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The Neutron Crystal Structure of 9-Methyladenine at 126 K

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Abstract

At 126 K, 9-methyladenine ($C_6H_7N_5$) is monoclinic, space group $P2_1/c$, with $a = 7.506$ (1), $b = 12.285$ (2), $c = 8.483$ (1) Å, $\beta = 122.83$ (1)°, and four molecules per unit cell. The structure has been refined using 2983 reflections with a measured neutron wavelength of 0.9085 Å ($\sin \theta/\lambda \leq 0.87$ Å⁻¹), and 373 reflections at a wavelength of 1.0474 Å ($\sin \theta/\lambda \leq 0.75$ Å⁻¹). The latter consist mainly of $2h,2k,2l$ reflections which were remeasured when it was found that the shorter wavelength was contaminated with 2λ neutrons produced by double Bragg diffraction at the Be monochromating crystal. The final $R(F^2)$ value was 0.049. Bond lengths and angles have e.s.d.'s of 0.001 Å, 0.08° for non-hydrogen atoms, otherwise 0.003 Å, 0.2°. Values are in general agreement with those of the previously reported room-temperature X-ray refinement. The hydrogen bonding of the amino group appears to cause displacement of the H atoms from the molecular plane. The largest thermal motion in the structure involves the methyl H atoms which are librating about the $N(9)-CH_3$ bond with r.m.s. amplitudes 0.28, 0.29, 0.30 Å. There is a short intermolecular distance of 2.52 Å between a methyl H atom and N(3).

Introduction

The crystal structure of 9-methyladenine was first determined by Stewart & Jensen (1964) and recently refined by Kistenmacher & Rossi (1977) using more extensive room-temperature X-ray data (Mo $K\alpha$, $\sin \theta/\lambda \leq 0.70$ Å⁻¹). A neutron structure has also been determined for the complex of 9-methyladenine with 1-methylthymine at room temperature (Frey, Koetzle, Lehmann & Hamilton, 1973). The present low-temperature neutron study was carried out as part of a study of the electronic charge density in the crystal

structure. 9-Methyladenine was chosen because it is a simple molecule having a charge distribution which must be closely related to that of the adenine moiety in nucleic acids.

Experimental

Crystals of 9-methyladenine were grown by the slow cooling (370 to 298 K) of an aqueous solution contained in a Dewar flask. The specimen selected for study is described in Table 1, together with the crystal data* and conditions for the diffraction measurements. The neutron diffraction data were measured on an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor. The neutron beam was obtained by (002) reflection from a beryllium crystal, at a wavelength determined by the least-squares

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* The unit cell was chosen to be consistent with the previous structure determinations. The reduced cell ($a = 7.506$, $b = 12.285$, $c = 7.698$ Å, $\beta = 112.19°$, space group $P2_1/n$; 126 K) can be obtained by the transformation matrix $(1,0,0/0,-1,0/-1,0,-1)$.

fit of $\sin^2 \theta$ data for a standard KBr crystal at 298 K ($a_0 = 6.6000$ Å). The data were measured at the shorter neutron wavelength, 0.90850 (14) Å, before it was suspected that the beam contained a significant 2λ component. Some measurements were then repeated using a longer wavelength, 1.04738 (13) Å. The 9-methyladenine crystal was mounted on a hollow aluminum pin and placed inside a closed-cycle helium refrigerator (Air Products and Chemicals, Inc; DISPLEX® Model CS-202) which was positioned with the χ circle of the diffractometer. The |100| scattering vector of the crystal was within 1° of the φ axis. The crystal was centered by adjusting translations of the cryostat stage until differences in 2θ and χ for four forms (Hamilton, 1974) of the 400 reflections, two at each $\pm\chi$, became negligibly small (ca 0.02°). Cooling of the crystal to 116 K produced no abrupt changes in the crystal lattice parameters.

