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# The Crystal Structures of Salts of Methylated Purines and Pyrimidines. III. 1-Methyluracil Hydrobromide

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Crystals of 1-methyluracil hydrobromide are orthorhombic with $a=13{\cdot}24$, $b=6{\cdot}82$, and $c=8{\cdot}35$ Å. The space group is *Pnma* with four molecules per unit cell, all atoms lying in the mirror plane at $y=\frac{1}{4}$ and $\frac{3}{4}$. Final bond lengths and angles have been determined from coordinates obtained by the least-squares method from *h*0*l* and *h*1*l* data, the estimated standard deviation for bond lengths being 0·05 Å and for bond angle 2°. The acidic proton has been identified as being attached to the carbonyl oxygen of C(4). No interpyrimidine hydrogen bonds are formed, the molecules being held together in layers by zigzag hydrogen bonds of the types O–H · · · Br and N–H · · · Br. The molecular packing is somewhat unusual, the bromide ions on one layer being sandwiched between the pyrimidine rings of the layers immediately above and below. The structure is remarkably similar to 1-methylcytosine hydrobromide done previously in this laboratory.

## Introduction

The present series of studies of the methylated purines and pyrimidines has been continued in this laboratory in an effort to provide additional information concerning the nature of hydrogen bonding of the nucleic acids at acidic *p*H. Such information is of help in understanding the structural chemistry of polynucleotides, an endeavor which is of great interest in modern biology. The crystal structure of 1-methyluracil hydrobromide was determined by two-dimensional X-ray diffraction methods in this present work. Previous crystal structures determined in this series were 1-methylcytosine hydrobromide (Bryan & Tomita, 1962*a*) and 9-methyladenine hydrobromide (Bryan & Tomita, 1962*b*).

## Experimental

Crystals of 1-methyluracil hydrobromide were prepared by adding an excess amount of concentrated hydrobromic acid to a powder preparation of 1-methyluracil†, and allowing the solution to evaporate at room temperature. The crystals so obtained are colorless needles elongated along the *b* axis and a crystal suitable for X-ray analysis, approximately 0·25 mm × 0·25 mm × 0·5 mm, was mounted in a 0·3 mm diameter glass capillary with some mother liquor. The unit-cell dimensions and space group were determined by 30° precession photographs with Cu $K\alpha$ radiation. Intensity data were collected at room temperature on an equi-inclination Weissenberg camera for the zero and first layers around the *b* axis, the multiple film technique being used. Intensities were estimated visually with a calibrated standard scale obtained by recording different time exposures of a selected single reflection. Lorentz polarization corrections were applied but no absorption correction was made. 109 *h*0*l* and 117 *h*1*l* non-zero reflections were recorded from the theoretical number of 146 *h*0*l* and 145 *h*1*l* unique reflections available.

*Crystal data*

1-Methyluracil hydrobromide, $C_5H_6N_2O_2.HBr$, mol. wt. 206·9.

Orthorhombic prismatic,

$a=13{\cdot}24\pm0{\cdot}03$, $b=6{\cdot}82\pm0{\cdot}04$, $c=8{\cdot}35\pm0{\cdot}04$ Å.

Volume of unit cell 754·0 Å$^3$, $D_m=1{\cdot}805$ g.cm$^{-3}$, $Z=4$, $D_x=1{\cdot}834$ g.cm$^{-3}$, $F(000)=408$.

The systematic absences required the crystal to be in space group *Pnma* or $Pna2_1$. Because of the close similarity of this crystal structure to that of 1-methylcytosine hydrobromide, it was assumed to be in the same space group as the latter, *Pnma*. This was subsequently verified during the course of the crystal structure determination.

