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A Refinement of the Crystal Structure of 9-Methyladenine

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Abstract. $C_6N_5H_7$, monoclinic, space group $P2_1/c$, with $a = 7{\cdot}682\,(2)$, $b = 12{\cdot}330\,(3)$, $c = 8{\cdot}501\,(2)$ Å, $\beta = 123{\cdot}12\,(2)°$, $V = 674{\cdot}43$ Å^3, $Z = 4$, $D_m = 1{\cdot}474\,(4)$, $D_c = 1{\cdot}469$ g cm^{-3}. Full-matrix least-squares refinement led to a final R value of 0·061. The X-ray crystal structure of $C_6N_5H_7$ has been previously studied by Stewart & Jensen [*J. Chem. Phys.* (1964), **40**, 2071–2075] employing a limited set of three-dimensional data (385 independent F_o's) and isotropic refinement of the nonhydrogen atoms. The results presented here are based on a more extensive set of data (1882 independent F_o's), with anisotropic refinement of the nonhydrogen atoms and inclusion of H atoms at the isotropic level.

Introduction. The crystal structure of 9-methyladenine (Stewart & Jensen, 1964) was first undertaken to establish whether the transition moment for the first UV band of 9-methyladenine was short-axis or long-axis polarized. Since such information can be deduced without high precision for the atomic parameters, the original structural investigation was based only on the 385 most intense reflections out of a possible 1572 accessible within the limiting sphere for Cu $K\alpha$ radiation (Stewart & Jensen, 1964). More recently, however, neutral 9-methyladenine (de Meester, Goodgame, Skapski & Warnke, 1973; Sletten & Thorstensen, 1974; Sletten & Ruud, 1975; McCall & Taylor, 1975; Szalda, Kistenmacher & Marzilli, 1975; Kistenmacher, Marzilli & Szalda, 1976) and the N(1)-protonated 9-methyladenine cation (Terzis, 1976) have been employed as models for the binding of adenine nucleosides and nucleotides to metal ions and metal complexes. One aspect of these studies, besides the position of the metal binding site, is the effect on the bond lengths and bond angles in the heterocyclic ring system due to the bonding of the metal ion or metal complex. Such detailed information requires a more precise determination of the atomic positions and derived bond lengths and angles for 9-methyladenine.

Crystals of 9-methyladenine were grown from an aqueous solution which was made slightly basic, pH = 8, by the addition of KOH. The crystal used in our diffractometer study was a prismatic needle with the following dimensions: (011)–$(0\bar{1}\bar{1})$ 0·25, $(01\bar{1})$–$(0\bar{1}1)$ 0·20 and (100)–$(\bar{1}00)$ 0·25 mm, with a as the prism axis. Precise cell dimensions and their associated standard deviations were obtained by a least-squares fit to the setting angles of 15 carefully centered reflections and are comparable to the values determined by Hoogsteen (1959) and employed by Stewart & Jensen (1964).

A total of 9156 reflections (the full sphere to $2\theta = 60°$) were measured on a Syntex $P1$ computer-controlled diffractometer; Mo graphite-monochromatized radiation was used. Intensity data were collected in the θ–2θ scan mode; individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) ranged from 2° min^{-1} (less than 100 counts during the rapid scan) to 24° min^{-1} (more than 1000 counts during the rapid scan). All reflections were assigned observational variances based on the equation: $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S, B_1 and B_2 are the scan and extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B = T_S/4$ for all reflections), and p was taken to be 0·03 and represents the expected error proportional to the diffracted intensity (Busing & Levy, 1957) as determined by the random variations in the standard intensities. The intensities and their standard deviations were corrected for Lorentz and polarization effects; the amplitudes of reflections with $I \leq 0{\cdot}2\ \sigma(I)$ were set equal to zero. No correction for absorption was deemed necessary ($\mu = 1{\cdot}1$ cm^{-1}). The data were then averaged to yield 1882 independent values [87 reflections with $I_{\rm AVE} \leq \sigma(I_{\rm AVE})/n$, where n is the number of independent observations contributing to the average, were considered statistically unobserved and removed from the data set].

The refinement of the structure was initiated from the final parameters of Stewart & Jensen (1964). Three cycles of full-matrix isotropic least-squares refinement, minimizing the quantity $\Sigma\, w(\,|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, plus one cycle in which all the non-hydrogen atoms were refined with anisotropic thermal parameters reduced the R value ($= \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$) to 0·108. A difference Fourier map was computed at this stage, and on the basis of this map the seven H atoms in the asymmetric unit were assigned positional parameters.

