*for X-ray Crystallography*, 1974). Table 1 lists atomic positional parameters for compound (6). Tables 2–4 list bond lengths, valence angles and interplanar angles, respectively.*

**Discussion.** The structures of compounds (5) and (6) are shown in Figs. 1 and 2. The corresponding distances around the ring systems in the two independent molecules of (5) are statistically equivalent. The orientations of the $-CO_2CH_3$ groups differ in the two molecules; this leads to different degrees of conjugation with the C(1)—C(10) double bond and to variations in the side-chain bond lengths. The distances in compound (6) are not as internally consistent, which may reflect the neglect of absorption. The benzene ring imparts different geometrical constraints at C(1)—C(10) leading to some difference between (5) and (6). The C(1)—C(10) double-bond systems deviate slightly from planarity, with interplanar angles of 175·0 (5), 178·3 (5) and 178·2 (5)° in (5*a*), (5*b*) and (6), respectively; however, molecular-mechanics calculations (Allinger & Yuh, 1980) predict deviations of less than 1°. The central double-bond system in *syn*-sesquinorborenes deviates from planarity by 16–22° (Watson, 1983) and is readily oxidized to the diketone. The eight-membered ring of the diketone exhibits a flattened crown conformation which maintains the general shape of the parent compound, *i.e.* the interplanar angles between C(2)C(3)C(8)C(9) and C(3)C(4)C(7)C(8) are 161·4 (5), 163·0 (5) and 173·5 (5)° for (5*a*), (5*b*) and (6), respectively. The H(11)···H(12) separations between methano bridge H atoms range from 1·91 to 2·00 Å for the three compounds. These short contacts prevent the carbonyl system from becoming planar. The methano bridges might be expected to bend away from each other to minimize this interaction and allow the central portion of the eight-membered ring to flatten; however, the interplanar angles 2–3 and 4–6 (see Table 4) range from 95·8 to 100·6° while the angles 1–3 and 5–6 range from 151·2 to 156·2°. The 1–3 angles are consistently larger than the 5–6 angles indicating possible repulsion by the π system of the C(1)—C(10) bond (the ethylene bridge) or torsional interactions *via* substituents on C(1)—C(10) (Watson, 1983). The calculated values for 2–3 and 4–6 are 96·1 and 97·7° while those for 1–3 and 5–6 are 156·2 and 151·5°, respectively.

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### References

ALLINGER, N. L. & YUH, Y. H. (1980). *MM*2 with *MMPI* subroutines for IBM PC. Updated by L. C. ROHREN (1984); adapted by J. J. GAJEWSKI & K. E. GILBERT from copy supplied by O. NELSON & C. SCOTT OWEN. Obtained from Serena Software, 489 Serena Lane, Bloomington, IN 47401.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Nicolet Instrument Corporation (1986). *SHELXTL for Desktop* 30 (*Microeclipse*), PN269–1040340. Nicolet Instrument Corporation, Madison, Wisconsin.

PAQUETTE, L. A. & CARR, R. V. C. (1980). *J. Am. Chem. Soc.* **102**, 7553–7559.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. C. HECK, H. & FLACK, A. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUBRAMANYAM, R., BARTLETT, P. D., MOLTRASIO IGLESIAS, G. Y., WATSON, W. H. & GALLOY, J. (1982). *J. Org. Chem.* **47**, 4491–4498.

WATSON, W. H. (1983). *Stereochemistry and Reactivity of π-Electron Systems.* Deerfield Beach, Florida: Verlag Chemie.

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43744 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Structure of 3-Methyladenine Hydrochloride

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(*Received* 6 *December* 1986; *accepted* 16 *February* 1987)

**Abstract.** $C_6H_8N_5^+.Cl^-$, $M_r = 185{\cdot}62$, monoclinic, $P2_1$, $a = 8{\cdot}656$ (5), $b = 5{\cdot}321$ (1), $c = 9{\cdot}500$ (4) Å, $\beta = 108{\cdot}13$ (4)°, $V = 415{\cdot}9$ (3) Å$^3$, $Z = 2$, $D_m = 1{\cdot}475$ (5), $D_x = 1{\cdot}482$ Mg m$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 3{\cdot}74$ mm$^{-1}$, $F(000) = 192$, $T = 298$ K, $R = 0{\cdot}034$ for 689 observed reflections. The 3-methyladenine molecule

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is protonated at N(7) and the bond lengths and angles of the protonated compound are different from those of related adenine bases. The $Cl^-$ ion is hydrogen bonded to the protonated N(7) atom and to the amino N(6) atom, which is also linked to the neighbouring $Cl^-$ ion related by a symmetry operation.

