	0.0679 (3)	-0.0400 (5)	-0.1258 (4)	3.2 (12)
C(2)	0.1238 (4)	-0.0801 (6)	-0.0174 (6)	3.7 (16)
N(3)	0.1701 (2)	0.0114 (5)	0.0741 (4)	3.0 (11)
C(4)	0.1532 (3)	0.1658 (6)	0.0447 (4)	2.3 (3)
C(5)	0.0966 (3)	0.2283 (5)	-0.0610 (4)	2.3 (3)
C(6)	0.0519 (3)	0.1173 (6)	-0.1507 (5)	2.7 (3)
N(6)	-0.0052 (3)	0.1562 (5)	-0.2577 (4)	3.1 (15)
N(7)	0.0976 (2)	0.3954 (4)	-0.0577 (4)	2.8 (9)
C(8)	0.1545 (3)	0.4300 (6)	0.0491 (5)	3.0 (5)
N(9)	0.1897 (2)	0.2958 (5)	0.1152 (3)	2.5 (3)
C(11)	0.2582 (3)	0.2891 (7)	0.2297 (4)	2.8 (8)
C(12)	0.3437 (3)	0.2328 (7)	0.1875 (5)	3.2 (8)
S	0.38575 (8)	0.3588 (2)	0.0624 (1)	3.31 (138)
C(6')	0.4486 (4)	0.5062 (8)	0.1700 (6)	4.0 (16)
C(4')	0.3952 (3)	0.6035 (6)	0.2526 (4)	3.1 (14)
N(3')	0.3333 (3)	0.7114 (5)	0.1940 (4)	3.8 (16)
C(2')	0.2981 (4)	0.7772 (7)	0.2954 (5)	4.1 (15)
N(1')	0.3340 (3)	0.7155 (6)	0.4157 (4)	3.8 (16)
C(5')	0.3952 (3)	0.6066 (7)	0.3900 (5)	3.6 (12)

intensities designated as zero-reflexions; standard deviations estimated by $\sigma^2(F_o) = \sigma_p^2(F_o) + q|F_o|^2$, where $\sigma_p(F_o)$ was evaluated by counting statistics and q estimated to be 1.0×10^{-4} . Structure solved by direct method and refined by full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/\sigma^2(F_o)$; zero-reflexions with $|F_c| > F_{lim}$ ($F_{lim} = 3.161$) included in the least-squares calculation with the assumption that $F_o = F_{lim}$ and $w = w(F_{lim})$; all H atoms found on a difference map and included in subsequent refinement; final $R = 0.069$ for 1496 reflexions with $F_o > 3\sigma$ ($wR = 0.045$, $S = 1.38$); max. $\Delta/\sigma = 0.1$ for non-H atoms; max. $\Delta\rho = 0.37 \text{ e \AA}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs used were *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *LSAP80* (Takenaka & Sasada, 1980), *DCMS82* (Takenaka & Sasada, 1982), *LISTUP* (Takenaka & Sasada, 1983) and *FDINCOR* (Takeda, Irimajiri & Tanaka, 1982). Final atomic parameters are given in Table 1.*

Discussion. Fig. 1 shows the conformation of the molecule with the atom numbering, bond distances and angles. The dimensions of the adenine moiety, the imidazolyl group and the linking part [from C(11) to

C(6')] are in good agreement with those in the related compounds (Kistenmacher & Rossi, 1977; Takimoto, Takenaka & Sasada, 1981; Edington & Harding, 1974; Madden, McGrandy & Seeman, 1972; Prout, Critchley, Ganellin & Mitchell, 1977). The molecule is folded and the torsion angles N(9)–C(11)–C(12)–S, C(11)–C(12)–S–C(6') and C(12)–S–C(6')–C(5') are $60.1 (5)$, $87.8 (4)$ and $-62.4 (4)^\circ$, respectively. The dihedral angle between the imidazolyl group and the adenine moiety is $57.7 (2)^\circ$. An H atom is attached to N(1') [N(ϵ) in the nomenclature for histidine]. In neutral histidine and histamine derivatives, the H atom is attached to N(ϵ) predominantly (Prout, Critchley & Ganellin, 1974; Itoh, Yamane & Ashida, 1977).