The refinement was then continued adding suc-

cessively to the parameter list: (1) positional parameters on the hydrogen atoms and (2) the isotropic temperature factors for each of the H atoms. In these last cycles, the 200 reflection was excluded, as it was obviously affected by secondary extinction. Four cycles in such a mode led to convergence and to a final R index of 0·061. The final weighted R value $\{R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}\}$ and goodness-of-fit $\{[\Sigma\, w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = 1882 independent observations and NV = 128 variables$\}$ were 0·048 and 2·6 respectively.

The scattering curves for the nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964), while the scattering curve for H was that of Stewart, Davidson & Simpson (1965). The real part of the scattering curves for all nonhydrogen atoms was corrected for anomalous dispersion effects (Cromer & Liberman, 1970). Final positional parameters and thermal parameters are given in Table 1.*

The structure factor and least-squares calculations were carried out with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); Fourier maps were computed with *FORDAP* (Zalkin, 1965); the illustrations were prepared with the aid of *ORTEP* (Johnson, 1965); best planes were computed with *MEAN PLANE* (Pippy & Ahmed, 1968). Calculations not cited were performed with locally written programs.

Discussion. Our refinement of the structure of 9-methyladenine provides a much more precise result

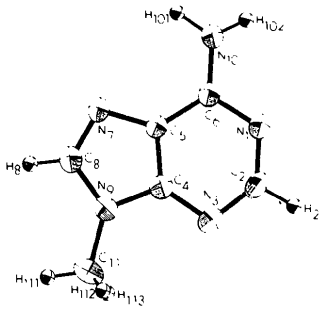

Fig. 1. The 9-methyladenine molecule viewed along the normal to the mean plane of the nine-atom framework. The thermal ellipsoids are drawn at the 50% probability level. The isotropic thermal parameters for the hydrogen atoms have been set to 1·0 Å^2.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32038 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates* ($\times 10^4$ *for nonhydrogen atoms and* $\times 10^3$ *for hydrogen atoms*) *and thermal parameters* ($\times 10^4$ *for anisotropic atoms*)

Estimated standard deviations are in parentheses. Values enclosed in square brackets are those of Stewart & Jensen (1964). The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	2425 (2)	1305 (1)	7290 (1)	247 (4)	47 (1)	119 (2)	−6 (1)	110 (2)	−4 (1)
	[2409 (7)]	[1305 (3)]	[7264 (6)]						
N(3)	2885 (2)	−598 (1)	6970 (2)	252 (4)	48 (1)	134 (2)	4 (1)	110 (2)	15 (1)
	[2887 (7)]	[−593 (4)]	[6975 (7)]						
N(7)	1993 (2)	687 (1)	2810 (2)	305 (4)	45 (1)	138 (2)	2 (1)	146 (3)	0 (1)
	[2004 (7)]	[683 (4)]	[2819 (7)]						
N(9)	2585 (2)	−991 (1)	4035 (2)	235 (3)	39 (1)	154 (2)	2 (1)	120 (2)	−4 (1)
	[2592 (7)]	[−981 (4)]	[4023 (7)]						
N(10)	1911 (2)	2610 (1)	5130 (2)	394 (5)	38 (1)	160 (3)	1 (1)	185 (3)	−4 (1)
	[1915 (8)]	[2623 (4)]	[5123 (7)]						
C(2)	2747 (2)	267 (1)	7823 (2)	250 (4)	55 (1)	112 (3)	−5 (2)	104 (3)	10 (1)
	[2759 (9)]	[260 (5)]	[7865 (9)]						
C(4)	2603 (2)	−308 (1)	5314 (2)	174 (3)	40 (1)	130 (3)	−3 (1)	88 (3)	0 (1)
	[2610 (8)]	[−320 (5)]	[5321 (8)]						
C(5)	2244 (2)	720 (1)	4556 (2)	194 (4)	40 (1)	109 (2)	−3 (1)	92 (3)	0 (1)
	[2221 (8)]	[700 (4)]	[4549 (7)]						
C(6)	2194 (2)	1573 (1)	5637 (2)	196 (4)	41 (1)	116 (2)	−6 (1)	96 (3)	−4 (1)
	[2178 (8)]	[1558 (5)]	[5610 (8)]						
C(8)	2201 (2)	−345 (1)	2575 (2)	292 (5)	48 (1)	157 (3)	0 (2)	149 (3)	−8 (1)
	[2230 (8)]	[−350 (5)]	[2558 (8)]						
C(11)	2889 (3)	−2159 (1)	4224 (3)	343 (6)	37 (1)	237 (4)	16 (2)	169 (4)	−2 (2)
	[2891 (10)]	[−2169 (6)]	[4242 (9)]						

	x	y	z	B		x	y	z	B
H(2)	285 (2)	12 (1)	900 (2)	3·2 (3)	H(111)	289 (3)	−248 (2)	320 (3)	6·4 (5)
H(8)	214 (2)	−65 (1)	153 (2)	3·6 (3)	H(112)	169 (3)	−251 (2)	423 (3)	7·6 (6)
H(101)	196 (2)	285 (1)	405 (2)	4·8 (4)	H(113)	421 (3)	−233 (2)	543 (3)	7·6 (6)
H(102)	204 (2)	310 (1)	593 (2)	3·8 (4)					

Table 2. *Nonhydrogen atom bond lengths and angles*

SJ: Stewart and Jensen (1964). KR: This study.