## Structure determination

The choice of the space group *Pnma* required that the molecule lie on a mirror plane at $y=\frac{1}{4}$ and $\frac{3}{4}$, and therefore only the two positional parameters, $x$ and $z$, needed to be determined to specify the structure completely. The structure was solved by the heavy atom method. The Patterson function $(u,w)$ was calculated and the Br–Br peaks identified, locating the bromine position at $x=0{\cdot}1184$, $z=0{\cdot}1988$. The phases calculated from the bromide position were then used for the first Fourier (010) synthesis. Although all the light atom peaks were identified, considerable distor-

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† Obtained from the Cyclo Chemical Corporation, Los Angeles, California, U.S.A.

tion of the uracil molecule was encountered owing to overlap of the pyrimidine ring by the bromine ion projected from the planes immediately above and below. Subsequent Fourier synthesis failed to give any improvement and attempts to refine the coordinates of this structure isotropically by the least-squares procedure were without success. Difference Fourier synthesis revealed that the bromine ion had a large anisotropic component of thermal vibration in the $z$ direction (Fig. 1). It was therefore decided to attempt first an anisotropic refinement for the bromine thermal parameters using the initial approximate coordinates obtained from the first Fourier synthesis.

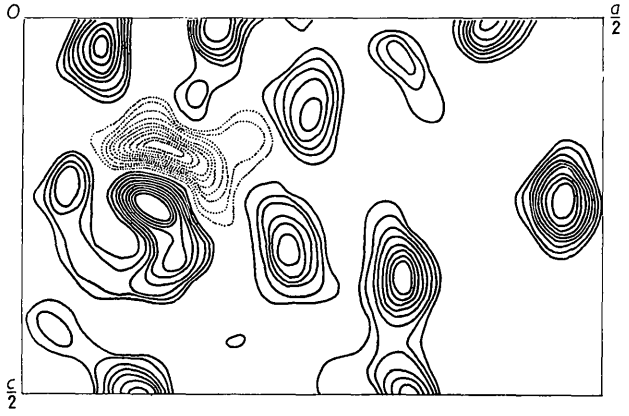



Fig. 1. Difference Fourier (010) synthesis showing marked anisotropic thermal vibration of bromine ion predominantly in $z$ direction. Light atom electron density peaks are apparent. Contours are drawn at equal but arbitrary levels of electron density.

The least-squares refinement based on $h0l$ $F$'s began with a residual of 0·259. After two cycles of anisotropic refinement in which the coordinates of all the atoms, the scale factor, and $\beta_{11}$, $\beta_{33}$, $\beta_{13}$ were varied, the residual was 0·169. Four cycles of refinement were next calculated, keeping the scale factor and anisotropic temperature factors fixed, and varying the atomic positions. The residual dropped quickly to 0·123. At this point, structure factors for $hll$ were introduced into the refinement. The final residual after individual light atom and bromine thermal anisotropic refinements was 0·122 excluding zeros, 0·141 including zeros. The weighted residual, with an arbitrary weighting scheme (Hughes, 1941), was 0·150 omitting zeros and 0·173 including zeros. A comparison between the initial values of coordinates from the first electron density projection and the final values as computed from least-squares refinement is presented in Table 1. The final thermal parameters are presented in Table 2, and the final $F_o$ and $F_c$ values are shown in Table 3. The final $(F_o - F_{Br})$ synthesis after anisotropic refinement is shown in Fig. 2.


Fig. 2. Final $(F_o - F_{Br})$ Fourier (010) synthesis after anisotropic refinement. Contours are drawn at equal but arbitrary levels of electron density.

Table 2. *Final anisotropic thermal parameters after least-squares refinement*

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{13}$ |
|---|---|---|---|---|
| N3 | 0·0007 | 0·0031 | 0·0110 | 0·0012 |
| C2 | 0·0005 | 0·0075 | 0·0116 | −0·0016 |
| N1 | 0·0014 | 0·0080 | 0·0077 | −0·0012 |
| C6 | 0·0016 | 0·0110 | 0·0139 | −0·0022 |
| C5 | 0·0005 | 0·0126 | 0·0102 | 0·0021 |
| C4 | 0·0020 | 0·0080 | 0·0095 | 0·0013 |
| O(4) | 0·0009 | 0·0139 | 0·0087 | 0·0007 |
| O(2) | 0·0011 | 0·0176 | 0·0121 | −0·0006 |
| C(7) | 0·0037 | 0·0142 | 0·0091 | −0·0012 |
| Br | 0·0020 | 0·0286 | 0·0143 | −0·0030 |

