

molecule are given in Fig. 3. There are some notable differences between the values obtained here and those obtained previously. The C—O distances are now significantly different: C=O 1.222 (2) and C—O(H) 1.308 (2) Å, compared with 1.23 (3) and 1.26 (3) Å respectively (Holtzberg *et al.*, 1953). The new dimensions are also in closer agreement with those obtained for other carboxyl compounds (Nahringbauer, 1970*b*).

The length of the hydrogen bond is 2.624 (2) Å. The previously reported value of 2.58 (3) Å is shorter, but not significantly so. The present hydrogen-bond distance is similar to that found in acetic acid: 2.626 (6) and 2.625 (4) Å at 278 and 83 K respectively (Nahringbauer, 1970*a*). Replacement of CH<sub>3</sub> by only a slightly more electronegative H atom would not be expected to cause a significant change in the hydrogen bond, as seen from a comparison of the hydrogen-bond situations in ammonium acetate and ammonium formate (Nahringbauer, 1967, 1968).

In the case of acetic acid, the hydrogen bond is accepted in the *trans* position with respect to the hydroxyl group. The same is also true of the formic acid molecules in HCOOH.HCONH<sub>2</sub> (Nahringbauer & Larsson, 1968). A molecular-orbital treatment by EHT and CNDO/2 methods (Murthy, Davis & Rao, 1969) suggests that the  $\beta$  form is more stable than the  $\alpha$  form. *Ab initio* LCAO—MO—SCF calculations of the conformation of protonated formic acid made by Hopkinson, Yates & Csizamadia (1970) also indicate that a similar arrangement of the two protons is the most stable.

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### 3-Methyl-8-azaguanine Hydrobromide Monohydrate

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**Abstract.** C<sub>3</sub>H<sub>7</sub>N<sub>6</sub>OBr.H<sub>2</sub>O, monoclinic, *P*2<sub>1</sub>/*m*, *a* = 10.120 (6), *b* = 6.654 (4), *c* = 7.508 (4) Å,  $\beta$  = 109.91 (4)°, *U* = 475.4 Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.85, *D<sub>m</sub>* = 1.82 g cm<sup>-3</sup> (by flotation in CHBr<sub>3</sub>/CCl<sub>4</sub>),  $\mu$ (Mo *K* $\alpha$ ) =

42.6 cm<sup>-1</sup>. The crystal has a layer structure with the cations, anions and water molecules all lying on crystallographic mirror planes perpendicular to the *b* axis, the distance between the layers being 3.327 Å.

The negatively charged bromide ions in one layer lie on top of the positively charged six-membered heteroaromatic ring in the layer below. In each layer, bromide anions and water molecules lie between rows of the 3-methyl-8-azaguanine cations parallel to the *c* axis. Protons on the heterocyclic ring are attached to atoms N(1) and N(8).

**Introduction.** Single crystals of the title compound were grown in the form of thick irregular colorless plates by dissolving 3-methyl-8-azaguanine (obtained from Heterocyclic Chemical Corporation, Harrisonville, Missouri) in conc. HBr and evaporating at room temperature. The crystal used for data collection had the approximate dimensions 0.60 × 0.45 × 0.30 mm. Precession and Weissenberg photographs only showed absences for *Ok0* with *k* odd, indicating the space group to be either  $P2_1$  or  $P2_1/m$ . The intensity data were collected using graphite-monochromatized Mo  $K\alpha$  radiation on a four-circle Picker automatic diffractometer equipped with a scintillation counter and a pulse-height analyzer. The cell constants were determined by a least-squares procedure using the diffractometer coordinates of 12 reflections with  $2\theta(\text{Mo})$  values in the range 23 to 37°.  $\lambda(\text{Mo } K\alpha)$  was assumed to be 0.7093 Å. The intensities were collected up to  $2\theta = 55.5^\circ$  by the  $\theta/2\theta$  scan technique at a scan speed of  $2^\circ (\text{Mo}) \text{ min}^{-1}$ , with stationary background measurements of 20 s on each side of a peak. To allow for the presence of both  $K\alpha_1$  and  $K\alpha_2$  radiation, the scan range for each reflection was from  $1.0^\circ$  below the calculated  $K\alpha_1$  peak position to  $1.0^\circ$  above the calculated  $K\alpha_2$  position. The data were corrected for the usual geometrical factors and for absorption. The absorption correction was calculated using Hamilton's GONO9 program; for the sample used, the transmission coefficients ranged from 0.22 to 0.45 with an average value of 0.38. 1294 reflections were recorded, of which 1055 had  $I > 3\sigma(I)$ ; only these latter reflections were used in the refinement.

