

I thank Dr Robert Battershell for the sample of the compound.

#### References

- BRITTON, D. (1981a). *Cryst. Struct. Commun.* **10**, 1509–1512.  
 BRITTON, D. (1981b). *Cryst. Struct. Commun.* **10**, 1501–1508.  
 BRITTON, D. (1988). *Acta Cryst.* **C44**, 1020–1022.  
 DUNITZ, J. D., SCHWEIZER, W. B. & SEILER, P. (1982). *Helv. Chim. Acta*, **66**, 123–133.  
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.  
 Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.  
 NYBURG, S. C. & FAERMAN, C. H. (1985). *Acta Cryst.* **B41**, 274–279.  
 RIJ, C. VAN & BRITTON, D. (1981). *Cryst. Struct. Commun.* **10**, 175–178.  
 SEILER, P., SCHWEIZER, W. B. & DUNITZ, J. D. (1984). *Acta Cryst.* **B40**, 319–327.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1991). **C47**, 2474–2476

## Redetermination of the Structure of Guanine Hydrochloride Monohydrate

BY J. MAIXNER

*Institute of Chemical Technology, Praha, Czechoslovakia*

AND J. ZACHOVÁ

*Institute of Physics, Charles University, Praha, Czechoslovakia*

(Received 30 July 1990; accepted 1 May 1991)

**Abstract.**  $C_5H_6N_5O^+ \cdot Cl^- \cdot H_2O$ ,  $M_r = 205.6$ , monoclinic,  $P2_1/c$ ,  $a = 4.479$  (1),  $b = 9.995$  (1),  $c = 19.304$  (2) Å,  $\beta = 107.90$  (1)°,  $V = 819.1$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.664$ ,  $D_x = 1.667$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 4.38$  cm<sup>-1</sup>,  $F(000) = 424$ ,  $T = 293$  (1) K,  $R = 0.034$ ,  $wR = 0.043$  for 1736 observed reflections with  $I > 1.96 \sigma(I)$ . The guanine molecule is non-planar with a dihedral angle of  $1.7$  (1.5)° between the imidazole and the pyrimidine rings. The base rings are protonated at N(7) and form a hydrogen network with two modes of pairing [N(7)—H7···O(1) and N(10)—H101···N(3)]. Several interactions of the type  $D—H \cdots A$  are noted between purine cations, water and chlorine anions.

**Experimental.** Crystals were grown by cooling a solution of the title compound in 18% hydrochloric acid in a special crystallizer with reversible stirring of the crystal seeds (starting temperature was about 308 K, cooling gradient 0.1 K per day). As grown the crystals are isometric, colourless and very often twinned, with maximal crystal dimensions of  $5 \times 5 \times 3$  mm. The density was determined by flotation in toluene–methylene iodide mixtures. A crystal of size  $0.2 \times 0.3 \times 0.45$  mm was selected and mounted on an Enraf–Nonius CAD-4 diffractometer. The unit-cell parameters were determined by a least-squares fit of the adjusted angular settings of 25 reflections with  $17 < \theta < 18^\circ$  constrained to a monoclinic cell. The space group was determined by systematic absences ( $0k0$

with  $k$  odd,  $h0l$  with  $l$  odd) in the diffractometer-collected intensity data. Intensities were collected with graphite-monochromated Mo  $K\alpha$  radiation. The  $\omega-2\theta$  technique was used with a scan width of  $(0.75 + 0.35 \tan \theta)^\circ$  extended 25% on each side for background measurement. The set of 2234 unique reflections, 1736 of which had  $I > 1.96 \sigma(I)$ , was obtained from 2810 reflections measured in the range  $1 < 2\theta < 60^\circ$  ( $0 < h < 8$ ,  $0 < k < 13$ ,  $-30 < l < 30$ ,  $\sin \theta / \lambda < 0.7027$  Å<sup>-1</sup>,  $R_{int} = 0.02$ ). The angular positions of three standard reflections (0,0,18, 0,10,0, 5,2,14) were checked after measuring 500 reflections, the intensity of reflection 121 was monitored after every 6000 s. The position of the crystal was stable and the monitored intensities showed a very slight decrease of about 0.2%. The intensity data were corrected for Lorentz and polarization but not for absorption effects.