Table 1. *Comparison between atomic coordinates at the beginning and end of least-squares refinement*

| | Initial coordinates from first Fourier synthesis | | | Final coordinates after anisotropic least-squares refinement | | |
|---|---|---|---|---|---|---|
| Atom | $x/a$ | $y/b$ | $z/c$ | $x/a$ | $y/b$ | $z/c$ |
| N3 | 0·0580 | 0·2500 | 0·0520 | 0·0702 | 0·2500 | 0·0521 |
| C2 | 0·0408 | 0·2500 | 0·2391 | 0·0491 | 0·2500 | 0·2142 |
| N1 | 0·1181 | 0·2500 | 0·3361 | 0·1311 | 0·2500 | 0·3152 |
| C6 | 0·2216 | 0·2500 | 0·2987 | 0·2257 | 0·2500 | 0·2632 |
| C5 | 0·2535 | 0·2500 | 0·1122 | 0·2467 | 0·2500 | 0·1053 |
| C4 | 0·1642 | 0·2500 | 0·0157 | 0·1704 | 0·2500 | −0·0008 |
| O(4) | 0·1741 | 0·2500 | −0·1401 | 0·1733 | 0·2500 | −0·1540 |
| O(2) | −0·0378 | 0·2500 | 0·2677 | −0·0392 | 0·2500 | 0·2605 |
| C(7) | 0·0968 | 0·2500 | 0·5016 | 0·1098 | 0·2500 | 0·4884 |
| Br | 0·3843 | 0·2500 | −0·3030 | 0·3830 | 0·2500 | −0·2989 |