The location of the Br atom was deduced from a Patterson function. The Fourier map phased only by the Br atom showed all the non-hydrogen atoms at the same *y* coordinate as that assumed for Br (0.25). The structure was, therefore, refined initially in the centrosymmetric space group  $P2_1/m$  with all the non-hydrogen atoms constrained to lie on the mirror plane at *y* = 0.25. The H atoms were located from a difference Fourier map. All except the methyl H atom H1C(3) were found to lie on the mirror plane. The non-hydrogen atoms were refined with anisotropic temperature factors, and the H atoms with isotropic temperature factors. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , the weights *w* being taken as  $4F_o^2/\sigma^2(F_o^2)$ . The scattering factors for Br were taken from Cromer & Waber (1965), for C, N and O from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965).

Corrections for the anomalous dispersion of Br were taken from Cromer & Liberman (1970). Four of the eight independent H atoms, *i.e.* H2N(2), H1C(3), H1O(*W*) and H2O(*W*), could not be refined properly and were, therefore, fixed at the original positions obtained from the difference Fourier map. A secondary-extinction correction (Zachariasen, 1968) was applied, but the agreement between the observed and calculated structure factors for reflection 020 could not be improved satisfactorily. This reflection was more than twice as intense as any other reflection, and since  $|F_c|$  was much larger than  $|F_o|$  we conclude that our scintillation counter was flooded by this intensity. It was, therefore, removed from the data set. The final agreement indices  $R = \sum (|F_o| - |F_c|)/\sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$  were 0.039 and 0.050, respectively, based on 1054 observations and 98 variables. The value of the extinction coefficient was  $7(1) \times 10^{-8}$ .

An attempt was made to refine the structure in the noncentrosymmetric space group  $P2_1$ . Initially, only the heavy atoms were refined (using full-matrix techniques), and after convergence the H atoms were located in a difference Fourier map and included in the refinement. At no stage of the refinement were the agreement factors *R* and  $R_w$  lower than at the analogous stage of the centrosymmetric refinement. The final values of *R* and  $R_w$  were essentially the same as in the  $P2_1/m$  model (0.039 and 0.049 respectively), but none of the H atoms could be refined satisfactorily in space group  $P2_1$ . This suggests to us that the correct choice of space group is  $P2_1/m$ .

The positional parameters (and their estimated

Table 1. *Positional parameters* ( $\times 10^4$ , for H  $\times 10^3$ ) for 3-methyl-8-azaguanine hydrobromide monohydrate