Reflection intensity data were measured at 126 ± 1 K by a $\theta/2\theta$ step-scan procedure in which counts at each step were accumulated for a preset monitor count of the direct beam. Contributions to the scan profiles

Table 1. *Crystal data for 9-methyladenine* ($C_6H_7N_5$)

(a) Unit-cell data: monoclinic, space group $P2_1/c$, $Z = 4$ molecules/cell

	298 K					
	X-ray* (Cu $K\alpha$)	X-ray† (Mo $K\alpha$)	136 ± 1 K Neutron	126 ± 1 K Neutron‡		116 ± 1 K Neutron
λ (Å)	1.5418	0.7107	1.0474	1.0474	0.9085	1.0474
a (Å)	7.67 (3)	7.682 (2)	7.514 (1)	7.506 (1)	7.505 (1)	7.499 (1)
b (Å)	12.24 (4)	12.330 (3)	12.288 (2)	12.285 (2)	12.285 (2)	12.283 (3)
c (Å)	8.47 (3)	8.501 (2)	8.483 (1)	8.483 (1)	8.482 (1)	8.481 (1)
β (°)	123.12 (2)	123.12 (2)	122.85 (1)	122.84 (1)	122.82 (1)	122.83 (1)
V (Å³)	663.62	674.38	658.01	657.22	657.20	656.42
d_c (Mg m⁻³)	1.493	1.469	1.506	1.507	1.508	1.509
Number of observations used in refinement			28	28	88	28

(b) Description of crystal

Faces	{100}, {011}	Volume	5.01 mm³ (=wt/d_c at 298 K)	Absorption	16.2 mm⁻¹ at $\lambda = 0.9085$ Å
Dimensions	2.40 × 1.20 × 1.20 mm		4.98 mm³ (from dimensions of faces	coefficients	17.4 mm⁻¹ at $\lambda = 1.047$ Å
Weight	7.36 mg		at 298 K)		

(c) Intensity data measurements

	Set (I)	Set (II)			Set (I)	Set (II)
Neutron wavelength	$\lambda = 0.9085$ Å	$\lambda = 1.0474$ Å	Number of observations		3906	433
Monochromator	Be(002)	Be(002)	Number of unique observations		3444	373
Temperature	126 ± 1 K	126 ± 1 K	Agreement on averaging symmetry-		0.022	0.012
$(\sin \theta/\lambda)_{max}$	0.87 Å⁻¹	0.75 Å⁻¹	related intensities§			
Scan width	3.2–5.9°	3.2–5.9°	Calculated neutron transmission			
Average number of steps/scan	65	65	factors:			
Counting time/step	2.75 s	2.17 s	minimum		0.854	0.839
			maximum		0.742	0.737

* Stewart & Jensen (1964).

† Kistenmacher & Rossi (1977). This paper also reports $d_{obs} = 1.474$ (4) Mg m⁻³ at 298 K.

‡ The average values of these two sets of unit-cell parameters were used in the structure determination.

§ The agreement factor is given as $\sum (\langle F_{obs} \rangle^2 - F_{obs}^2) / \sum F_{obs}^2$.

from scattering by the aluminum pin and cryostat were examined over the entire 2θ range at $\chi = 0, 45, 90°$ and at φ (or ω) values that avoided Bragg reflections from the sample. This scattering, being diffuse and relatively weak, was neglected in evaluating intensities from the scan data.

The integrated intensity (I) for each reflection was obtained by subtracting the background (B) evaluated from the first and last tenth parts of the total scan. The variance in an intensity was derived from counting statistics. Neutron absorption corrections were applied using an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973). The linear absorption coefficient ($\mu = 17\cdot4$ mm^{-1}) at wavelength $\lambda = 1\cdot0474$ Å was calculated using the value $\sigma_a = 2\cdot39$ mm^2 mg^{-1} for the mass absorption of chemically bonded hydrogen (McMullan, Fox & Craven, 1978). The value $\mu = 16\cdot2$ mm^{-1} at $\lambda = 0\cdot9085$ Å was derived with the assumption $\sigma_a \propto 1/V$ where V is the neutron velocity. When absorption corrections were applied to the intensity of the 200 reflection ($\lambda = 1\cdot0474$ Å) measured at 10° intervals of crystal rotation about $\mathbf{a}^*$, the maximum difference from the average value was reduced from 11 to 3%.