Table 3. *Observed and calculated structure factors*

| h 0 l | $F_o$ | $F_c$ | h 0 l | $F_o$ | $F_c$ | h 0 l | $F_o$ | $F_c$ | h 1 l | $F_o$ | $F_c$ | h 1 l | $F_o$ | $F_c$ | h 1 l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 0 | 104.0 | 117.8- | 6 3 | 62.3 | 51.5- | 1 6 | 27.6 | 29.1- | 2 0 | 17.4 | 15.3 | 16 2 | 21.4 | 22.9 | 10 5 | 20.0 | 23.1 |
| 6 | 36.2 | 36.5- | 7 | 25.8 | 26.4- | 2 | 13.1 | 10.9- | 4 | 50.9 | 51.1 | 0 3 | 31.5 | 32.5- | 11 | 51.0 | 40.9 |
| 8 | 64.3 | 62.4 | 8 | 31.3 | 25.8- | 3 | 46.5 | 51.7- | 6 | 80.1 | 82.2- | 1 | 42.8 | 46.2- | 12 | 7.0 | 4.6 |
| 12 | 39.7 | 45.7- | 9 | 49.9 | 41.4- | 4 | 41.0 | 40.3- | 8 | 26.6 | 23.2- | 2 | 8.5 | 4.5 | 1 6 | 30.2 | 30.9 |
| 14 | 51.9 | 45.5- | 10 | 38.9 | 31.3 | 5 | 12.1 | 11.8 | 10 | 65.9 | 70.3 | 3 | 54.3 | 57.8- | 2 | 13.2 | 9.1- |
| 16 | 26.4 | 32.7 | 11 | 12.5 | 6.1 | 6 | 18.4 | 23.1 | 12 | 40.7 | 42.6 | 4 | 62.6 | 57.0 | 3 | 31.0 | 30.1- |
| 1 1 | 37.9 | 48.3 | 12 | 22.7 | 19.0 | 7 | 22.9 | 20.1 | 14 | 42.9 | 35.5- | 5 | 56.8 | 45.1 | 5 | 36.1 | 38.1- |
| 2 | 162.2 | 135.0- | 13 | 50.1 | 40.1 | 8 | 19.2 | 13.1 | 16 | 15.9 | 14.6- | 6 | 48.7 | 36.9 | 6 | 11.6 | 8.0- |
| 3 | 34.5 | 34.7- | 14 | 13.7 | 13.0- | 11 | 31.1 | 26.9- | 0 1 | 24.5 | 29.0 | 7 | 65.8 | 54.0 | 7 | 23.5 | 22.3 |
| 4 | 36.1 | 30.0- | 16 | 24.8 | 22.7- | 12 | 11.3 | 9.4- | 1 | 9.7 | 12.4- | 8 | 44.5 | 38.5- | 8 | 11.7 | 9.6- |
| 6 | 99.6 | 99.3 | 0 4 | 54.6 | 60.4 | 1 7 | 24.6 | 25.5- | 2 | 14.8 | 13.4- | 9 | 27.2 | 21.2- | 9 | 59.6 | 47.0 |
| 8 | 62.8 | 54.7 | 1 | 16.9 | 22.9 | 2 | 28.6 | 31.0- | 3 | 43.4 | 37.5 | 10 | 36.5 | 31.2- | 10 | 24.4 | 17.3 |
| 9 | 8.9 | 10.6- | 2 | 34.8 | 30.4 | 4 | 12.5 | 12.5- | 4 | 117.3 | 124.4- | 11 | 40.7 | 37.1- | 11 | 7.1 | 7.7- |
| 10 | 73.2 | 70.0- | 3 | 58.5 | 57.7 | 5 | 39.7 | 41.0 | 5 | 36.7 | 34.6- | 13 | 27.7 | 21.8 | 12 | 18.9 | 15.1- |
| 12 | 12.5 | 11.5- | 4 | 23.2 | 21.5- | 6 | 25.0 | 23.1 | 6 | 5.5 | 5.4 | 14 | 19.5 | 16.2 | 13 | 27.2 | 28.9- |
| 14 | 43.1 | 37.2 | 5 | 28.2 | 25.0- | 9 | 30.6 | 31.5- | 7 | 51.1 | 46.7- | 15 | 17.2 | 16.9 | 0 7 | 23.1 | 24.8 |
| 16 | 21.6 | 21.2 | 6 | 23.7 | 19.3- | 10 | 22.5 | 20.4- | 8 | 56.0 | 55.0 | 16 | 18.3 | 19.7- | 1 | 23.1 | 26.7- |
| 0 2 | 117.7 | 122.9- | 7 | 54.9 | 46.2- | 0 8 | 17.5 | 15.4- | 9 | 17.9 | 16.6 | 1 4 | 64.0 | 73.7- | 2 | 8.2 | 7.9- |