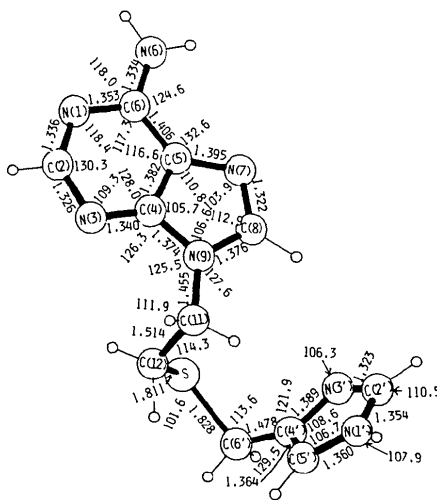


Fig. 1. Atomic numbering and molecular structure of the title compound. E.s.d.'s are 0.005–0.008 Å for bond distances (Å) and 0.3–0.5° for bond angles (°).

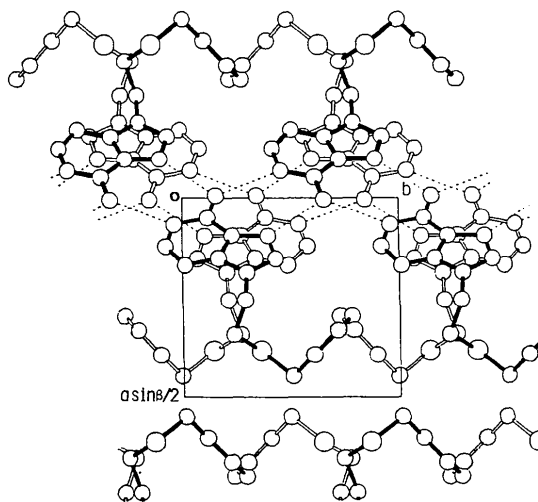


Fig. 2. Crystal structure of the title compound projected along the *c* axis.

* Lists of structure factors, anisotropic thermal parameters and atomic parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42685 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Hydrogen bonds in the title compound*

E.s.d.'s are given in parentheses and refer to the last decimal places.

$X-H\cdots Y$	$X\cdots Y(\text{\AA})$	$\angle HXY(^{\circ})$
$N(6)-H(6A)\cdots N(1')$	2.903 (5)	163 (4)
$N(6)-H(6B)\cdots N(7^{ii})$	3.080 (5)	175 (4)
$N(1')-H(1')\cdots N(3^{iii})$	2.831 (6)	158 (5)

Symmetry codes: (i) $-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (ii) $-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The crystal structure viewed along the c axis is shown in Fig. 2 and the geometry of the hydrogen bonds is listed in Table 2. The adenine moieties are arranged so as to form ribbons along the twofold screw axis through the $N(6)H\cdots N(7)$ and $N(6)H\cdots N(1)$ hydrogen bonds. Such a ribbon structure of adenines has often been found in crystals of adenine derivatives (e.g., Takimoto, Takenaka & Sasada, 1981). The imidazolyl groups are connected to each other along the c axis by the $N(1')H\cdots N(3')$ hydrogen bonds. As seen from Fig. 2, a double molecular sheet is formed parallel to the bc plane. In the sheet, close contacts are $C(4)\cdots C(11)$ [$3.720(6)$ Å] and $C(5)\cdots C(11)$ [$3.452(6)$ Å] between the molecules related by the c glide. The double sheets are loosely packed, the shortest contact being $3.911(8)$ Å for $C(6')\cdots C(6')$.

There are no direct interactions between the neutral imidazolyl group and the adenine moiety. This is in contrast with the stacking interaction between the protonated imidazolyl group and the adenine moiety in the crystal of 3-(9-adeninyl)propionhistamide hydrochloride. Such a difference in interaction patterns explains well the experiments in solution; the biological consequence of this has already been mentioned in a previous paper (Takenaka, Takimoto & Sasada, 1984).

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Structure of Tris(4-methoxyphenyl)phosphine

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Abstract. $C_{21}H_{21}O_3P$, $M_r = 352.37$, monoclinic, $P2_1/c$, $a = 9.881(3)$, $b = 9.636(3)$, $c = 19.801(3)$ Å, $\beta = 91.83(2)^\circ$, $V = 1884.4$ Å³, $Z = 4$, $D_m = 1.24(1)$, $D_x = 1.242$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å (graphite monochromated), $\mu(\text{Cu } K\alpha) = 1.408$ mm⁻¹, $F(000) =$

744, $T = 293$ K, final $R = 0.039$ for 1422 unique nonzero reflections. The geometry around P is pyramidal with C–P–C angles of $99.6(2)$ – $102.9(2)^\circ$ and P–C distances of $1.824(4)$ – $1.830(4)$ Å. One of the phenyl rings is more distorted from planarity than

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