The structure was refined by minimizing $\sum w(F_o^2 - F_c^2)^2$ with a modified version of the full-matrix least-squares computer program of Busing, Martin & Levy (1962). Each observation was assigned a weight $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sin 2\theta\sigma(I)]^2 + (0\cdot01F_o^2)^2$. Values assumed for the neutron coherent scattering lengths for C, H and N were 6·65, −3·74, 9·40 fm (Koester, 1977). Initial values of the atomic parameters were those of Kistenmacher & Rossi (1977) for positions and an assumed uniform isotropic temperature factor ($U = 0\cdot019$ Å^2). The atomic parameters and a scale factor were refined using data set (I) (Table 1); an isotropic extinction factor and anisotropic thermal factors were introduced as variable parameters and the refinement was carried to convergence.

It became obvious at this point that the F_o^2 values of the $2h,2k,2l$ reflections were grossly inconsistent with the structural model. Such reflections gave values of $(F_{obs}^2 - F_{calc}^2)/\sigma(F_{obs}^2)$ which were positive and very large (up to +80), with values increasing in proportion to the F_{obs}^2 value for the corresponding hkl reflection. Similar effects were observed in refinements of deuterated cytosine monohydrate (Weber, Craven & McMullan, 1980) where the neutron data had been collected using the same equipment with a similar wavelength ($\lambda = 0\cdot9094$ Å). It appeared that the neutron beam reflected from the Be crystal contained both λ and 2λ components. The implied reflection of 2λ neutrons from the space-group-absent (001) of Be could arise from a double Bragg reflection, as proposed by Hay (1959). Further verifications were sought. First, selected pairs of $2h,2k,2l$ and hkl reflections were remeasured using a crystal of parabanic acid for which

Table 2. Atomic positional parameters with e.s.d.'s

All values are fractional coordinates $\times 10^5$ with e.s.d.'s given in parentheses.

	x	y	z
N(1)	24201 (10)	13133 (4)	72368 (7)
N(3)	29363 (10)	−5933 (4)	69429 (7)
N(7)	19280 (10)	6806 (4)	27356 (7)
N(9)	25919 (10)	−9994 (4)	39923 (8)
N(10)	18300 (11)	26268 (4)	50511 (8)
C(2)	27760 (14)	2712 (6)	78014 (10)
C(4)	26137 (13)	−3143 (6)	52777 (10)
C(5)	22169 (13)	7235 (6)	44924 (10)
C(6)	21502 (13)	15808 (6)	55727 (9)
C(8)	21559 (14)	−3623 (6)	25045 (10)
C(11)	29211 (15)	−21696 (6)	42025 (13)
H(2)	29745 (38)	1264 (15)	91586 (26)
H(8)	20304 (39)	−7080 (15)	12765 (27)
H(101)	19286 (34)	28784 (14)	39513 (24)
H(102)	19353 (37)	31829 (13)	59900 (26)
H(111)	29889 (50)	−24957 (18)	30585 (34)
H(112)	16171 (45)	−25581 (18)	41957 (43)
H(113)	44018 (43)	−23501 (18)	55130 (32)

a satisfactory neutron structure determination had already been carried out (Craven & McMullan, 1979) with longer-wavelength neutrons ($\lambda = 1\cdot0470$ Å) reflected from the same Be crystal. At the shorter wavelength, parabanic acid reflections had the same kind of systematic intensity differences as in 9-methyladenine. Also, pairs of reflections $2h,2k,2l$ and hkl for parabanic acid were measured after small rotations of up to 0·5° of the Be crystal about $\mathbf{c}^*$. For pairs with strong hkl reflections, the ratio of the integrated intensities changed by ca 10%. These tests strongly indicated the presence of double Bragg scattering in the Be crystal. Time did not permit the identification of the actual reflections involved, apart from 002_λ. However, if for example the reciprocal-lattice point $02\bar{2}_\lambda$ was also on the Ewald sphere, then so would be $001_{2\lambda}$ and $01\bar{1}_{2\lambda}$. Double Bragg scattering would also involve $02\bar{4}_\lambda$, $0\bar{1}2_{2\lambda}$ and would occur with both λ and 2λ neutrons. Of the various reflections, only 001 is space-group forbidden. Among the 9-methyladenine reflections, only those of the type $2h,2k,2l$ are affected. Using data set (I) (Table 1), a least-squares refinement was carried out minimizing the function $\sum_H w\{F_o^2(H) - |F_c^2(H) + mF_c^2(H/2)|\}$ where the mixing parameter m was a variable only for the parity group of reflections with all indices even (otherwise $m = 0$). With $m = 0\cdot48$ (4), the agreement index† $R_w(F^2)$ decreased from 0·36 to 0·08, the smaller value being consistent with the agreement for reflections of other parities.