| 1 | 31.2 | 34.1- | 8 | 9.6 | 6.1 | 1 | 18.4 | 20.1 | 10 | 54.2 | 53.3 | 2 | 14.3 | 17.2 | 3 | 16.4 | 12.5- |
| 2 | 21.0 | 22.4- | 9 | 28.3 | 22.5 | 3 | 17.5 | 18.5 | 11 | 42.6 | 43.1 | 3 | 54.5 | 61.7 | 5 | 28.7 | 26.8 |
| 3 | 51.4 | 45.3- | 10 | 17.7 | 14.5 | 4 | 27.3 | 27.0 | 12 | 18.5 | 19.1- | 4 | 17.9 | 13.2 | 7 | 22.8 | 19.8 |
| 4 | 53.7 | 50.4 | 11 | 63.8 | 49.5 | 7 | 12.7 | 13.5- | 13 | 19.8 | 15.7- | 5 | 60.2 | 52.0 | 8 | 19.0 | 18.3 |
| 5 | 22.7 | 18.7- | 12 | 18.3 | 21.2- | 8 | 18.9 | 18.2- | 14 | 31.8 | 27.5- | 6 | 15.8 | 11.9- | 10 | 9.2 | 7.0- |
| 6 | 21.5 | 16.5 | 13 | 7.6 | 8.6- | 11 | 12.7 | 12.8 | 15 | 9.2 | 6.7- | 7 | 33.4 | 26.9- | 11 | 18.6 | 18.4- |
| 7 | 66.8 | 52.3 | 14 | 15.4 | 16.4- | 2 9 | 23.2 | 24.6 | 16 | 20.8 | 20.9 | 9 | 48.9 | 43.8- | 12 | 12.4 | 12.2- |
| 8 | 72.5 | 55.2- | 15 | 34.6 | 32.3- | 5 | 8.3 | 8.1- | 1 2 | 42.9 | 54.5 | 10 | 14.3 | 7.1 | 1 8 | 11.6 | 9.8- |
| 9 | 25.9 | 22.2- | 1 5 | 39.7 | 41.7 | 6 | 15.5 | 16.8- | 2 | 85.0 | 105.4- | 11 | 16.4 | 14.2 | 2 | 18.3 | 18.6- |
| 10 | 15.5 | 12.4- | 2 | 15.4 | 15.7- | 9 | 5.8 | 7.2 | 3 | 86.9 | 74.2- | 12 | 31.4 | 22.4 | 4 | 11.3 | 8.7 |
| 11 | 22.7 | 21.0- | 3 | 32.7 | 32.3- | 0 10 | 14.1 | 15.6 | 4 | 58.9 | 45.5- | 13 | 33.8 | 28.8 | 5 | 17.4 | 16.4 |
| 12 | 68.8 | 55.7 | 5 | 38.6 | 38.0- | 4 | 15.0 | 16.2- | 5 | 37.4 | 31.4- | 15 | 10.7 | 7.7- | 6 | 21.4 | 21.7 |
| 13 | 9.8 | 10.2 | 6 | 11.6 | 8.4- | 5 | 3.8 | 3.9- | 6 | 71.0 | 58.5 | 0 5 | 36.2 | 37.0- | 9 | 21.5 | 18.3- |
| 14 | 34.3 | 29.5 | 7 | 23.0 | 17.8 | | | | 7 | 54.9 | 43.9 | 1 | 48.8 | 52.4 | 10 | 17.5 | 15.4- |
| 15 | 27.0 | 24.8 | 8 | 14.3 | 20.0 | | | | 8 | 24.3 | 20.6 | 3 | 41.6 | 43.9 | 0 9 | 18.0 | 16.9- |
| 16 | 8.7 | 10.1- | 9 | 28.9 | 24.6 | | | | 9 | 36.9 | 33.7 | 4 | 7.1 | 7.7- | 3 | 10.0 | 9.3 |
| 1 3 | 46.0 | 54.0- | 10 | 20.3 | 17.7 | | | | 10 | 33.9 | 30.8- | 5 | 31.5 | 31.3- | 6 | 8.6 | 7.5 |
| 2 | 49.4 | 53.4 | 12 | 6.4 | 6.3- | | | | 11 | 11.7 | 9.2- | 6 | 10.9 | 8.7- | 7 | 12.3 | 9.9- |
| 3 | 50.4 | 45.8 | 13 | 32.5 | 33.8- | | | | 12 | 40.6 | 35.8- | 7 | 79.7 | 72.8- | 8 | 15.5 | 15.0- |
| 4 | 20.3 | 13.7- | 14 | 10.2 | 14.6- | | | | 13 | 39.0 | 30.8- | 8 | 16.4 | 15.5 | 9 | 12.2 | 13.2- |
| 5 | 59.9 | 51.4 | 0 6 | 20.5 | 19.7 | | | | 14 | 20.6 | 19.7 | 9 | 20.3 | 22.2 | 2 10 | 12.0 | 11.0 |