|                 | <i>x</i>   | <i>y</i> | <i>z</i>  |
|-----------------|------------|----------|-----------|
| Br              | 2372 (0.5) | 2500     | 1035 (1)  |
| N(1)            | 8993 (4)   | 2500     | 8908 (5)  |
| C(2)            | 8427 (5)   | 2500     | 10311 (6) |
| N(2)            | 9292 (5)   | 2500     | 12081 (6) |
| N(3)            | 7040 (4)   | 2500     | 9894 (5)  |
| C(3)            | 6393 (6)   | 2500     | 11371 (8) |
| C(4)            | 6224 (5)   | 2500     | 8007 (6)  |
| C(5)            | 6785 (5)   | 2500     | 6552 (6)  |
| C(6)            | 8267 (5)   | 2500     | 6973 (7)  |
| O(6)            | 8920 (4)   | 2500     | 5860 (5)  |
| N(7)            | 5725 (4)   | 2500     | 4895 (6)  |
| N(8)            | 4621 (4)   | 2500     | 5443 (6)  |
| N(9)            | 4837 (4)   | 2500     | 7301 (6)  |
| O( <i>W</i> )   | 1802 (6)   | 2500     | 5905 (9)  |
| NH(1)           | 997 (7)    | 250      | 939 (9)   |
| H1N(2)          | 1025 (9)   | 250      | 1246 (12) |
| H2N(2)          | 890        | 250      | 1307      |
| H1C(3)          | 677        | 110      | 1224      |
| H2C(3)          | 550 (9)    | 250      | 1090 (10) |
| HN(8)           | 390 (8)    | 250      | 454 (10)  |
| H1O( <i>W</i> ) | 88         | 250      | 607       |
| H2O( <i>W</i> ) | 265        | 250      | 710       |

standard deviations) derived from the last cycle of refinement in the centrosymmetric space group  $P2_1/m$  are presented in Table 1.\* A difference Fourier map calculated at the end of the refinement did not reveal any significant residual electron density.

**Discussion.** We have previously reported the structure of protonated 8-azaguanine (Kozłowski, Singh & Hodgson, 1974, 1975) which shows the triazole proton to be attached to N(8) (I, see Fig. 1 for numbering system), while the extra proton goes to N(3). A similar result was observed for the protonated 8-aza-2,6-diaminopurine cation (Singh & Hodgson, 1975). In neutral 8-azaguanine, however, the triazole proton was found to be at N(9) (Macintyre, Singh & Werkema, 1965). It was, therefore, of interest to determine the protonation sites in the crystals of the protonated 3-methyl-8-azaguanine cation. The results show that the triazole proton is again attached to N(8) (II, and Fig. 1), while the extra proton goes to N(1). The tautomers shown in (I) and (II) each have two resonance contributors, with the positive charge delocalized over N(1) and N(3); the contributors shown appear to predominate over those with the charge at N(1), since N(1)–C(2) is slightly longer than N(3)–C(2) in both cations.

A view of the protonated 3-methyl-8-azaguanine cation normal to the molecular plane is shown in Fig. 1. All atoms lie in a crystallographic mirror plane except the two methyl protons, H1C(3) and H1'C(3), which

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32966 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

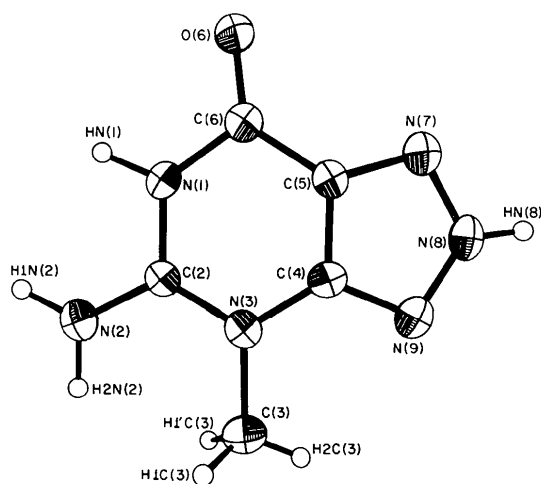
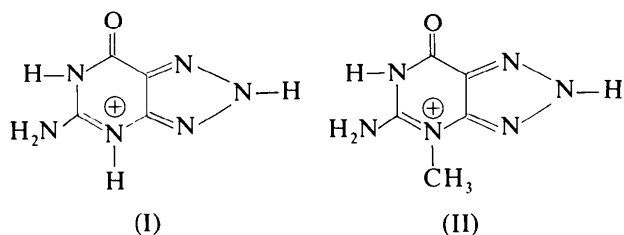


