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Crystal Structure of 1-Methyluracil from Neutron Diffraction at 15, 60 and 123 K

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Abstract

The crystal structure of 1-methylpyrimidine-2,4-dione (1-methyluracil, $C_5H_6N_2O_2$) has been determined at 15, 60 and 123 K from neutron diffraction data. Molecules lie in the eightfold special positions (symmetry m) of space group $Ibam$, with $a = 13.213$ (2), $b = 13.172$ (2), $c = 6.163$ (1) Å at 15 K. Full-matrix least-squares refinements based on 807 (15 K), 805 (60 K) and 815 (123 K) reflections with $\sin\theta/\lambda < 0.69$ Å⁻¹ converged with $R(F^2) = 0.023$, 0.024 and 0.024 respectively. Bond lengths and angles have e.s.d.'s less than 0.002 Å and 0.2°. Detailed analysis of the anisotropic thermal parameters gives estimates of the zero-point internal vibrations for all nuclei and also for molecular rigid-body thermal vibrations at 15, 60 and 123 K. With thermal-vibration corrections there is good agreement in bond lengths and angles at the three temperatures.

Introduction

The crystal structure of 1-methyluracil (Fig. 1) was determined by Green, Mathews & Rich (1962) from X-ray diffraction data, presumably at room temperature. Neither the details of the analysis, nor the atomic parameters have been published. This is an important crystal structure because it contains the uracil moiety in an environment with similarities to that of uracil in ribonucleic acids. It was chosen for a study aimed at providing highly accurate molecular dimensions because the structure is simple and good quality crystals are easily grown. The structure has been determined from neutron diffraction data collected at

15, 60 and 123 K. The purpose in obtaining the structure at a sequence of low temperatures was to aid our efforts in understanding the thermal vibrations in the crystal and the effects which they have on the apparent molecular dimensions.

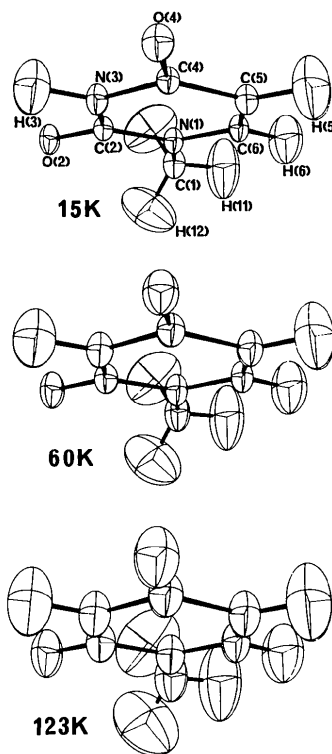


Fig. 1. Atomic labeling and thermal ellipsoids for 1-methyluracil shown at 95% probability level (Johnson, 1976).

Experimental

Plate-like crystal from aqueous solution, forms {001}, {010}, {210}, (0.010 × 0.036 × 0.352 cm); weight 2.47 mg; volume 1.62 mm³; BNL H6-S four-circle diffractometer; germanium (022) monochromator; $\lambda = 1.599$ (1) Å, from least-squares fit of $32 \sin\theta/\lambda$ values KBr ($a_0 = 6.6000$ Å at 298 K); sample crystal c axis $\sim 3^\circ$ to diffractometer ϕ axis; temperature control $< \pm 0.5$ K* by Displex model CS-202 closed-cycle refrigerator; crystal cooling rate 2 K min⁻¹; order of measurements: 123, 15, 60 K; lattice parameters from least-squares fit of $32 \sin\theta/\lambda$ values at each temperature (Table 1). Intensities in one quadrant from $\omega/2\theta$ step-scans, fixed widths $\Delta 2\theta = 3.0^\circ$ for $\sin\theta/\lambda < 0.40$ Å⁻¹; $\Delta 2\theta = (1.48 + 3.11 \tan\theta)^\circ$ for $0.4 < \sin\theta/\lambda < 0.69$ Å⁻¹; points in scans: 59–87; count time/point: ≈ 1.9 s as determined by preset monitor count of direct beam; two reflections monitored at ~ 3 h intervals, intensities constant within 2%; number of observations (including standards): 843 (15 K), 878 (60 K), 1007 (123 K), with ψ scans for 004 at 60 K and 002 at 123 K, and space-group-extinguished reflections ($\sin\theta/\lambda < 0.40$ Å⁻¹) at 123 K. Background (B) taken as first and last tenths of each scan, thus $\sigma^2(I) = I + 5B$; absorption corrections by analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973), mass absorption 2643 mm² g⁻¹ for bound hydrogen (McMullan & Koetzle, 1979), linear absorption 1.979 cm⁻¹. Minimum and maximum transmission: 0.76 and 0.93; non-symmetry-related reflections for refinement: 807 (15 K), 805 (60 K), 815 (123 K); of these 12 (15 K), 20 (60 K) and 37 (123 K) had $F_o^2 < 0.0$.