	SJ	KR		SJ	KR
N(1)–C(2)	1·348 (8) Å	1·335 (2) Å	C(5)–N(7)	1·379 (11) Å	1·389 (2) Å
C(2)–N(3)	1·322 (9)	1·326 (2)	N(7)–C(8)	1·311 (9)	1·311 (2)
N(3)–C(4)	1·338 (10)	1·351 (2)	C(8)–N(9)	1·354 (10)	1·365 (2)
C(4)–C(5)	1·365 (9)	1·380 (2)	N(9)–C(4)	1·359 (10)	1·370 (2)
C(5)–C(6)	1·395 (10)	1·411 (2)	C(6)–N(10)	1·348 (9)	1·329 (2)
C(6)–N(1)	1·348 (11)	1·357 (2)	N(9)–C(11)	1·468 (10)	1·453 (3)
N(1)–C(2)–N(3)	126·5 (9)°	129·9 (2)°	C(8)–N(9)–C(4)	107·9 (7)°	105·4 (1)°
C(2)–N(3)–C(4)	112·4 (8)	110·0 (1)	N(9)–C(4)–C(5)	104·7 (7)	106·4 (1)
N(3)–C(4)–C(5)	126·6 (8)	127·4 (1)	C(4)–C(5)–N(7)	111·2 (7)	110·3 (1)
C(4)–C(5)–C(6)	117·2 (8)	116·8 (1)	N(10)–C(6)–C(5)	125·7 (9)	124·3 (1)
C(5)–C(6)–N(1)	117·4 (8)	117·3 (1)	N(10)–C(6)–N(1)	116·9 (7)	118·4 (1)
C(6)–N(1)–C(2)	119·8 (8)	118·7 (1)	C(8)–N(9)–C(11)	128·3 (9)	128·4 (1)
C(5)–N(7)–C(8)	104·2 (6)	103·5 (1)	C(11)–N(9)–C(4)	123·8 (8)	126·1 (1)
N(7)–C(8)–N(9)	112·0 (7)	114·4 (2)			

Table 3. *Bond lengths and angles involving the hydrogen atoms*

C(2)–H(2)	0·98 (2) Å	C(11)–H(112)	1·02 (2) Å
C(8)–H(8)	0·94 (2)	C(11)–H(113)	0·99 (2)
C(11)–H(111)	0·96 (2)	N(10)–H(101)	0·98 (2)
		N(10)–H(102)	0·87 (2)
N(1)–C(2)–H(2)	115 (1)°	N(9)–C(11)–H(113)	110 (1)°
N(3)–C(2)–H(2)	115 (1)	H(111)–C(11)–H(112)	106 (2)
N(7)–C(8)–H(8)	126 (1)	H(111)–C(11)–H(113)	110 (2)
N(9)–C(8)–H(8)	120 (1)	H(112)–C(11)–H(113)	109 (2)
N(9)–C(11)–H(111)	113 (1)	C(6)–N(10)–H(101)	120 (1)
N(9)–C(11)–H(112)	109 (1)	C(6)–N(10)–H(102)	119 (1)
		H(101)–N(10)–H(102)	118 (2)

than the previous study of Stewart & Jensen (1964). Our analysis, which is based on about five times the number of data, has led to positional uncertainties which are about three to four times lower than those of the initial work. An illustration of the 9-methyladenine molecule and its thermal ellipsoids is presented in Fig. 1.

We present in Table 2 our derived bond lengths and angles and compare them with the earlier work of Stewart & Jensen (1964). The largest bond-length difference, –0·019 Å, is in the exocyclic bond length to the amino group, C(6)–N(10)H_2. There are also seven other bond lengths where the difference exceeds 0·01 Å (Table 2). The largest bond-angle difference, 3·4°, is in the N(1)–C(2)–N(3) bond angle, and there are four other bond angles where the difference exceeds 2° (Table 2). The bond lengths and bond angles involving the hydrogen atoms are collected in Table 3. As is typical of purines in an asymmetric environment in the crystalline solid (Sletten & Jensen, 1969; Voet & Rich, 1970), the purine is folded about the C(4)–C(5) bond by an angle of 1·5 (1)°.