The structure was solved from Patterson and  $\Delta\rho$  maps and refined on  $F$  by the full-matrix least-squares method with anisotropic thermal motion. All H-atom positions were found from  $\Delta\rho$  maps and included in the model. Final refinement was performed with 151 variables including all positional parameters, anisotropic displacement parameters for the non-H atoms, isotropic displacement parameters for the H atoms, one scale factor and the isotropic secondary-extinction coefficient of  $4.3 \times 10^{-7}$ . The final agreement factors were  $R = 0.034$ ,  $wR = 0.043$  and  $S = 1.42$ . The ratio of the maximum least-

squares shift to e.s.d. in the final refinement cycle was less than 0.07. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = [\sigma^2(F_o) + (0.015F_o)^2 + 2.5]^{-1}$ . The final  $\Delta\rho$  map was almost featureless with the highest peak at 0.36 (2) and the lowest peak at  $-0.29$  (2)  $e \text{ \AA}^{-3}$ . All calculations were carried out on a PDP11/73 microcomputer using the Enraf-Nonius *SDP* (Frenz, 1985) software. Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The fractional atomic coordinates and equivalent  $B$  values are listed in Table 1, the bond distances and angles are in Table 2.\*

**Related literature.** Protonation of guanine as well as the other nucleic acid bases has been the subject of both extensive theoretical and experimental studies, because it plays an important role in biological processes like mutation.

There are two guanine salts that crystallize from hydrochloric acid solutions: guanine hydrochloride monohydrate and guanine hydrochloride dihydrate. The structure determination of guanine hydrochloride dihydrate, which crystallizes more easily, was performed by Iball & Wilson (1963). The crystal structure of the monohydrate was determined by Broomhead (1951), using photographic recording techniques. Broomhead had no possibility of locating the position of the H atoms and therefore suggested four tautomers for the  $(\text{HG})^+$  cation. The unambiguous determination of the positions of the H atoms and the lengths of the bonds of the ring system has established that the true tautomer of guanine is protonated at N(7), as shown in the present work (Fig. 1). This result agrees with similar guanine compounds: guanine hydrochloride dihydrate (Iball & Wilson, 1963), 9-methylguanine hydrobromide (Sobell & Tomita, 1964), 9-ethylguanine hemihydrochloride (Mandel & Marsh, 1975) and guanosine hydrobromide hemihydrate (Tougaard & Chantot, 1974). The crystal packing is shown in Fig. 2.

The most favourable protonation site of the guanine molecule, at N(7), has been determined by Taylor & Kennard (1982) using structural data retrieved from the Cambridge Structural Database. They found significant changes in the geometry of the purine skeleton produced by the influence of protonation, especially changes in the angle C(5)—

Table 1. Fractional atomic coordinates for non-H atoms and their equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$B_{\text{eq}} = (4/3) \sum_i \beta_i \mathbf{a}_i \cdot \mathbf{a}_i$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Cl	0.0580 (1)	0.94680 (5)	0.77136 (2)	3.036 (8)
O(1)	0.1613 (3)	0.5549 (1)	0.92890 (7)	2.85 (3)
O(W)	0.5223 (3)	0.6333 (2)	0.79498 (7)	3.20 (3)
N(1)	0.4979 (3)	0.7249 (2)	0.92688 (7)	2.15 (3)
N(3)	0.7344 (3)	0.8727 (1)	1.02550 (7)	2.02 (2)
N(7)	0.2760 (3)	0.6443 (2)	1.08964 (7)	2.14 (2)
N(9)	0.5846 (3)	0.8135 (2)	1.13232 (7)	2.20 (3)
N(10)	0.8273 (4)	0.8947 (2)	0.91523 (8)	2.57 (3)
C(2)	0.6844 (3)	0.8316 (2)	0.95700 (8)	1.91 (9)
C(4)	0.5763 (3)	0.7982 (2)	1.06075 (8)	1.79 (3)
C(5)	0.3812 (4)	0.6917 (2)	1.03392 (8)	1.91 (3)
C(6)	0.3274 (4)	0.6476 (2)	0.96107 (8)	1.98 (3)
C(8)	0.4009 (4)	0.7184 (2)	1.14767 (9)	2.32 (3)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