Structure refinement by full-matrix least squares (modified ORFLS, Busing, Martin & Levy, 1962); $\sum w(F_o^2 - F_c^2)^2$ minimized with $w = \{[\sin(2\theta)\sigma(I)]^2 + (0.01F_o^2)^2\}^{-1}$ in which the factor 0.01 was determined from the variability in the monitor reflections. Initial coordinates for the 123 K refinement derived from Fig. 2 of Green *et al.* (1962); coherent neutron-scattering lengths from Koester (1977). Variable parameters: nuclear coordinates, anisotropic thermal factors, scale factor, anisotropic secondary-extinction parameters g_{ij} [type I crystal, Becker & Coppens (1974); Lorentzian distribution and spread anisotropy, Thornley & Nelves (1974)]. 91 variables (P) at each temperature. Shift $P_i/\sigma(P_i) < 0.04$ in final cycles. $R(F_o^2)$, $wR(F_o^2)$, S : 0.023, 0.033, 1.29 (15 K); 0.024, 0.033, 1.24 (60 K); 0.024, 0.038, 1.09 (123 K). Extinction parameters ($\times 10^{-4}$): g_{11} , g_{22} , g_{33} ($g_{12} = g_{13} = g_{23} = 0$, constrained); 25 (6), 4.5 (2), 15 (1) (15 K); 23 (7), 4.8 (2), 17 (1) (60 K); 35 (9), 4.6 (3), 17 (1) (123 K). Greatest extinc-

Table 1. Lattice parameters (Å) and cell volume (Å³) for 1-methyluracil

	15 K	60 K	123 K	293 K*
a	13.213 (2)	13.213 (3)	13.214 (3)	13.200 (3)
b	13.172 (3)	13.172 (3)	13.193 (3)	13.226 (2)
c	6.163 (1)	6.174 (1)	6.213 (1)	6.372 (2)
V	1072.6 (6)	1074.5 (7)	1083.1 (7)	1112.4 (8)

* Values from X-ray data (Mo K α radiation) determined by Swaminathan (1982).

Table 2. Nuclear positional parameters ($\times 10^5$)

The atoms are in eightfold (f) positions $x, y, 0$ on the mirror plane of space group $Ibam$, except for H12 which is in 16-fold (k) general position. The values for each atom are in the order 15, 60 and 123 K.

	x	y	z
N1	28611 (4)	12738 (4)	0
	28609 (4)	12729 (4)	0
	28629 (4)	12702 (4)	0
C2	23241 (5)	3763 (6)	0
	23237 (6)	3753 (6)	0
	23270 (6)	3729 (6)	0
N3	12863 (4)	4747 (4)	0
	12872 (4)	4748 (4)	0
	12895 (4)	4724 (4)	0
C4	7445 (5)	13743 (6)	0
	7450 (6)	13736 (6)	0
	7481 (6)	13704 (6)	0
C5	13558 (6)	22795 (6)	0
	13566 (6)	22780 (6)	0
	13612 (6)	22739 (6)	0
C6	23792 (6)	21938 (6)	0
	23785 (6)	21921 (6)	0
	23821 (6)	21874 (6)	0
C1	39635 (6)	12063 (6)	0
	39633 (6)	12048 (6)	0
	39647 (6)	12027 (7)	0
O2	27440 (7)	-4554 (6)	0
	27428 (7)	-4547 (7)	0
	27437 (7)	-4567 (7)	0
O4	-1942 (6)	13526 (6)	0
	-1938 (6)	13526 (7)	0
	-1884 (7)	13514 (7)	0
H3	8855 (12)	-2070 (11)	0
	8853 (12)	-2048 (12)	0
	8866 (13)	-2048 (12)	0
H5	10103 (13)	30236 (13)	0
	10098 (14)	30200 (13)	0
	10137 (15)	30151 (14)	0
H6	28647 (13)	28607 (12)	0
	28667 (13)	28576 (12)	0
	28677 (14)	28534 (13)	0
H11	42650 (14)	19705 (14)	0
	42646 (15)	19684 (15)	0
	42653 (15)	19633 (16)	0
H12	42131 (9)	7954 (11)	14346 (24)
	42136 (10)	7973 (12)	14319 (26)
	42151 (10)	7948 (13)	14106 (31)

tion, yF_c^2 , for (002), y : 0.351 (15 K), 0.354 (60 K), 0.365 (123 K). Final difference map residual $|\Delta\rho|$ as % of nitrogen peak height: 1.12 (15 K), 1.20 (60 K), 1.33 (123 K). Final nuclear positional parameters are given in Table 2, anisotropic thermal parameters in Table 3.*

Additional refinements were carried out to test for possible anharmonic nuclear vibrations. Third- and fourth-order thermal parameters for all nuclei were

* The reported temperatures include a correction of +2.5 K based on a prior calibration with reference to the magnetic phase transition in FeF₂ at 78.4 K (Hutchings, Schulhof & Guggenheim, 1972).