The atomic scattering factors for carbon, nitrogen, and oxygen were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and for the bromide ion from Thomas & Umeda (1957). The following anisotropic temperature factor, $\exp(-\beta)$ was used: $\beta=\beta_{11}h_1^2+\beta_{22}h_2^2+\beta_{33}h_3^2+2\beta_{12}h_1h_2+2\beta_{13}h_1h_3+2\beta_{23}h_2h_3$, where $\beta_{ij}$ are the six anisotropic temperature factors, $h_i$ the Miller indices. The symmetry of the space group *Pnma* requires $\beta_{12}$ and $\beta_{23}$ to be zero (Levy, 1956; Trueblood, 1956).

## Discussion

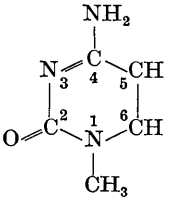
The crystal structure of 1-methyluracil hydrobromide bears a striking resemblance to that of 1-methylcytosine hydrobromide done earlier in this laboratory (Bryan & Tomita, 1962*a*). Both crystals belong to space group *Pnma* with four molecules per unit cell. The cell constants for 1-methylcytosine hydrobromide are

$$a=12{\cdot}98,\ b=6{\cdot}80,\ c=8{\cdot}83\ \text{Å},$$

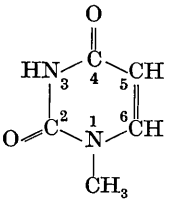
as compared with 1-methyluracil hydrobromide

$$a=13{\cdot}24,\ b=6{\cdot}82,\ c=8{\cdot}35\ \text{Å}.$$

This might be expected, since the structures of 1-methylcytosine and 1-methyluracil are closely related, the essential difference being that in the former an amino group, and in the latter a carbonyl oxygen atom, is attached to C(4).