The experimental conditions might have been altered to achieve monochromation by a complete reorien-

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† $R_w(F^2) = (\sum w\Delta^2/\sum wF_o^4)^{1/2}$ where $\Delta = F_o^2 - F_c^2$ and $w = 1/\sigma^2(F_o^2)$.

tation of the Be crystal. However, it was more expeditious to recollect the $2h,2k,2l$ reflections at the longer wavelength, giving data set (II) (Table 1). In the subsequent least-squares refinements, $2h,2k,2l$ reflections were deleted from data set (I), and data set (II) was included with a separate scale factor. In the combined data set (3356 reflections) there were 382 reflections from data set (II). Convergence was obtained with $R(F^2) = 0.049$, $R_w(F^2) = 0.051$ and $[\sum w\Delta^2/(n_{obs} - n_{param})]^{1/2} = 1.120$. The final atomic parameters are in Table 2.* The value for the isotropic extinction parameter $g = 459$ (31) rad^{-1} was small, so that only four reflections had correction factors of 0.90 or less, the most severely affected being 200 with $0.79F_{calc}^2$. Scattering lengths for the five N nuclei were included as least-squares variables. The average of final values was 9.33 fm with a maximum deviation (0.02 fm) which was less than the least-squares $\sigma = 0.03$ fm.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35103 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Values from other recent structure determinations range from 9.24 to 9.30 fm (Weber, Craven & McMullan, 1980) and are consistently smaller than the value 9.36 (2) fm tabulated by Koester (1977).

Additional least-squares refinements were carried out using various subsets of the complete data in order to explore the stability of the structure parameters. Among the five refinements (Table 3), the greatest effect on the reported atomic parameter values was produced either by omitting the 382 reflections of data set (II) or by omitting the 21 reflections having the worst agreement F_o^2 vs F_c^2. In the former refinement, the maximum changes Δ/σ were 2.39 and 2.20 in individual positional and thermal parameters, respectively. In the latter refinement, the corresponding values were 2.15 and 1.93. These are only possibly significant. Most of the 21 omitted reflections with poor agreement were clustered in a wedge $\Delta\varphi \sim 50°$ of reciprocal space near b^* and had $F_o^2 < F_c^2$. The cause of the intensity disagreement could not be found. From the various least-squares refinements it is concluded that the neutron intensity data include some systematic errors. However, the atomic parameters (Table 2) appear to be only marginally affected.

Table 3. Summary of least-squares refinements

All refinements involved the same 165 variables: two scale factors, isotropic extinction parameter, atom positional parameters and anisotropic thermal parameters. In these final refinements, the scattering length of N was fixed at the average value of 9.3 fm determined in earlier refinement cycles.

(1) Refinement using the complete data set (3356 reflections) for which parameters are reported (Table 1).
(2) Omit 21 reflections with $[|F_o^2 - F_c^2|/\sigma^2(F^2)] \geq 5$ (worst agreement).
(3) Omit 156 reflections with (sin θ/λ) ≤ 0.3 Å^{-1} (lowest scattering angle).
(4) Omit 1441 reflections with (sin θ/λ) ≥ 0.7 Å^{-1} (highest scattering angle).
(5) Omit 1018 reflections with $F_o^2/\sigma(F^2) \leq 3$ (weak reflections).
(6) Omit 382 reflections with all indices even (i.e. data set II).