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51575 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Nuclear anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

The values for each atom are in order 15, 60, 123 K. The temperature factor is: $T = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	48 (2)	42 (2)	78 (2)	-3 (2)	0	0
	73 (2)	56 (2)	117 (2)	-6 (2)	0	0
	124 (2)	89 (2)	187 (3)	-6 (2)	0	0
C2	46 (3)	38 (3)	62 (3)	-1 (2)	0	0
	75 (3)	52 (3)	93 (3)	1 (2)	0	0
	123 (3)	86 (3)	166 (4)	-3 (3)	0	0
N3	52 (2)	38 (2)	84 (2)	1 (2)	0	0
	76 (2)	57 (2)	112 (3)	-5 (2)	0	0
	127 (2)	83 (2)	184 (3)	-11 (2)	0	0
C4	43 (3)	39 (3)	59 (3)	-2 (2)	0	0
	69 (3)	56 (3)	84 (3)	-5 (3)	0	0
	114 (3)	84 (3)	151 (4)	-10 (3)	0	0
C5	51 (3)	44 (3)	80 (3)	0 (3)	0	0
	78 (3)	53 (3)	117 (4)	-9 (3)	0	0
	132 (3)	82 (3)	187 (4)	-7 (3)	0	0
C6	48 (3)	41 (3)	78 (3)	-3 (2)	0	0
	69 (3)	50 (3)	105 (4)	-4 (3)	0	0
	128 (4)	82 (3)	182 (4)	-18 (3)	0	0
C1	57 (3)	65 (3)	132 (4)	0 (3)	0	0
	80 (3)	86 (3)	192 (4)	-4 (3)	0	0
	124 (3)	145 (4)	354 (5)	-14 (3)	0	0
O2	67 (3)	38 (3)	104 (4)	9 (3)	0	0
	96 (4)	54 (4)	152 (4)	10 (3)	0	0
	161 (4)	92 (4)	268 (5)	18 (3)	0	0
O4	38 (4)	57 (3)	89 (4)	-3 (3)	0	0
	69 (4)	70 (4)	126 (4)	-4 (3)	0	0
	119 (4)	113 (4)	236 (5)	-6 (3)	0	0
H3	151 (6)	104 (7)	245 (8)	-28 (6)	0	0
	179 (7)	134 (8)	274 (8)	-21 (6)	0	0
	240 (7)	148 (8)	378 (10)	-32 (6)	0	0
H5	193 (8)	115 (7)	331 (10)	34 (6)	0	0
	231 (8)	124 (7)	368 (11)	38 (6)	0	0
	295 (9)	157 (7)	493 (12)	37 (7)	0	0
H6	155 (7)	118 (8)	275 (9)	-50 (5)	0	0
	182 (8)	130 (8)	323 (10)	-51 (6)	0	0
	240 (8)	179 (8)	409 (11)	-63 (6)	0	0
H11	170 (8)	152 (8)	544 (13)	-55 (6)	0	0
	199 (8)	167 (8)	621 (15)	-60 (7)	0	0
	250 (9)	257 (9)	897 (20)	-76 (8)	0	0
H12	221 (6)	398 (7)	311 (7)	33 (5)	-67 (5)	141 (6)
	247 (6)	422 (8)	386 (8)	37 (5)	-84 (6)	135 (7)
	317 (7)	577 (9)	632 (11)	43 (6)	-131 (7)	194 (9)

included in the model, assuming the Gram-Charlier expansion for the temperature factor [Johnson & Levy, 1974, §5.2.3.1, equation (9)]. Full-matrix least-squares refinement (Lundgren, 1979), but restricted so that the variables for only five nuclei were involved in each cycle. With the addition of 220 variables, giving a total of 311, small reductions in agreement factors were obtained for the data at each temperature. However, according to the *R*-factor ratio test (Hamilton, 1974), none of these is significant at the 99.5% confidence level. Individual parameters most likely to be significantly non-zero were $c(3333)$ for N1 having values

-48 (14), -39 (13), -23 (12) $\times 10^{-9}$ at 123, 60 and 15 K respectively. Although anharmonic effects may be present, they are small and cannot be described adequately with the available neutron data extending only to $\sin\theta/\lambda < 0.69 \text{ \AA}^{-1}$.