In accord with the original structure of Stewart & Jensen (1964), we find two principal modes of interaction in the crystal: (1) interpurine hydrogen bonds of the type N(10)–H(101)···N(1)(x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) [N(10)–H(101) = 0·98 (2), N(10)···N(1) = 2·969 (2) Å, N(10)–H(101)···N(1) = 164 (1)°] and N(10)–H(102)···N(7) (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)[N(10)–H(102) = 0·87 (2), N(10)3···N(7) = 3·074 (2) Å, N(10)–H(102)···N(7) = 173 (1)°], and (2) stacking of the 9-methyladenine molecules about the inversion center at 0,0,$\frac{1}{2}$, with a mean separation of 3·34 Å and significant contacts as follows: N(1)···N(9′) 3·391 (2), N(1)···C(4′) 3·463 (2), N(3)···C(5′) 3·413 (2), N(3)···C(6) 3·484 (2), C(2)···C(5) 3·435 (2), and C(2)···C(4) 3·469 (2) Å.

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Rubidium Trichloromanganate

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Abstract. $RbMnCl_3$, hexagonal, $P6_3/mmc$, $a = 7{\cdot}16$ (1), $c = 17{\cdot}83$ (4) Å, $D_o = 3{\cdot}09$, $D_x = 3{\cdot}11$ g cm^{-3}, $Z = 6$. The unit cell accommodates six close-packed layers of composition $RbCl_3$ with Mn ions situated between the layers, being octahedrally coordinated by Cl ions. The structure differs from that of $CsMnCl_3$ in that it has a six-layer, rather than nine-layer, stacking sequence.

Introduction. Many complex chlorides of composition $XMCl_3$, where X represents an alkali ion and M a metal in the first transition series, have structures which are based on hexagonally close-packed layers of composition XCl_3 with the M ions situated between the layers, being octahedrally coordinated by Cl ions. In such structures the XCl_3 layers are of three types (*A*, *B* or *C*) according to the position of the cross-section of the hexagonal cell (see Fig. 1). The structure of $CsNiCl_3$ consists of layers in the sequence *BABA*---, whilst that of $CsMnCl_3$ (Goodyear & Kennedy, 1973) has the nine-layer sequence *BABACACBC*---. The unit-cell dimensions of $RbMnCl_3$ suggested that the crystal structure of this compound should have a six-layer sequence.

The material was prepared by heating stoichiometric amounts of RbCl and $MnCl_2$ in an evacuated silica tube until molten and then cooling the sample to room temperature at about 5°C h^{-1}. Orange crystals were formed, most of which were intimately twinned and unsuitable for single-crystal study. After much searching a single crystal was found which, although of unfavourable shape, permitted a Weissenberg study to be made of the crystal structure. Because of the very hygroscopic nature of the material, the selected crystal was mounted in a sealed Lindemann glass tube containing phosphorus pentoxide.

The dimensions of the unit cell were determined from α_1–α_2 doublet separations on a zero-layer Weissenberg photograph taken with Cu $K\alpha$ radiation. The volume of the unit cell and the observed density indicated six formula units per cell, which is what would be required for a six-layer structure.

Intensity data were collected from equi-inclination photographs taken about the *a* axis with Mo $K\alpha$ radiation. The intensities of 125 symmetrically independent reflexions were measured, both visually and with a flying-spot microdensitometer, on layer lines 0–6 from accurately timed film exposures. The systematically absent reflexions were of the type *hhl* with $l = 2n + 1$, and about 250 reflexions were too weak to be observed. The observed data were corrected for the Lorentz–polarization factor and a very approximate correction was made for absorption by assuming the crystal to be cylindrical in shape with a μr value of 0·8. Because of the relatively small range in the magnitudes of the observed structure factors, each reflexion was given unit weight in the refinement procedure.

Initially, the structure was assumed to consist of the six-layer stacking sequence *BCBACA*---. The idealized positional parameters suggested the space group $P6_3/mmc$, consistent with the absent reflexions. Several cycles of least-squares refinement reduced the residual, $R = \Sigma\,|F_o| - |F_c|\,/\Sigma\,|F_o|$, to 16%, at which stage it was apparent that the two strongest reflexions, 110 and 220, were suffering from extinction. The latter were then removed from the refinement and after they were corrected for primary extinction, the final value of R was 11·8%. In the last cycle of refinement the shifts in the positional parameters were less than $\frac{1}{50}$ of a standard deviation and for the isotropic temperature terms the shifts were less than $\frac{1}{15}$ of a standard deviation. Furthermore, the calculated structure factor for each