The effect of each refinement on the atomic parameter is expressed as the average value of $[\Delta^2/(\sigma_i^2 + \sigma_j^2)]^{1/2}$, where Δ is the change in a parameter and σ_i, σ_j are the e.s.d.'s in the ith and jth refinements, as listed above. In the table, entries above the diagonal refer to atomic positional parameters, and those below to atomic thermal parameters. The ith term in the final column is the r.m.s. value for all positional parameter terms involving the ith refinement. The jth term in the final row is the corresponding value for thermal parameters.

	(1)	(2)	(3)	(4)	(5)	(6)	i
(1)	0	0.72	0.40	0.32	0.14	0.76	0.52
(2)	0.53	0	0.64	0.74	0.73	0.97	0.77
(3)	0.22	0.49	0	0.49	0.43	0.83	0.58
(4)	0.61	0.78	0.65	0	0.28	0.69	0.56
(5)	0.13	0.50	0.21	0.59	0	0.69	0.51
(6)	0.58	0.86	0.65	0.60	0.50	0	0.79
j	0.46	0.65	0.49	0.65	0.43	0.65	

Discussion

The values of the anisotropic thermal parameters have been used to obtain rigid-body thermal-motion tensors (Schomaker & Trueblood, 1968). The non-H-atom

Table 4. Rigid-body thermal motion

Tensor components are with respect to orthogonal crystal axes a, b, c^*, with the origin at the molecular centroid. Only C and N atoms were included.

(a) Translational tensor

$$T (\text{Å}^2) = \begin{pmatrix} 0.0142\,(3) & -0.0004\,(2) & 0.0031\,(2) \\ & 0.0095\,(2) & 0.0003\,(1) \\ & & 0.0112\,(2) \end{pmatrix}$$

R.m.s. principal values (Å) = 0.127, 0.099, 0.099.

(b) Librational tensor

$$L (\text{deg}^2) = \begin{pmatrix} 3.1\,(2) & -1.3\,(2) & -1.5\,(1) \\ & 5.8\,(3) & 1.8\,(2) \\ & & 4.5\,(2) \end{pmatrix}$$

R.m.s. principal values (°) = 2.8, 1.9, 1.5.

(c) Cross-tensor

$$S (\text{deg Å}) = \begin{pmatrix} 0.029\,(5) & -0.019\,(3) & -0.026\,(3) \\ -0.006\,(3) & -0.005\,(7) & -0.034\,(5) \\ -0.001\,(3) & 0.007\,(5) & -0.024 \end{pmatrix}$$

The r.m.s. difference between observed and calculated (rigid-body) U_{ij} values was 0.0004 Å^2. This value increased to 0.0063 Å^2 when H atoms were included in the rigid body.
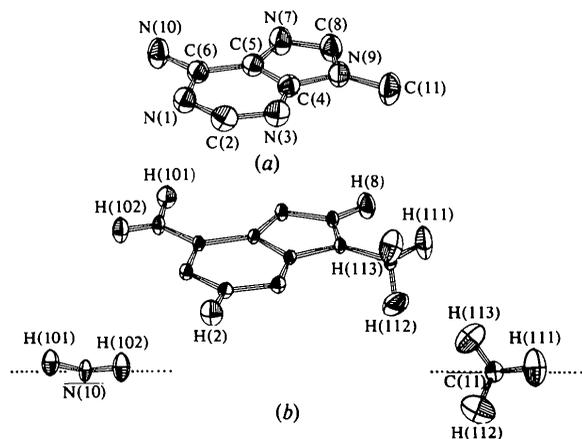
Fig. 1. Atomic nomenclature and thermal motion for 9-methyl-adenine. The ellipsoids are at 50% probability (Johnson, 1976). (a) The molecular framework with thermal ellipsoids from the X-ray study at 298 K (Kistenmacher & Rossi, 1977). (b) The present neutron results (126 K). The amino group (right) and the methyl group (left) are also shown in projection down each extra-annular bond.

framework can be fitted to rigid-body behavior (Table 4) with no significant discrepancies in terms of the experimental errors, $\sigma(U_{ij}) \simeq 0.0002$ Å^2. The H atoms appear to have considerable motion independent of the ring (Fig. 1b), which would account for the poor fit of the complete molecule to rigid-body behavior. The methyl H atoms have r.m.s. amplitudes 0.28, 0.29, 0.39 (3) Å in directions of a torsional motion about the N(9)—C(11) bond.