Results and discussion

The molecular arrangement

Molecules of 1-methyluracil (Fig. 1) form sheets lying in the crystallographic mirror planes of the space group *Ibam*. Within these sheets, the molecules are very efficiently packed, as shown in Fig. 2 of Green *et al.* (1962), where a van der Waals outline for each molecule is drawn. The molecular arrangement in sheets parallel to (001) is consistent with the observed (001) cleavage of the crystals, and the comparatively small temperature dependences of the cell dimensions *a* and *b* (Table 1). Between adjacent sheets, the intermolecular forces are weaker, so that there is considerable thermal expansion of the structure along *c* (0.21 \AA per unit cell over the range 15 to 293 K).

Within each sheet, the molecules form doubly hydrogen-bonded dimers having crystallographic symmetry *2/m*. The hydrogen bond N3-H3...O4 has an N3...O4 distance of 2.81 \AA , an H3...O4 distance of 1.77 \AA and an N-H...O angle of 179.4°. Similar dimers occur in the crystal structure of uracil itself (Parry, 1954; Stewart & Jensen, 1967) where the N3...O4 distance is 2.87 \AA . Note that the hydrogen bonding in the crystal structures of uracil and 1-methyluracil involves O4 as acceptor but not O2. In this respect, the hydrogen bonding resembles that of uracil in Watson-Crick-type interactions, as observed in the minihelical arrangement of sodium adenylyl-3',5'-uridine hexahydrate (Seeman, Rosenberg, Sudath, Kim & Rich, 1976). In 1-methyluracil, both O2 and O4 are involved in close interactions with C-H groups. These interactions are C6-H6...O2 and C1-H11...O4 having H...O distances 2.36 and 2.32 \AA and C-H...O angles 124 and 176°, respectively. They both occur within the closely packed sheets of

* These distances and angles are not quoted with the precision of the nuclear parameters because of the uncertainty in the proper correction owing to thermal-vibration effects.

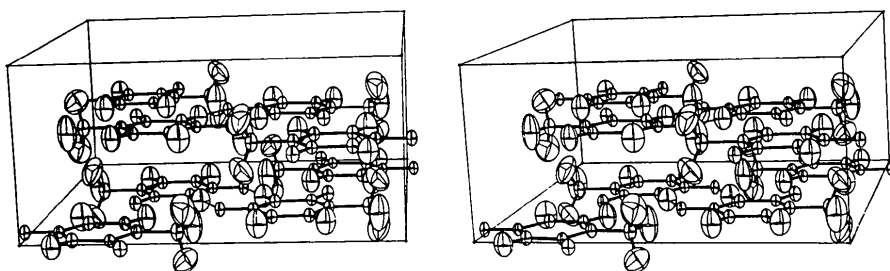


Fig. 2. The crystal structure of 1-methyluracil at 15 K with thermal ellipsoids shown at 95% probability level. Right-handed system with *c* axis vertical and *a* axis horizontal.

molecules and may thus be a consequence of the molecular arrangement rather than interactions of the hydrogen-bonding type.

The stacking of molecular sheets along *c* (with *d* spacing 3.082 Å at 15 K) occurs with no overlap of pyrimidine rings (Fig. 2). There are approximate superpositions of C2 on O2, O4 on O4, H5 on H11 and C6 on H6. The shortest interatomic distance between sheets is H12...H12 (2.50 Å at 15 K, Table 6b).

Analysis of molecular thermal librations

As expected, nuclear thermal ellipsoids (Fig. 1) are elongated normal to the pyrimidine-ring plane, which is the direction of weakest intermolecular force in the crystal. At each temperature, the probability ellipsoids for the H atoms are larger than for the others, but over the range 15 to 123 K, the H-atom mean-square (m.s.) vibrational amplitudes show a smaller temperature dependence. This indicates that H-atom internal molecular vibrations are significant. The nuclear anisotropic thermal parameters (Table 3) were used to calculate m.s. amplitudes of thermal vibration along the vectors between all pairs of covalently bonded atoms. Except for C—H and N—H, no highly significant differences were found within pairs of covalently bonded atoms.* The equality of such m.s. amplitudes is a necessary but not sufficient condition arising when a pair of nuclei are vibrating rigidly along the bond direction (Harel & Hirshfeld, 1975). Therefore, it was assumed that the molecular framework, excluding H atoms, was vibrating as a rigid body. With the rigid-body model (Schomaker & Trueblood, 1968) and using computer programs by Craven & He (1982) in order to minimize the residual $\sum_w \Delta U_{ij}^2$, reasonably good agreement was obtained at all three temperatures. For some atoms there were significant discrepancies ΔU_{33} between observed and rigid-body values at each temperature. It was considered that these could be due to the internal ring-puckering vibrations with the nuclei moving normal to the pyrimidine ring. Static molecular deformations of this kind appear to be readily induced since they are commonly observed in pyrimidine crystal structures. Thus, in the minihelical dinucleotide structure determined by Seeman *et al.* (1976), atomic displacements from the best least-squares plane of the uracil ring range up to 0.05 Å for C5. In crystals of 1-methyluracil, such deformations are likely to be dynamical rather than static since the molecules lie in mirror planes with the same environment on both sides. If we assume that there is no mixing between the internal and external (rigid body) modes of vibration for 1-methyluracil, then each type of vibration will give a positive contribution to the total m.s. amplitude U_{33} for

* The most significant differences (3.4σ , 3.1σ) were for C2—N1 and C2—O2 at 15 K. For C—H and N—H pairs the differences in m.s. amplitudes were in the range 6 to 10σ .