Fig. 1. View of the 3-methyl-8-azaguanine cation normal to the molecular plane. H atoms are shown as open circles of arbitrary size and others as 50% probability thermal ellipsoids (Johnson, 1965). H1'C(3) is directly below H1C(3) when viewed from above H1C(3).



are related by the mirror plane. The bond lengths and bond angles in the 3-methyl-8-azaguanine cation are compared with those in the previously published structure of the 8-azaguanine cation (Kozłowski *et al.*, 1974) in Table 2. It is obvious from these data that the substitution of a methyl group for a proton on N(3) has no discernible effect on the molecular geometry. This is consistent with the observations of Ringertz (1972), who has noted that the effects of H and CH<sub>3</sub>

Table 2. Bond lengths (Å) and bond angles (°), involving non-hydrogen atoms only, in 3-methyl-8-azaguanine hydrobromide monohydrate (MAG.HBr) compared with those in 8-azaguanine hydrochloride monohydrate (AG.HCl)

|                | MAG.HBr   | AG.HCl*   | $\Delta$<br>(MAG.HBr –<br>AG.HCl) |
|----------------|-----------|-----------|-----------------------------------|
| N(1)–C(2)      | 1.360 (6) | 1.365 (3) | –0.005                            |
| C(2)–N(2)      | 1.319 (8) | 1.306 (3) | 0.013                             |
| C(2)–N(3)      | 1.330 (6) | 1.344 (3) | –0.014                            |
| N(3)–C(3)      | 1.467 (7) |           |                                   |
| N(3)–C(4)      | 1.376 (8) | 1.369 (3) | 0.007                             |
| C(4)–C(5)      | 1.392 (7) | 1.391 (3) | 0.001                             |
| C(5)–C(6)      | 1.423 (7) | 1.449 (3) | –0.026                            |
| C(6)–O(6)      | 1.229 (7) | 1.221 (3) | 0.008                             |
| C(6)–N(1)      | 1.387 (8) | 1.387 (3) | 0.000                             |
| C(5)–N(7)      | 1.338 (9) | 1.334 (3) | 0.004                             |
| N(7)–N(8)      | 1.316 (6) | 1.309 (3) | 0.007                             |
| N(8)–N(9)      | 1.336 (6) | 1.345 (3) | –0.009                            |
| N(9)–C(4)      | 1.321 (7) | 1.326 (3) | –0.005                            |
| C(6)–N(1)–C(2) | 126.8 (4) | 127.5 (2) | –0.7                              |
| N(1)–C(2)–N(3) | 120.4 (5) | 119.8 (2) | 0.6                               |
| N(1)–C(2)–N(2) | 118.1 (4) | 118.5 (2) | –0.4                              |
| N(2)–C(2)–N(3) | 121.5 (5) | 121.7 (2) | –0.2                              |
| C(2)–N(3)–C(4) | 117.2 (5) | 117.9 (2) | –0.7                              |
| C(2)–N(3)–C(3) | 121.9 (5) |           |                                   |
| C(4)–N(3)–C(3) | 120.8 (4) |           |                                   |
| N(3)–C(4)–C(5) | 123.1 (4) | 122.9 (2) | 0.2                               |
| N(3)–C(4)–N(9) | 126.6 (5) | 127.5 (2) | –0.9                              |
| C(5)–C(4)–N(9) | 110.3 (5) | 109.6 (2) | 0.7                               |
| C(4)–C(5)–C(6) | 120.4 (5) | 120.8 (2) | –0.4                              |
| C(4)–C(5)–N(7) | 108.5 (4) | 108.6 (2) | –0.1                              |
| C(6)–C(5)–N(7) | 131.1 (5) | 130.5 (2) | 0.6                               |
| N(1)–C(6)–O(6) | 119.8 (4) | 120.6 (2) | –0.8                              |
| N(1)–C(6)–C(5) | 112.0 (5) | 111.1 (2) | 0.9                               |
| C(5)–C(6)–O(6) | 128.2 (5) | 128.3 (2) | –0.1                              |
| C(5)–N(7)–N(8) | 102.0 (4) | 102.9 (2) | –0.9                              |
| N(7)–N(8)–N(9) | 118.1 (5) | 117.1 (2) | 1.0                               |
| N(8)–N(9)–C(4) | 101.1 (5) | 101.7 (2) | –0.6                              |