The thermal ellipsoids from the room-temperature X-ray study (Kistenmacher & Rossi, 1977) have an orientation very similar to that of the present neutron determination (Fig. 1). The larger values of the X-ray thermal parameters are also well fitted by assuming rigid-body motion.*

In Table 5, atomic distances and angles are listed for the present neutron results and librationally corrected values for the assumed rigid-body framework are compared with those of Kistenmacher & Rossi (1977). The largest differences are in the N(3)—C(4) bond length (0.012 Å) and in the N(1)—C(2)—N(3) bond angle (1.0°). The latter may be significant, since the e.s.d. is 0.3° after the reported values are doubled to allow for uncertainty in the thermal corrections. All bond angles are within the range of values reported in a survey of adenine derivatives (Voet & Rich, 1970). However, the bond lengths are somewhat longer. The difference between each of the present neutron values and that of the corresponding averaged adenine moiety

* The r.m.s. difference between observed and calculated (rigid-body) U_{ij} values is 0.0013 Å, which is about 1.5σ. The rigid-body librational tensor has r.m.s. principal values of 5.0, 3.4 and 2.5°, which are almost double the corresponding low-temperature neutron values (Table 4).

Table 5. Atomic distances (Å) and angles (°)

(a) Nonhydrogen-atom bond lengths and angles

The neutron values (N) are given before and after correction for rigid-body librational motion. The third values (KR) are from the room-temperature X-ray results of Kistenmacher & Rossi (1977), which we have corrected for librational motion. The corrections for the latter ranged from 0.003 to 0.007 Å in bond distances and from −0.1 to +0.1° in bond angles. Since the neutron bond angle corrections are small (−0.04 to +0.04°) only corrected values are given. The uncorrected neutron values have e.s.d.'s of about 0.001 Å in distances and 0.08° in angles, while for uncorrected X-ray values the e.s.d.'s are about 0.002 Å and 0.1°.

	d(N)	d(N)$_{corr}$	d(KR)$_{corr}$
N(1)—C(2)	1.342	1.344	1.340
C(2)—N(3)	1.330	1.331	1.330
N(3)—C(4)	1.342	1.344	1.356
C(4)—C(5)	1.394	1.396	1.386
C(5)—C(6)	1.415	1.416	1.415
C(6)—N(1)	1.354	1.355	1.363
C(5)—N(7)	1.386	1.388	1.394
N(7)—C(8)	1.321	1.323	1.316
C(8)—N(9)	1.366	1.368	1.371
N(9)—C(4)	1.371	1.372	1.373
C(6)—N(10)	1.338	1.340	1.334
N(9)—C(11)	1.453	1.455	1.459

	θ(N)$_{corr}$	θ(KR)$_{corr}$
N(1)—C(2)—N(3)	128.8	129.8
C(2)—N(3)—C(4)	110.7	109.9
N(3)—C(4)—C(5)	127.4	127.5
C(4)—C(5)—C(6)	116.4	116.7
C(5)—C(6)—N(1)	117.2	117.2
C(6)—N(1)—C(2)	119.5	118.8
N(3)—C(4)—N(9)	126.7	126.2
C(5)—N(7)—C(8)	103.8	103.4
N(7)—C(8)—N(9)	113.9	114.4
C(8)—N(9)—C(4)	106.1	105.5
N(9)—C(4)—C(5)	105.9	106.3
C(4)—C(5)—N(7)	110.4	110.5
C(6)—C(5)—N(7)	133.2	132.8
N(10)—C(6)—C(5)	124.3	124.3
N(10)—C(6)—N(1)	118.5	118.5
C(8)—N(9)—C(11)	128.3	128.4
C(11)—N(9)—C(4)	125.6	126.1

(b) Hydrogen-atom bond lengths and angles

C(2)—H(2)	1.092 (3)	C(11)—H(111)	1.076 (3)
C(8)—H(8)	1.081 (3)	C(11)—H(112)	1.086 (3)
N(10)—H(101)	1.023 (2)	C(11)—H(113)	1.086 (3)
N(10)—H(102)	1.019 (2)		