Table 4. *Derived mean-square amplitudes* ($\text{Å}^2 \times 10^4$) *for internal vibrations*

Values are derived from the differences between observed U_{ij} (Table 3) and those calculated for the rigid-body vibrations of the molecular framework, excluding H atoms. For H atoms, values are averaged for 15, 60 and 123 K with e.s.d.'s from the distribution. M.s. amplitudes are referred to a local Cartesian axial system for each nucleus. The *z* axis is normal to the pyrimidine ring, except for the methyl H atom H12, where this axis is normal to the plane N1—C1—H12. The *x* axis is along the appropriate C—H or N—H bond. For non-H atoms, displacements occur only along *z* (see text).

	<i>x</i>	<i>y</i>	<i>z</i>
N1	0	0	23
C2	0	0	13
N3	0	0	26
C4	0	0	17
C5	0	0	32
C6	0	0	7
C1	0	0	24
O2	0	0	21
O4	0	0	12
H3	63 (9)	99 (2)	122 (9)
H5	60 (3)	152 (6)	257 (8)
H6	49 (5)	123 (3)	116 (26)
H11	55 (7)	156 (5)	399 (36)
H12	74 (3)	210 (16)	464 (63)

each nucleus. For each nucleus at 15 K, we write $U_{33}(\text{int.}) = \Delta U_{33} + U_0$, where ΔU_{33} are the discrepancies from the rigid-body model and U_0 is a constant with the same value for all framework nuclei. Although U_0 cannot be determined directly from the experimental data, the minimum for U_0 must be sufficient to give $U_{33}(\text{int.})$ a positive or zero value for all nuclei. At 15 K, ΔU_{33} is 3 (2), -7 (3), 6 (2), -4 (3), 12 (3), -13 (3), 4 (4), 1 (4) and -8 (4) $\text{Å}^2 \times 10^4$ for N1, C2, N3, C4, C5, C6, C1, O2 and O4 respectively, requiring $U_0 \geq 0.0013 \text{ Å}^2$. Arbitrarily, we chose $U_0 = 0.0020 \text{ Å}^2$, giving $U_{33}(\text{int.})$ in the range from 0.0007 Å^2 for C6 to 0.0032 Å^2 for C5, as shown in Table 4.* It should be noted that $U_{33}(\text{int.})$ alternates between large and small m.s. amplitudes at neighboring ring positions, consistent with certain ring-puckering modes being favored over others. However, details of these vibrations cannot be determined without elaborate lattice-dynamical calculations.

It was next assumed that $U_{33}(\text{int.})$ at 15 K for each atomic nucleus corresponds to the sum of m.s. amplitudes for the ground states of the internal modes, and because of their high frequencies, these modes remain in the ground state up to a temperature of 123 K. Accordingly, the rigid-body model was modified to include $U_{33}(\text{int.})$ determined at 15 K as fixed contributions to $U_{33}(\text{calc.})$ at each temperature. There

* Whatever value is chosen for U_0 subsequently becomes subtracted from the rigid-body translational tensor component, T_{33} . In principle, U_0 has an upper bound (0.0055 Å^2 in this case) where the translational tensor becomes non-positive definite. Note that the introduction of U_0 has no effect on the rigid-body librational and cross tensors (L, S).

Table 5. *Molecular thermal parameters*

Rigid-body calculations were carried out with respect to the orthogonal crystal axes with the origin at the molecular center of mass, which has fractional coordinates (0.1949, 0.1089, 0).