**Introduction.** Alkylations by many mutagenic and carcinogenic agents occur on some endo- or exocyclic heteroatoms of purine and pyrimidine bases. 3-Methyladenine is also found as one of the products (Brookes & Lawley, 1964). An X-ray structural analysis was performed on 3-methyladenine hydrochloride to obtain structural information on the positively charged 3-methyladenine base. The X-ray data are compared with those of related compounds.

**Experimental.** 3-Methyladenine, purchased from Sigma Chemical Co., St Louis, crystallized from 1*M* HCl solution as 3-methyladenine hydrochloride, density by flotation in a $C_6H_6$–$CCl_4$ mixture; crystal $0{\cdot}4 \times 0{\cdot}07 \times 0{\cdot}05$ mm, Rigaku automatic four-circle diffractometer, $\omega$–$2\theta$ scanning technique, $2\theta_{max} = 120°$, graphite-monochromatized Cu $K\alpha$ radiation; unit-cell dimensions by least-squares procedure based on $2\theta$ values $(41 < 2\theta < 53°)$ of 25 reflections; intensity fluctuation monitored periodically by three reflections ($020$, $\bar{1}03$, $211$): $<2\%$; 695 independent reflections $(-9 \leq h \leq 9, 0 \leq k \leq 5, 0 \leq l \leq 10)$, 689 observed with $F_o \neq 0$; Lorentz and polarization corrections, absorption ignored; direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); block-diagonal least-squares refinement with anisotropic temperature factors for all non-H atoms; all H atoms including H atom attached to N(7) located on a difference Fourier map; final refinement including H atoms with isotropic temperature factors reduced $R$ to 0·034 ($wR = 0{\cdot}050$, $S = 0{\cdot}73$) for 689 reflections and 142 variables; function minimized $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0{\cdot}0345|F_o| + 0{\cdot}00108|F_o|^2]$ and $k$ is the scale factor; highest residual in final difference Fourier map 0·14 e Å$^{-3}$; $(\Delta/\sigma)_{ave} = 0{\cdot}13$ and $(\Delta/\sigma)_{max} = 0{\cdot}49$, for non-H atoms; scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous-dispersion effects not considered; program system *UNICS* (1979) on an ACOS 850 computer of the Crystallographic Research Center, Institute for Protein Research, Osaka University.

**Discussion.** The final atomic parameters are listed in Table 1.* The crystal packing with atom numbering

Table 1. *Final atomic parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Cl | 0·71586 (9) | 0·92590 | 0·36928 (8) | 3·50 (2) |
| N(1) | 0·4109 (3) | 0·3853 (7) | 0·1217 (3) | 3·2 (1) |
| C(2) | 0·3503 (4) | 0·2267 (9) | 0·0123 (3) | 3·1 (1) |
| N(3) | 0·2494 (3) | 0·0377 (8) | 0·0099 (3) | 2·8 (1) |
| C(4) | 0·1998 (4) | 0·0087 (8) | 0·1330 (3) | 2·8 (1) |
| C(5) | 0·2598 (3) | 0·1702 (8) | 0·2503 (3) | 2·5 (1) |
| C(6) | 0·3658 (3) | 0·3630 (8) | 0·2485 (3) | 2·8 (1) |
| N(7) | 0·1855 (3) | 0·0872 (8) | 0·3533 (3) | 3·2 (1) |
| C(8) | 0·0923 (4) | −0·1075 (10) | 0·2913 (4) | 3·5 (1) |
| N(9) | 0·0957 (3) | −0·1662 (8) | 0·1554 (3) | 3·4 (1) |
| N(6) | 0·4318 (3) | 0·5234 (8) | 0·3569 (3) | 3·5 (1) |
| C(3) | 0·1858 (4) | −0·1246 (9) | −0·1210 (3) | 3·7 (1) |