N(1)—C(2)—H(2)	114.7 (1)	N(9)—C(11)—H(113)	109.8 (2)
N(3)—C(2)—H(2)	116.5 (1)	H(111)—C(11)—H(112)	108.3 (3)
N(7)—C(8)—H(8)	125.0 (2)	H(111)—C(11)—H(113)	108.9 (2)
N(9)—C(8)—H(8)	121.2 (2)	H(112)—C(11)—H(113)	109.6 (2)
N(9)—C(11)—H(111)	110.2 (2)	C(6)—N(10)—H(101)	120.2 (1)
N(9)—C(11)—H(112)	110.0 (2)	C(6)—N(10)—H(102)	117.5 (1)
		H(101)—N(10)—H(102)	119.8 (2)

(c) Intermolecular distances and angles

Corrections have not been applied for thermal-motion effects. Magnitudes of these corrections are uncertain, but are probably at least 0.005 Å.

(i) Hydrogen bonds

	d(N$\cdots$N)	d(H$\cdots$N)	θ(N—H$\cdots$N)
N(10)—H(101)$\cdots$N(1)'	2.956 (1) Å	1.954 (3) Å	165.6 (2)°
N(10)—H(102)$\cdots$N(7)''	3.055 (1)	2.037 (3)	176.1 (2)

(ii) Short distances involving H atoms

N(3)$\cdots$H(111)[x, $-\frac{1}{2}-y$, $\frac{1}{2}+z$]	2.524 (2)
H(2)$\cdots$H(8)[x, y, 1 + z]	2.482 (3)

(Voet & Rich, 1970) has an average value of +0.012 Å. Much of this may be attributed to thermal-motion effects.

Table 6. *Least-squares planes through selected atoms*

The planes are referred to the crystal axes and are of the form $Ax + By + Cz = D$, where x,y,z are fractional coordinates and the coefficients are in Å. The planes are as follows:

(1) All nonhydrogen atoms in the molecule;
(2) Central planar bridge between the two rings (five atoms);
(3) The molecular framework at the amino group (four atoms).

Plane coefficients

	A	B	C	D
(1)	6·6202	1·8410	−0·8719	1·2166
(2)	6·6839	1·7702	−1·0192	1·1506
(3)	6·6224	1·5902	−0·8321	1·2099

Distances (Å $\times 10^3$) of atoms from the planes (e.s.d.'s are 0·001 Å, or 0·002 Å for H atoms)

(a) Atoms used to calculate the planes

N(1)	−25	–	–	N(1)	−1
C(2)	−24	–	–	–	–
N(3)	18	N(3)	−1	–	–
C(4)	16	C(4)	3	–	–
C(5)	9	C(5)	1	C(5)	−1
C(6)	6	C(6)	−2	C(6)	2
N(7)	−18	–	–	–	–
C(8)	−24	–	–	–	–
N(9)	10	N(9)	−2	–	–
N(10)	25	–	–	N(10)	−1
C(11)	6	–	–	–	–

R.m.s. deviation 21   3   2

(b) Atoms not used to calculate the planes

H(2)	−51	N(1)	−38	H(101)	196
H(8)	−46	C(2)	−42	H(102)	79
H(101)	243	N(7)	−20	N(1)'	979*
H(102)	99	C(8)	−29	N(7)''	110*
H(111)	108	N(10)	23		
H(112)	−931	C(11)	−11		
H(113)	833				

* Distances for atoms N(1)' and N(7)'' which are H-bonded with H(101) and H(102), respectively.

The molecule is only approximately planar (Table 6). This is most notable for the amino group H atoms in projection down the N(10)—C(6) bond (Fig. 1). Torsion angles N(1)—C(6)—N(10)—H are 167·2 (2) and 5·3 (2)° at H(101) and H(102) respectively. While the three bonds formed at C(6) are coplanar, the amino H atoms are displaced from this plane on the side of the N atoms with which they are hydrogen bonded (Table 6b). The effect is to make both N—H···N hydrogen bonds more nearly collinear (Table 5c). Kistenmacher & Rossi (1977) found the ring system to be folded 1·5 (1)° about the bridging C(4)—C(5) bond. However, the conformation can be described more precisely (Table 6). The central five atoms, N(3), C(4), C(5), C(6) and N(9), are coplanar with a fold occurring across the pyrimidine ring at N(3)···C(6) and across the imidazole ring at N(9)···C(5). Remaining ring atoms fold towards the same side of the central plane.