	15 K			60 K			123 K		
Goodness of fit	1.879			2.069			2.574		
wR	0.063			0.056			0.053		
$\Omega_{\text{H,C}} (\text{deg}^2)^*$	125 (3)			125 (3)			163 (4)		
$T (\text{\AA}^2 \times 10^3)$	$\begin{bmatrix} 44 (1) & & \\ -2 (1) & 0 & \\ & 36 (2) & \end{bmatrix}$			$\begin{bmatrix} 69 (1) & & \\ -4 (1) & 0 & \\ & 50 (2) & \end{bmatrix}$			$\begin{bmatrix} 119 (2) & & \\ -8 (2) & 0 & \\ & 78 (2) & \end{bmatrix}$		
$L (\text{deg}^2)$	$\begin{bmatrix} 4.1 (3) & & \\ -1.6 (2) & 35 (2) & \\ & 0 & 0 \end{bmatrix}$			$\begin{bmatrix} 4.8 (4) & & \\ -1.5 (2) & 61 (2) & \\ & 0 & 0 \end{bmatrix}$			$\begin{bmatrix} 7.9 (5) & & \\ -1.4 (3) & 114 (3) & \\ & 0 & 0 \end{bmatrix}$		
$S (\text{deg } \text{\AA} \times 10^3)$	$\begin{bmatrix} 0 & & \\ 0 & 0 & -12 (4) \\ 5 (3) & 0 & -15 (3) \end{bmatrix}$			$\begin{bmatrix} 0 & & \\ 0 & 0 & -13 (4) \\ 8 (3) & 0 & -30 (3) \end{bmatrix}$			$\begin{bmatrix} 0 & & \\ 0 & 0 & -33 (5) \\ 10 (4) & 0 & -53 (4) \end{bmatrix}$		

* Torsional libration of methyl H atoms about the N1—C1 axis.

was an improved agreement with wR decreasing from 0.084 to 0.054 (15 K), from 0.073 to 0.041 (60 K) and from 0.054 to 0.034 (123 K).*

The m.s. amplitudes of the H nuclei resulting from the rigid-body vibrations of the molecular framework were then calculated and subtracted from the observed values. For each of the ring-substituent H atoms, these differences were found to be similar at all three temperatures. Furthermore, when transformed to local Cartesian axes with one axis along the appropriate C—H or N—H bond and another normal to the pyrimidine ring, principal values for these residual m.s. amplitude tensors were in directions close to those of the Cartesian axes. We attribute these differences to the internal vibrations of the H nuclei and characterize the average principal values for the three temperatures at each nucleus as the resultant of bond stretching, in-plane and out-of-plane internal modes (Table 4). The e.s.d. from the distribution of values at the three temperatures is comparable to the e.s.d. in the observed U_{ij} parameters of the H nuclei except for the out-of-plane motion of H6.† Since the residual m.s. amplitudes do not increase systematically with increasing temperature, it is assumed that they represent internal vibrations of the H nuclei in their ground state.

It should be noted that both in-plane and out-of-plane internal vibrations for H6 are significantly smaller than those for H5. This might be the result of the unusually short C6—H6...O2 interaction which has no counterpart for H5. For the methyl H atoms, m.s. amplitudes for internal vibrations are similar at each temperature, except for the torsional motion about the N1—C1 bond, which increases at 123 K. Comparison of the crystallographically distinct H11 and H12 atoms shows that the internal vibrations have smaller m.s. amplitudes for H11. As in the comparison of H5 and H6, this

difference might be a result of the short C1—H11...O4 interaction.

A least-squares fit of the complete molecule to the rigid-body model was carried out, including fixed values from Table 4 for the internal vibrations of all atomic nuclei. Libration of the methyl H nuclei about the N1—C1 axis was also included as a variable, according to the procedure of Dunitz & White (1973). This was done for convenience, although, as shown above, methyl H-nuclei internal vibrations are only approximately consistent with the motion of a symmetric rotor. With the inclusion of the H atoms, there is some deterioration in the overall agreement between observed and calculated U_{ij} parameters (Table 5). However, the agreement is considered to be satisfactory when the approximations in the model are taken into account. The resulting molecular-vibration tensors are in Table 5. The maximum rigid-body libration amplitude occurs about an axis which lies in the pyrimidine plane and is nearly perpendicular to the N3...C6 ring diagonal. This axis, which has direction cosines (0.8210, -0.5709, 0) with respect to the crystal axes, makes an angle of 21.3° with the axis corresponding to the minimum moment of inertia of the molecule, which has direction cosines (0.9722, -0.2343, 0).

Interatomic distances and angles

Bond lengths and angles for 1-methyluracil are shown in Table 6(a), both with and without harmonic thermal-vibration corrections. It can be seen that bond-length corrections not involving H atoms are small ($\leq 0.002 \text{ \AA}$) and have only a marginal effect on the agreement among values for the three temperatures, which is generally within the range of the e.s.d.'s (0.001 \AA). It is possible that the molecular internal vibrations might give rise to significant corrections for bond lengths involving ring substituents. The true correction cannot be estimated without knowledge of the correlated atomic motions in the internal modes. However, an approximation, which might be as

* $wR = [\sum w\Delta^2 / \sum w(U_{ij}^2)_{\text{obs}}]^{1/2}$ where $\Delta = [(U_{ij})_{\text{obs}} - (U_{ij})_{\text{calc}}]^2$ and $w = 1/\sigma^2(U_{ij})_{\text{obs}}$.