Table 2. *Comparison of bond lengths* (Å) *and angles* (°) *in* 3-*methyladenine hydrochloride with those of related compounds*

| | This work | e$^3$A$^{(a)}$ | m$^3$A-Pt$^{(b)}$ | Adenine$^{(c)}$ |
|---|---|---|---|---|
| N(1)–C(2) | 1·315 (5) | 1·314 | 1·316 | 1·338 |
| C(2)–N(3) | 1·328 (5) | 1·350 | 1·329 | 1·332 |
| N(3)–C(4) | 1·374 (5) | 1·371 | 1·362 | 1·342 |
| C(4)–C(5) | 1·375 (5) | 1·383 | 1·393 | 1·382 |
| C(5)–C(6) | 1·380 (5) | 1·402 | 1·407 | 1·409 |
| C(6)–N(1) | 1·382 (5) | 1·365 | 1·356 | 1·349 |
| C(5)–N(7) | 1·399 (5) | 1·379 | 1·382 | 1·385 |
| N(7)–C(8) | 1·333 (5) | 1·332 | 1·353 | 1·312 |
| C(8)–N(9) | 1·338 (5) | 1·363 | 1·343 | 1·367 |
| N(9)–C(4) | 1·357 (5) | 1·345 | 1·351 | 1·376 |
| C(6)–N(6) | 1·323 (5) | 1·330 | 1·328 | 1·337 |
| N(3)–C(3) | 1·473 (5) | 1·476 | 1·470 | — |
| | | | | |
| C(6)–N(1)–C(2) | 118·9 (3) | 118·9 | 119·5 | 118·8 |
| N(1)–C(2)–N(3) | 126·7 (3) | 126·4 | 126·3 | 129·0 |
| C(2)–N(3)–C(4) | 116·7 (3) | 115·9 | 116·6 | 110·8 |
| N(3)–C(4)–C(5) | 118·7 (3) | 120·8 | 120·5 | 126·9 |
| N(3)–C(4)–N(9) | 127·5 (3) | 127·6 | 128·2 | 127·4 |
| C(5)–C(4)–N(9) | 113·8 (3) | 111·6 | 111·4 | 105·7 |
| C(4)–C(5)–C(6) | 122·6 (3) | 119·5 | 119·0 | 116·9 |
| C(6)–C(5)–N(7) | 134·1 (3) | 132·2 | 134·1 | 132·3 |
| C(4)–C(5)–N(7) | 103·3 (3) | 108·4 | 107·0 | 110·7 |
| C(5)–C(6)–N(1) | 116·3 (3) | 118·5 | 117·8 | 117·6 |
| C(5)–C(6)–N(6) | 126·7 (3) | 122·9 | 124·0 | 123·4 |
| N(1)–C(6)–N(6) | 116·9 (3) | 118·6 | 118·3 | 119·0 |
| C(5)–N(7)–C(8) | 106·5 (3) | 101·5 | 103·9 | 103·9 |
| N(7)–C(8)–N(9) | 114·6 (4) | 118·3 | 115·6 | 113·8 |
| C(8)–N(9)–C(4) | 101·9 (3) | 100·3 | 102·7 | 105·9 |
| C(2)–N(3)–C(3) | 122·0 (3) | 122·8 | 122·6 | — |
| C(4)–N(3)–C(3) | 121·3 (3) | 121·2 | 120·8 | — |

References: (*a*) 3-ethyladenine (Petersen & Furberg, 1975); (*b*) *cis*-diamminebis(3-methyladenine)platinum(II) nitrate trihydrate (Orbell *et al.*, 1982); (*c*) Taylor & Kennard (1982).

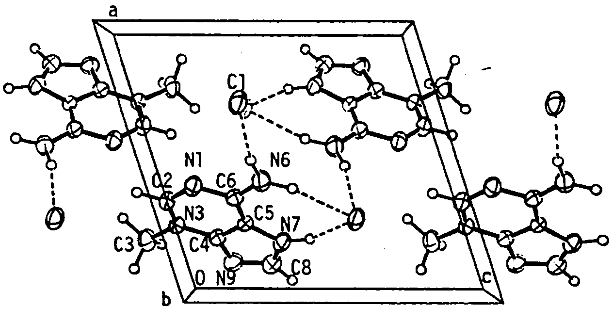

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the crystal packing viewed down the *b* axis. Dotted lines indicate the hydrogen bonds.