N(1)—C(2)	1.365 (2)	C(4)—C(5)	1.370 (2)
N(1)—C(6)	1.386 (2)	C(5)—C(6)	1.422 (2)
N(3)—C(2)	1.336 (2)	N(7)—C(5)	1.382 (2)
N(3)—C(4)	1.345 (2)	N(7)—C(8)	1.314 (2)
C(6)—O(1)	1.227 (2)	N(9)—C(4)	1.379 (2)
N(10)—C(2)	1.331 (3)	N(9)—C(8)	1.346 (2)
C(2)—N(1)—C(6)	125.7 (2)	N(9)—C(4)—C(5)	106.3 (2)
C(2)—N(3)—C(4)	112.2 (1)	N(7)—C(5)—C(4)	107.5 (1)
C(5)—N(7)—C(8)	108.3 (1)	N(7)—C(5)—C(6)	132.0 (2)
C(4)—N(9)—C(8)	108.2 (1)	C(4)—C(5)—C(6)	120.4 (2)
N(1)—C(2)—N(3)	123.7 (2)	N(1)—C(6)—C(5)	110.4 (1)
N(1)—C(2)—N(10)	117.0 (1)	N(1)—C(6)—O(1)	120.9 (2)
N(3)—C(2)—N(10)	119.3 (2)	C(5)—C(6)—O(1)	128.6 (2)
N(3)—C(4)—N(9)	126.1 (1)	N(7)—C(8)—N(9)	109.6 (2)
N(3)—C(4)—C(5)	127.5 (2)		

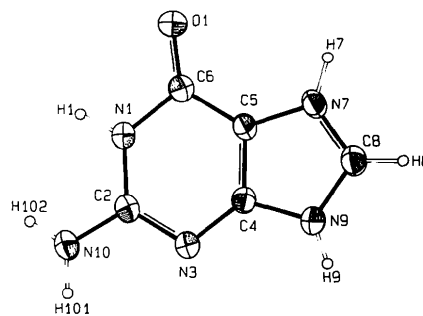


Fig. 1. A perspective view of the guanine ion (ORTEP; Johnson, 1976). Thermal ellipsoids are drawn at the 50% probability level.

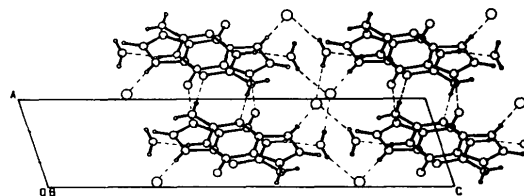


Fig. 2. Molecular packing viewed down  $b$ . Dashed lines indicate hydrogen bonding.

\* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, bond distances and angles involving H atoms, least-squares-planes details and hydrogen-bond contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54221 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N(7)—C(8). Its value is  $104.2(3)^\circ$  in the neutral guanine molecule and  $108.0(2)^\circ$  in the protonated molecule.

Del Bene (1983) optimized the geometry of both the neutral and the protonated guanine molecules and calculated the protonation energies for four different protonation sites. Del Bene came to the same conclusions as Taylor & Kennard (1982), *i.e.* the most favourable site is N(7) with C(5)—N(7)—C(18) angles of  $104.0$  and  $109.1^\circ$ , respectively.

All bond distances and angles presented in this work are in agreement with the above results, *i.e.* the value of the angle C(5)—N(7)—C(8) is  $108.3(1)^\circ$ .

*Acta Cryst.* (1991). **C47**, 2476–2478

## Structure of 3-Amino-5-nitro-1,2,4-triazole Hydrate\*

BY DON T. CROMER† AND CARLYLE B. STORM

*INC-4, MSC346, Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545, USA*

(Received 6 November 1990; accepted 25 March 1991)

**Abstract.**  $C_2H_3N_5O_2 \cdot H_2O$ ,  $M_r = 147.09$ , monoclinic,  $P2_1/c$ ,  $a = 11.129(3)$ ,  $b = 15.227(3)$ ,  $c = 7.130(2)$  Å,  $\beta = 101.29(2)^\circ$ ,  $V = 1184.88$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.649$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å,  $\mu = 1.4$  cm<sup>-1</sup>,  $F(000) = 608$ , room temperature, final  $R = 0.028$  for the 989 observed reflections with  $I > 3\sigma(I)$  from 1540 independent reflections. There are two formula units in the asymmetric unit. The geometries of the two molecules are very similar. Rings are planar within  $0.006$  Å. All H atoms take part in hydrogen bonds.