\* Kozłowski *et al.* (1974) [see also Kozłowski *et al.* (1975)].

substituents on the internal angles of purines are very similar. The only difference in the bond lengths and angles greater than  $3\sigma$  occurs in C(5)—C(6), which is shorter in the methyl derivative by 0.026 Å.

The packing and hydrogen bonding in the crystal are depicted in Fig. 2. The distances and angles associated with the hydrogen bonds are given in Table 3. All the

cations, anions and water molecules are arranged in layers parallel to the *ac* plane at  $y = \pm 0.25$ , the distance between the layers being  $b/2$ , *i.e.* 3.327 Å. In each layer the bromide anions and the water molecules are situated between rows of the 3-methyl-8-azaguanine cations running parallel to the *c* axis and hold the rows together through extensive hydrogen bonding. Every available N and O atom, except N(7), is involved in hydrogen bonding. The layers are held together by weak van der Waals forces and electrostatic interactions only, the latter between the bromide anions and the pyrimidine moiety of the cations as indicated in Fig. 2. It is seen that Br<sup>-</sup> interacts mainly with C(2), N(3) and C(4), and probably N(1), the respective distances (corresponding van der Waals separations in parentheses) being 3.49 (3.65), 3.49 (3.55), 3.59 (3.65) and 3.61 (3.55) Å.

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Table 3. Probable A—H...B hydrogen bonds

| A    | H      | B    | A...B<br>(Å) | H...B<br>(Å) | A—H...B<br>(°) |
|------|--------|------|--------------|--------------|----------------|
| N(1) | HN(1)  | Br   | 3.24         | 2.32         | 171            |
| N(2) | H1N(2) | Br   | 3.46         | 2.71         | 141            |
| N(2) | H1N(2) | O(W) | 3.12         | 2.53         | 123            |
| N(2) | H2N(2) | O(6) | 2.99         | 2.09         | 156            |
| N(8) | HN(8)  | Br   | 3.32         | 2.56         | 157            |
| O(W) | H1O(W) | O(6) | 2.91         | 1.94         | 169            |
| O(W) | H2O(W) | N(9) | 2.89         | 2.17         | 127            |

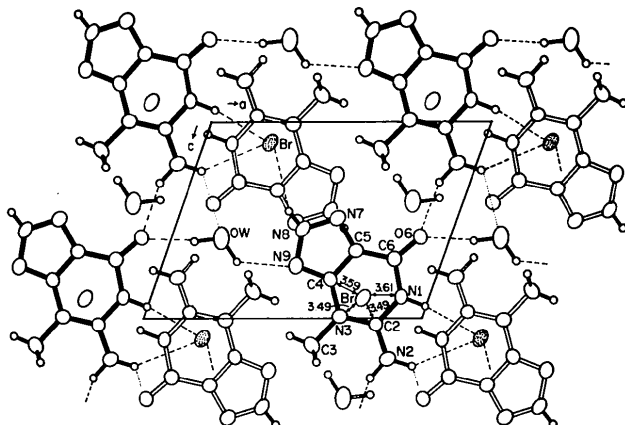


Fig. 2. Packing and hydrogen bonding projected on the *ac* plane. One unit cell is outlined. Molecules in the top layer are shown with full bonds; bromide anions in the top layer are shown as stippled ellipsoids. Hydrogen bonds (only in the top layer) are shown as dashed lines; probable N(2)—H...O(W) interactions are shown as dotted lines. Interactions of bromide ions with atoms of the six-membered rings from adjacent layers are also shown, the numbers indicating distances in Å.

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