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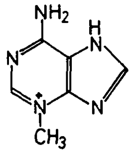
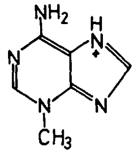
* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and best planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43791 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

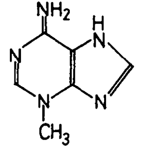
viewed down the *b* axis is illustrated in Fig. 1. The 3-methyladenine molecule takes a cationic form with N(7) protonated. The bond lengths and angles of the present structure together with those of related compounds are shown in Table 2. The observed bond lengths are consistent with those calculated for the predominant resonance structures (I)–(III). The charge-density distributions of N atoms calculated by using the *INDO* method (Pople & Segal, 1966) are −0·275, −0·051, −0·062, −0·269 and −0·185 e for N(1), N(3), N(7), N(9) and N(6), respectively.



(I)



(II)



(III)

The overall molecular dimensions of 3-methyladenine with N(7) protonated are significantly different from the standard values proposed for adenine (Taylor & Kennard, 1982) as well as those found in two 3-alkylated adenine derivatives, *cis*-diamminebis(3-methyladenine)platinum(II) ($m^3A$-Pt; Orbell, Solorzano, Marzilli & Kistenmacher, 1982) and 3-ethyladenine ($e^3$ A; Petersen & Furberg, 1975). The N(1)—C(2) and N(9)—C(4) bonds in 3-alkylated adenine derivatives are commonly shorter than those in adenine, whereas the N(3)—C(4) and N(7)—C(8) bonds are somewhat longer. Also the ring angles at N(3), N(9) and C(4) differ considerably from those of adenine. Some geometric differences are observed in the 3-alkylated adenine derivatives. The considerable changes occur at internal ring angles of N(7) and the ajacent C(5) and C(8) atoms. The variance is probably a direct result of the different environment about each N(7) atom. Indeed, the values in the 3-methyladenine with N(7) coordinated to a metal ($m^3A$-Pt) are intermediate between those of 3-methyladenine with N(7) protonated and free 3-ethyladenine ($e^3$ A). The nine-membered purine ring is essentially planar. The maximum deviation from the least-squares plane is 0·011 (4) Å for C(2). C(3) is displaced from this plane by 0·037 (5) Å. As shown in Fig. 1, the 3-methyladenine molecule is connected by three N—H···Cl type hydrogen bonds, forming an infinite hydrogen-bonded column along the *b* axis. The hydrogen-bonding distances are 3·086 (3) Å for N(7)···$Cl^i$, 3·277 (3) Å for N(6)···$Cl^i$ [(i) $1-x,\ -\frac{1}{2}+y,\ 1-z$] and 3·235 (3) Å for N(6)···Cl.

## References

Brookes, P. & Lawley, P. D. (1964). *J. Cell. Comp. Physiol.* **64**, Suppl. 1, 111–128.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–75. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Orbell, J. D., Solorzano, C., Marzilli, L. G. & Kistenmacher, T. J. (1982). *Inorg. Chem.* **21**, 2630–2636.

Petersen, C. S. & Furberg, S. (1975). *Acta Chem. Scand. Ser. B*, **29**, 37–40.

Pople, J. A. & Segal, G. A. (1966). *J. Chem. Phys.* **44**, 3289–3296.

Taylor, B. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 3209–3212.

*UNICS* (1979). *The Universal Crystallographic Computing System – Osaka.* Library of Programs, Computation Center, Osaka Univ.

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# Thermally Induced Acyl Migration in Salicylamides. 1. Structures of the Reactants, *O*-Acetylsalicylamide and *O*-Benzoylsalicylamide[*]

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**Abstract.** *O*-Acetylsalicylamide (I*a*), $C_9H_9NO_3$, $M_r = 179\cdot18$, monoclinic, $P2_1/c$, $a = 8\cdot155\ (5)$, $b = 8\cdot571\ (2)$, $c = 13\cdot092\ (3)$ Å, $\beta = 99\cdot54\ (5)^\circ$, $V = 902\cdot4\ (6)$ Å$^3$, $Z = 4$, $D_m = 1\cdot31$, $D_x = 1\cdot319$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 1\cdot08$ cm$^{-1}$, $F(000) = 376$, $T = 295$ K, $R = 0\cdot076$ for 1604 reflections. *O*-Benzoylsalicylamide (I*b*), $C_{14}H_{11}NO_3$, $M_r = 241\cdot2$, monoclinic, $P2_1/c$, $a = 9\cdot423\ (1)$, $b = 5\cdot116\ (1)$, $c = 26\cdot424\ (2)$ Å, $\beta = 103\cdot97\ (1)^\circ$, $V = 1236\cdot2\ (3)$ Å$^3$, $Z$

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