Fig. 2. The crystal structure of 9-methyladenine in projection down a*. Spheres of decreasing size represent N, C, and H atoms. The molecules of one almost planar sheet are shown with solid spheres. Molecules are H-bonded in ribbons extending up and down the page, parallel to c.

N(10) is displaced on the opposite side so as to maintain planarity of the bonds formed at C(6). In the crystal complex with 1-methyladenine (Frey, Koetzle, Lehmann & Hamilton, 1973), with the assumed space group $P2_1/m$, the 9-methyladenine molecule lies in an apparent mirror plane. It was recognized that slight molecular puckering might be present, but taken up in the anisotropic thermal parameters. However, attempts to refine a model in the lower-symmetry space group $P2_1$ were unsuccessful.

The crystal structure of 9-methyladenine (Fig. 2) consists of slightly puckered sheets of molecules parallel to the crystal planes (100). Two NH···N hydrogen bonds link molecules in ribbons along the c direction. The hydrogen-bonding distances and angles are not remarkable (Table 5c). It is notable that N(3) is not hydrogen bonded. However, N(3) is close (2·52 Å) to a methyl H atom of another molecule in the same sheet. This approach is somewhat shorter than the van der Waals distance (N···H, 2·7 Å) proposed by Pauling (1960). As part of an X-ray study, it will be of interest to determine whether the charge distribution around this C—H···N interaction differs from that of a typical hydrogen bond.

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Ethyl-18 Hydroxy-17β Nor-19 Pregnène-4 Yne-20 One-3*

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Abstract

$C_{22}H_{30}O_2$, orthorhombic, space group $P2_12_12_1$, $a = 21\cdot279$ (4), $b = 13\cdot820$ (3), $c = 6\cdot660$ (2) Å, $Z = 4$. The structure was solved by direct methods. Full-matrix least-squares refinement, with identical weights, converged at $R = 0\cdot050$ and $R_w = 0\cdot042$ for all 2272 observed reflexions. The structure of the title compound is compared with those of norethindrone and norgestrel.

Introduction

L'étude de la structure cristalline du présent stéroïde (RU1364) fait suite à celle de la noréthindrone (Mornon, Lepicard & Delettré, 1976) et s'insère dans le cadre de notre étude générale sur les stéroïdes progestogènes. Un échantillon de RU1364 nous a été confié par la Société Roussel–Uclaf. Ce composé est décrit par un brevet (Roussel–Uclaf, 1962).

Les trois stéroïdes noréthindrone, norgestrel et RU1364 diffèrent uniquement les uns des autres par la

nature du substituant sur le C(13) à savoir respective-ment méthyle, éthyle et propyle. Cette variation structurale s'accompagne de variations sensibles du comportement biochimique de ces stéroïdes (Raynaud, Philibert & Azadian-Boulanger, 1974). La structure cristalline du norgestrel est décrite par ailleurs (DeAngelis, Doyne & Grob, 1975).

Détermination de la structure et résultats

Les structures cristallines de la noréthindrone et du norgestrel sont isomorphes, celle de RU1364 sans être isomorphe de celles-ci s'en rapproche beaucoup. Les paramètres de maille pour ces trois composés sont respectivement de $a = 20{,}80$, $b = 12{,}12$, $c = 6{,}54$ Å; $a = 20{,}67$, $b = 12{,}80$, $c = 6{,}57$ Å; $a = 21{,}28$, $b = 13{,}82$, $c = 6{,}66$ Å.

Les mesures d'intensités ont été effectuées sur diffractomètre Philips PW 1100 en utilisant la radiation Cu $K\alpha$. Seules les intensités ont été mesurées, le fond continu résultant d'une série unique de mesures en fonction de θ. La structure de RU1364 a été déterminée sans difficulté à l'aide du programme *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). L'affinement a été effectué par moindres carrés avec

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