**Experimental.** Pale straw-colored crystals of the title compound were prepared according to Hartman & Silloway (1955) and grown from water. Selected crystal  $ca$   $0.20 \times 0.15 \times 0.10$  mm, CAD-4 diffractometer,  $\theta$ - $2\theta$  scan, scan range  $(1 + 0.34 \tan \theta)^\circ$ , scan speed  $1.6$  to  $5.5^\circ \text{ min}^{-1}$ , background first and last  $\frac{1}{6}$  of scan, graphite-monochromated Mo  $K\alpha$  radiation. Unit cell from 25 reflections with  $10 < \theta < 18^\circ$ . No absorption corrections.  $(\sin \theta)/\lambda_{\text{max}} = 0.540$  Å<sup>-1</sup>. Index range  $-12 \leq h \leq 12$ ,  $0 \leq k \leq 16$ ,  $-7 \leq l \leq 7$ , 3070 reflections measured and averaged to yield 1540 unique reflections of which 989 were observed with  $I > 3\sigma(I)$ ,  $R_{\text{int}} = 0.012$ . Standard reflections ( $\bar{1}18$  and  $40\bar{4}$ ) showed no significant variation. Least squares

## References

- BROOMHEAD, J. M. (1951). *Acta Cryst.* **4**, 92–99.  
 DEL BENE, J. E. (1983). *J. Phys. Chem.* **87**, 267–371.  
 FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.  
 IBALL, J. & WILSON, H. R. (1963). *Proc. R. Soc. London*, **288**, 418–429.  
 JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 MANDEL, G. S. & MARSH, R. E. (1975). *Acta Cryst.* **B31**, 2862–2867.  
 SOBELL, A. M. & TOMITA, K. (1964). *Acta Cryst.* **17**, 126–131.  
 TAYLOR, R. & KENNARD, O. (1982). *J. Mol. Struct.* **78**, 1–28.  
 TOUGARD, P. & CHANTOT, J. F. (1974). *Acta Cryst.* **B30**, 214–220.

minimized  $\sum w(\Delta F)^2$  with  $w = [\sigma_c^2(F) + 0.015F^2]^{-1}$ ,  $\sigma_c^2(F)$  based on counting statistics. Structure solved by *MULTAN* (Germain, Main & Woolfson, 1971). Scale factor, extinction parameter  $[2.9(3) \times 10^{-6} \text{ mm; Larson, 1969}]$ , positional parameters, anisotropic thermal parameters for C, N, O, and isotropic thermal parameters for H atoms were refined (222 parameters). Final  $R = 0.028$ ,  $wR = 0.030$ ,  $S = 2.0$ , max.  $\Delta/\sigma = 0.0004$ . Final  $\Delta F$  Fourier synthesis  $-0.17 < \Delta\rho < 0.13$  e Å<sup>-3</sup>. Scattering factors  $f$  (RHF for C, N, O and SDS for H),  $f'$ ,  $f''$  from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations on CDC-7600 using the Los Alamos Crystal Structure System developed primarily by A. C. Larson.

Fig. 1. is an *ORTEP* drawing (Johnson, 1965) to show the atom-numbering scheme of molecule (1). Final parameters are given in Table 1. ‡ Bond lengths and angles are given in Table 2. Nitro-group parameters are in the range of values found in other compounds. In molecule (1) the nitro group is twisted out of plane by  $4.3(1)^\circ$  and the amino group by  $2.1(8)^\circ$ . In molecule (2) these twists are  $2.2(1)$

‡ Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54111 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Work performed under the auspices of the US Department of Energy.

† Author to whom correspondence should be addressed.