† For H6, the residual out-of-plane m.s. amplitudes are 0.0130 (9), 0.0138 (10) and 0.0080 (11) \AA^2 at 15, 60 and 123 K, the latter being anomalously small.

Table 6. *Interatomic distances (Å) and angles (°)*

For each parameter, entries are for 15 K (top), 60 K (middle) and 123 K (bottom).

(a) Intramolecular

Values on the left are uncorrected and those on the right are corrected for rigid-body libration or, for C–H and N–H distances, by assuming H-atom vibrations in the riding mode (Busing & Levy, 1964).

N1–C6	1.369 (1)	1.370	C4–C5	1.440 (1)	1.442
	1.368 (1)	1.369		1.440 (1)	1.441
	1.367 (1)	1.369		1.441 (1)	1.444
N1–C2	1.379 (1)	1.380	C4–O4	1.241 (1)	1.242
	1.379 (1)	1.381		1.241 (1)	1.242
	1.380 (1)	1.382		1.238 (1)	1.240
N1–C1	1.459 (1)	1.460	C5–H5	1.081 (2)	1.100
	1.459 (1)	1.461		1.079 (2)	1.099
	1.459 (1)	1.461		1.080 (2)	1.103
C2–O2	1.228 (1)	1.229	C5–C6	1.357 (1)	1.358
	1.226 (1)	1.226		1.355 (1)	1.356
	1.225 (1)	1.227		1.354 (1)	1.356
C2–N3	1.377 (1)	1.378	C6–H6	1.088 (2)	1.103
	1.376 (1)	1.377		1.088 (2)	1.105
	1.377 (1)	1.379		1.088 (2)	1.105
N3–H3	1.043 (2)	1.056	C1–H11	1.083 (2)	1.108
	1.041 (2)	1.054		1.082 (2)	1.109
	1.040 (1)	1.055		1.079 (2)	1.112
N3–C4	1.384 (1)	1.385	C1–H12	1.088 (1)	1.116
	1.384 (1)	1.385		1.086 (2)	1.115
	1.384 (1)	1.386		1.080 (2)	1.119
C6–N1–C2	121.31 (5)	121.32	N3–C4–C5	114.74 (6)	114.76
	121.26 (6)	121.27		114.67 (6)	114.68
	121.41 (6)	121.41		114.67 (6)	114.67
C6–N1–C1	121.21 (6)	121.19	H5–C5–C6	119.75 (12)	119.72
	121.29 (6)	121.26		119.92 (12)	119.72
	121.20 (6)	121.18		119.99 (13)	119.97
C2–N1–C1	117.48 (6)	117.50	H5–C5–C4	120.91 (12)	120.92
	117.45 (6)	117.47		120.73 (12)	120.74
	117.39 (6)	117.41		120.64 (13)	120.65
O2–C2–N3	122.26 (7)	122.23	C6–C5–C4	119.35 (7)	119.36
	122.33 (8)	122.31		119.36 (7)	119.38
	122.18 (8)	122.16		119.37 (7)	119.38
O2–C2–N1	122.17 (6)	122.18	H6–C6–C5	121.37 (11)	121.38
	122.16 (7)	122.17		121.55 (12)	121.57
	122.41 (7)	122.41		121.31 (12)	121.32
N3–C2–N1	115.57 (6)	115.59	H6–C6–N1	116.15 (11)	116.16
	115.51 (6)	115.53		115.89 (11)	115.90
	115.42 (7)	115.44		116.16 (12)	116.16
H3–N3–C2	115.12 (11)	115.15	C5–C6–N1	122.48 (7)	122.47
	115.21 (11)	115.23		122.56 (7)	122.53
	115.32 (11)	115.34		122.54 (7)	122.52
H3–N3–C4	118.34 (11)	118.34	H11–C1–H12	110.55 (10)	110.55
	118.14 (11)	118.15		110.34 (11)	110.33
	118.08 (11)	118.08		110.51 (12)	110.50
C2–N3–C4	126.54 (6)	126.51	H11–C1–N1	108.10 (12)	108.12
	126.65 (6)	126.62		108.07 (13)	108.09
	126.59 (6)	126.58		108.10 (14)	108.12
O4–C4–N3	119.82 (7)	119.79	H12–C1–H12'	108.73 (18)	108.76
	119.90 (7)	119.88		109.00 (19)	109.05
	119.96 (8)	119.95		108.43 (21)	108.49
O4–C4–C5	125.44 (8)	125.45	H12–C1–N1	109.44 (8)	109.43
	125.42 (8)	125.44		109.53 (8)	109.52
	125.36 (8)	125.38		109.64 (9)	109.62

(b) Intermolecular

Values on the left are uncorrected and those on the right are corrected for atoms with uncorrelated thermal vibrations (Busing & Levy, 1964).