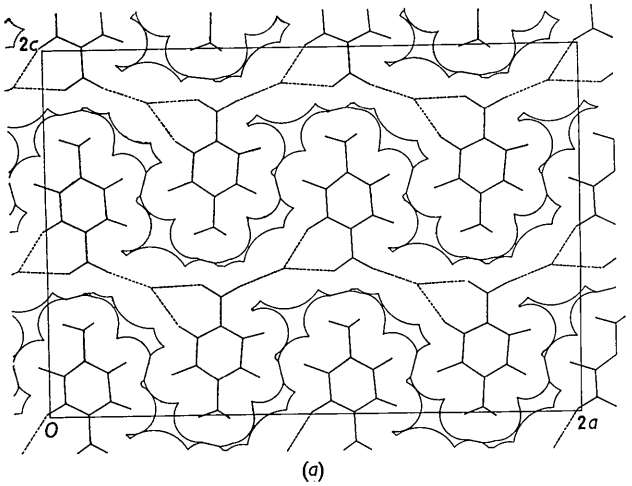



1-Methylcytosine

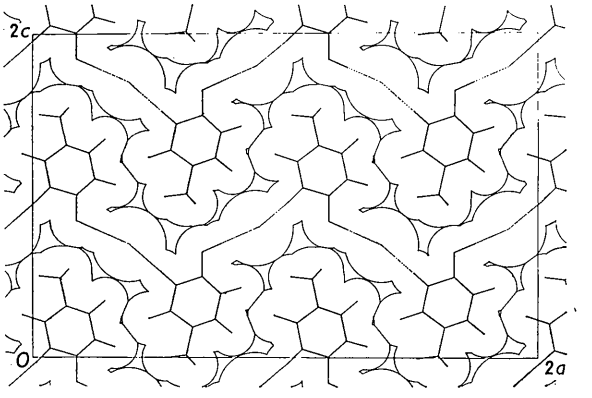



1-Methyluracil

In 1-methylcytosine hydrobromide the acidic proton is attached directly to the pyrimidine ring at N(3) and hydrogen bonding of the type N(3) · · · Br(1), and Br(2) · · · H–N–H · · · Br(1) occurs which forms a planar zigzag chain along the *a* axis (Fig. 3*a*). This is to be compared with 1-methyluracil hydrobromide where protonation occurs on the carbonyl oxygen attached to C(4), hydrogen bonding occurring between N(3)–H · · · Br(1), and O(4)-H · · · Br(2), again forming a planar zigzag chain along the *a* axis (Fig. 3*b*). Here the hydrogen bonds are straight to within 1 or 2°, while those which are formed in 1-methylcytosine deviate from linearity by as much as 25°. If one compares the relative orientation of these molecules in the unit cell, it appears that the uracil molecule is inclined more acutely to the *a* axis, and this allows it to make two straight hydrogen bonds. 1-Methylcytosine hydrobromide, however, has an amino group which may hinder it from assuming such a position, and the molecule forms three non-linear hydrogen bonds instead. This probably explains why the *a* axis in 1-methyluracil hydrobromide (13·24 Å) is slightly




(a)




(b)

Fig. 3. (*a*) Packing diagram of 1-methylcytosine hydrobromide with conventional van der Waals radii inscribed. Each molecule makes three non-linear hydrogen bonds of the type N–H · · · Br shown by broken lines. (*b*) Packing diagram of 1-methyluracil hydrobromide with conventional van der Waals radii inscribed. Each molecule makes two linear hydrogen bonds of the type N–H · · · Br and O–H · · · Br shown by broken lines.

longer than that of 1-methylcytosine hydrobromide (12·98 Å) and the *c* axis slightly shorter (*i.e.* 8·35 Å compared with 8·83 Å).

The bond lengths and angles found in the present analysis for 1-methyluracil hydrobromide are shown in Fig. 4. The standard deviation of light atom coordinates from the least-squares refinement, when only diagonal elements of the inverse matrix are used, is approximately 0·02 Å; however, since there is considerable overlap between some of the atoms in the pyrimidine ring and the bromine ion, this figure probably represents an underestimation. We suggest therefore that our standard deviation involving bond length between light atoms is probably around 0·05 Å and bond angle around 2°. A more accurate determination of 1-methyluracil was done recently in this laboratory (Green, Mathews, & Rich, 1962).

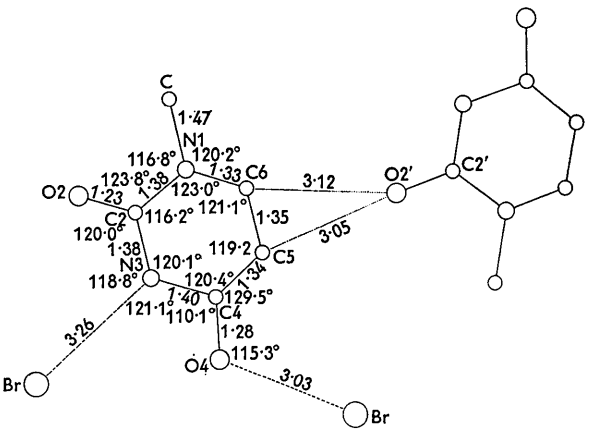
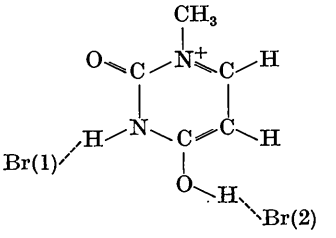
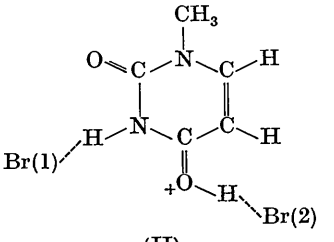



Fig. 4. Schematic diagram of 1-methyluracil hydrobromide showing bond distances and angles. Hydrogen bonds are indicated by broken lines. Other interatomic distances are shown by dotted lines.

Although we hesitate to be too confident of the bond distances and angles obtained from this analysis, it appears to us that there is significant shortening of the N(1)–C(6), C(6)–C(5), C(5)–C(4) bonds indicating partial double bond character. This suggests the following as predominant resonant structures:




(I)




(II)

Compatible with these resonant forms is the observation that the O–H · · · Br(2) bond is 3·03 Å, a value which is considerably shorter than the expected hydrogen bond distance of about 3·35 Å. The shortness of this bond suggests that it has a large electrostatic energy component which is associated with the resonant form (II). The N(3)–H · · · Br(1) bond of 3·26 Å appears to be a normal hydrogen bond distance.

The distance between the molecular planes is 3·31 Å.

The bromine ion on one plane is situated directly above the pyrimidine ring of uracil on the plane below. The distances are as follows: Br–N(1) 3·45 Å, Br–C(6) 3·65 Å, Br–C(5) 3·82 Å, Br–C(4) 3·78 Å, Br–N(3) 3·59 Å, Br–C(2) 3·43 Å. If one considers the half thickness of the aromatic molecule to be 1·7 Å, and the ionic radius of bromine to be 1·95 Å, it is evident that the observed distance of 3·43 Å must reflect a shortening of the carbon van der Waals radius in the direction of the center of the pyrimidine ring. The Br–N(1) distance of 3·45 Å is considerably shorter than the other bromine–light atom distances. This may be due to electrostatic interaction between the bromine ion and the positively charged nitrogen N(1) atom associated with resonant form (I).

The O(2) oxygen of an adjacent molecule is roughly equidistant from C(6) and C(5), the O(2) · · · C(6) distance being 3·12 Å and the O(2) · · · C(5) distance 3·05 Å. The angle subtended by atoms

$$C(4)\text{–}O(4) \cdots Br(1)$$

is 115·3°, which is in good agreement with the C–O · · · O angle of 114° found in formic acid (Jones & Templeton, 1958).

We wish to express our thanks to Dr David P. Shoemaker for the use of his MIFR1 Fourier program and to Dr Henri Levy and Dr William Busing for use of their full-matrix anisotropic least-squares program. We also wish to thank the M.I.T. Computation Center for providing us with a generous amount of calculating time on the IBM 7090. Our sincerest thanks are extended to Prof. Alexander Rich for his helpful advice and discussion of this work, as well as to Dr Scott Mathews, whose help in computer programing was deeply appreciated.

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# The Crystal Structures of Salts of Methylated Purines and Pyrimidines. IV. 9-Methylguanine Hydrobromide

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Crystals of 9-methylguanine hydrobromide are monoclinic, with $a = 4{\cdot}54$, $b = 17{\cdot}46$, and $c = 10{\cdot}68$ Å, $\gamma = 90°$. The space group is $P2_1/b$ with four molecules per unit cell. The molecular structure has been determined by the heavy atom method and refined isotropically and anisotropically by the least-squares method using partial three-dimensional data. Bond lengths and angles are given; the estimated standard deviations for bond lengths and angles involving light atoms are 0·03 Å and 2° respectively. The acidic proton has been identified as being attached directly to the purine ring at N(7). The crystal structure is quite interesting in that the bromide ions are stacked one on another to form neighboring pairs of infinite columns through the crystal. Each pair of bromide columns is surrounded in turn by six columns consisting of guanine molecules stacked 3·37 Å apart in a tilted arrangement. Each guanine molecule participates in two hydrogen bonds of the N–H · · · Br involving the ring nitrogen N(7) and the amino nitrogen N(10), forming a continuous zigzag hydrogen bonded network along the *c* axis. There are no inter-purine hydrogen bonds formed.

## Introduction

This is the fourth in a series of articles describing the crystal structures of salts of the methylated purines and pyrimidines. The purpose of these studies was to investigate the nature of hydrogen bonding in crystal structures of nucleic acid derivatives and to relate this to hydrogen bonding in polynucleotide fibers drawn in acidic solution. It was of particular interest to ascertain the first site of protonation on the guanine molecule and to determine the predominant resonant

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