O2...H5 ($\frac{1}{2}-x, -\frac{1}{2}+y, 0$)	2.593 (2)	2.605
	2.599 (2)	2.613
	2.600 (2)	2.621
O2...H6 ($\frac{1}{2}-x, -\frac{1}{2}+y, 0$)	2.359 (2)	2.371
	2.364 (2)	2.379
	2.371 (2)	2.393
O4...H11 ($-\frac{1}{2}+x, \frac{1}{2}-y, 0$)	2.322 (2)	2.340
	2.324 (2)	2.347
	2.338 (2)	2.372
H5...H11 ($-\frac{1}{2}+x, \frac{1}{2}-y, 0$)	2.306 (4)	2.331
	2.306 (4)	2.334
	2.311 (4)	2.350
H12...H12 ($1-x, y, \frac{1}{2}-z$)	2.459 (4)	2.490
	2.461 (4)	2.496
	2.477 (4)	2.527
H12...H12 ($x, -y, \frac{1}{2}-z$)	2.473 (4)	2.501
	2.480 (4)	2.511
	2.496 (4)	2.541

appropriate as the rigid-body correction, is to assume the riding-mode correction (Busing & Levy, 1964), which gives C2–O2 bond lengths 1.231, 1.229 and 1.231 Å and C4–O4 bond lengths 1.243, 1.243 and 1.242 Å, respectively. Whether either or neither correction is assumed, the C4–O4 bond length is significantly longer than C2–O2. The difference (~0.01 Å) could be an inherent property of the molecule, but could also be induced by the hydrogen bond which occurs at O4 but not O2 (Craven, Cusatis, Gartland & Vizzini, 1973).

The riding-mode corrections for N–H and C–H bonds range up to 0.03 Å. For the methyl group, they give improved agreement among methyl C–H bond lengths determined at the three temperatures. Small differences in the average bond lengths are found when comparing C5–H5 with C6–H6 (0.003 Å) and C1–H11 with C1–H12 (0.007 Å). Although the former difference is only marginally significant, the longer bond in both cases is associated with a larger m.s. amplitude for the C–H stretching vibration (Table 4). The effect is consistent with a stretching force constant which decreases slightly with increasing bond length. In addition to these bond-length differences, there are also significant differences in N1–C1–H and H–C1–H bond angles ($\leq 1.4^\circ$, Table 6) which cause small deviations from an ideally threefold symmetric methyl group. Such effects may all be correlated with the short intermolecular interaction C1–H11...O4 and differences in methyl-H nuclear thermal parameters.

The bond lengths and angles presently reported are probably the most accurate values available for a uracil derivative. They agree with results from other accurate room-temperature studies, with allowance for uncorrected shortening of bond lengths resulting from thermal-vibration effects. These crystal structures include uracil (Stewart & Jensen, 1967), uridine (Green, Rosenstein, Shiono, Abraham, Trus & Marsh, 1975), 5-nitrouracil (Craven, 1967) and 1-methylthymine (Kvick, Koetzle & Thomas, 1974). It is of interest that in all these structures, including 1-methyluracil, the internal ring angle at N1 is about 5° less than the angle at N3, irrespective of whether there is a ring substituent at N1.

In Table 6(b), we show the closest intermolecular distances with corrections for uncorrelated thermal vibrations (Busing & Levy, 1964), these being the most appropriate for weak van der Waals interactions. It should be noted that such corrections may be appreciable (~0.05 Å) for interactions involving H atoms.

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Spirocyclohexane Oxazines, Thiazines and Selenazines. Crystal Structures and NMR Comparative Study

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Abstract

The crystal structures of cyclohexanespiro-2-{4-phenyl-5-aza-3-oxabicyclo[4.4.0]deca-1(6),4-diene} (I) and the corresponding spirothiazine (II) were solved by direct methods using three-dimensional X-ray diffraction data. Compound (I), $C_{19}H_{23}NO$, $M_r = 281.4$, monoclinic, space group $P2_1/c$, $a = 15.157$ (9), $b =$

10.584 (3), $c = 9.745$ (3) Å, $\beta = 96.38^\circ$, $V = 1553.6$ Å³, $Z = 4$, $D_x = 1.20$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.39$ mm⁻¹, $F(000) = 608$, $T = 293$ K, $R = 0.058$ for 1782 reflections with $I > 3\sigma(I)$. Compound (II), $C_{19}H_{23}NS$, $M_r = 293.5$, monoclinic, space group $P2_1/a$, $a = 9.901$ (3), $b = 19.074$ (9), $c = 9.411$ (3) Å, $\beta = 114.10^\circ$, $V = 1622.3$ Å³, $Z = 4$, $D_x = 1.20$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu =$

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