

that molecules of pentabromobenzyl bromide enter the crystal lattice in an ordered manner due to their asymmetrical shape. If we ascribe the difference in  $\Delta S_f$  solely to entropy differences in the solid state, then for random disorder in (I) we expect an entropy difference of  $R \ln 6 = 3.54$  e.u. This stands in reasonable agreement with the 3.4 e.u. difference in the experimental  $\Delta S_f$  values, thereby supporting the deduction of random disorder in pentabromotoluene from the crystal-structure study.

G. C. W. wishes to express his appreciation for an NDEA title IV fellowship. Computer calculations were assisted by a National Science Foundation grant to the Triangle Universities Computation Center. We are indebted to Dr C. K. Johnson of the Oak Ridge National Laboratory for providing program *ORTEP* used to prepare Fig. 2, and especially to Dr F. R. Ahmed of the National Research Council of Canada for the computer programs used throughout the structure determination and refinement.

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## The Crystal Structure of Guanine Monohydrate

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(Received 21 December 1970)

The crystal structure of guanine monohydrate ( $C_5H_5N_5O \cdot H_2O$ ) has been determined from three-dimensional diffractometer and visual data and refined by full-matrix least-squares to an  $R$  index of 0.101 for 530 reflexions. The crystals are monoclinic, space group  $P2_1/n$ , with cell dimensions  $a = 16.510$  (8),  $b = 11.277$  (8),  $c = 3.645$  (5) Å,  $\beta = 96.8$  (1)° and  $Z = 4$ . The hydrogen bonding between bases is similar to that found in the crystal structures of guanosine and inosine. The molecules are stacked along  $c$  with an interplanar spacing of 3.30 Å. The crystal structure of guanine is almost identical to that of 8-azaguanine.

#### Introduction

The determination of the crystal structure of guanine was long a goal of this Laboratory. Guanine has properties, such as low solubility in most solvents, that are not characteristic of the other nucleic acid bases.

Of particular interest to us was the tautomeric form that guanine might choose – that is, which two of the four ring nitrogen atoms are protonated. It has been assumed that the favored positions for these two protons are at N(1) and N(9); however, other tautomeric forms can be represented by satisfactory valence-bond structures, and could lead to interesting hydrogen bonding and base pairing arrangements.

We have recently been successful in obtaining small crystals of guanine. Although the size of these crystals did not allow us to obtain highly accurate intensity data, we have been able to carry out a moderately

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† Contribution No 4178 from the A. A. Noyes Laboratories of Chemical Physics. This investigation was supported in part by Public Health Service Research Grant No. HE-02143, from the National Heart Institute.

accurate structure determination. A preliminary report of our results was published earlier (Bugg, Thewalt & Marsh, 1968); we report here the details.

### Experimental

After many attempts at crystallization, using various solvents and techniques, crystals in the form of very small needles, elongated along *c*, were obtained by evaporating a dimethylamine-water solution at room temperature. One crystal was considerably larger than the others – about 0.015 mm in diameter and about 0.3 mm in length. It was cut into two pieces, about 0.2 and 0.09 mm long; these two fragments were used in collecting all of our data.

Weissenberg and oscillation photographs showed Laue symmetry  $2/m$ ; the systematic absence of reflections  $0k0$  with *k* odd and  $h0l$  with  $h+l$  odd indicated the space group  $P2_1/n$ . Unit-cell dimensions were obtained by a least-squares fit to  $2\theta$  values measured on a diffractometer. Because of the small size of the remaining crystals, we were unable to measure the density. Crystal data are collected in Table 1.

Table 1. *Crystal data*

$C_5H_5N_5O \cdot H_2O$	F.W. 169.15
Monoclinic	Space group, $P2_1/n$
$a = 16.510$ (8) Å	$Z = 4$
$b = 11.277$ (8)	$F(000) = 352$ e
$c = 3.645$ (5)	$D_x = 1.67$
$\beta = 96.8$ (1)°	$D_m$ – not measured

One set of intensity data, from the smaller crystal fragment, was collected on a Datex-automated General Electric diffractometer, using nickel-filtered  $Cu K\alpha$  radiation, a scintillation counter, and a  $\theta$ - $2\theta$  scanning technique at a scan rate of  $\frac{1}{2}$  degree (in  $2\theta$ ) per minute; background was collected for 30 seconds at each end of the scan range. Data were collected out to  $2\theta = 90^\circ$ , the effective limit of measurable intensities. A total of 467 independent reflections were surveyed in this manner.

In order to increase the number of meaningful data, and in particular to obtain more accurate measurements for the large number of weak reflections, additional intensity data were collected photographically using the larger crystal fragment. Multiple-film Weissenberg photographs for levels  $l=0, 1,$  and  $2$  were prepared from the second crystal, again using  $Cu K\alpha$  radiation; the exposure times were approximately 150 hours for each layer. The intensities were estimated visually by comparison with a calibrated strip.

The intensity values measured on the diffractometer were assigned observational variances,  $\sigma^2(I)$ , according to the statistics of the scan and background counts plus an additional term  $(0.02S)^2$ ,  $S$  being the scan counts, that has seemed to be appropriate in this Laboratory. The intensities measured from films were assigned variances on the basis of the agreement between values measured on successive films (see Duchamp & Marsh, 1968). The diffractometer and film data were corrected for Lorentz and polarization factors, averaged together, and standard deviations  $\sigma(I)$  were calculated. Intensities too weak to be observed on the photographs were assigned threshold values and included in subsequent least-squares calculations only if the calculated value exceeded the threshold, except that all unobserved reflections with net scan counts less than one standard deviation above background were assigned zero weight regardless of  $F(\text{cal})$ . Finally the averaged intensities and their estimated standard deviations were placed on an approximately absolute scale by means of a Wilson (1942) plot.

A total of 924 reflections were surveyed; of these, 490 were either observed on photographs or had scan counts greater than one standard deviation above background. The relatively small number of measurable intensities is a reflection of the small size of the crystals.

### Determination and refinement of the structure

A satisfactory trial structure for guanine was quickly found by analogy with the structures of guanosine and inosine (Thewalt, Bugg & Marsh, 1970). For all three

Table 2. *Final heavy-atom parameters and their standard deviations*

The values have been multiplied by  $10^4$ .

The temperature factors are in the form  $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$

The final value for the extinction parameter  $g$  was  $0.5(0.4) \times 10^{-6}$

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
N(1)	2901 (4)	6502 (6)	3896 (23)	19 (3)	40 (7)	276 (111)	5 (8)	-60 (34)	-17 (54)
C(2)	3647 (5)	6773 (8)	5778 (30)	23 (4)	51 (11)	267 (151)	-8 (11)	-2 (47)	11 (71)
N(2)	3838 (4)	7923 (6)	5891 (27)	27 (4)	30 (7)	946 (126)	-8 (8)	-169 (38)	67 (56)
N(3)	4167 (4)	5989 (6)	7350 (24)	13 (3)	38 (7)	283 (107)	2 (8)	-89 (32)	70(59)
C(4)	3887 (5)	4858 (8)	6803 (30)	16 (4)	48 (9)	484 (151)	-6 (11)	-27 (45)	12 (77)
C(5)	3144 (5)	4494 (9)	4931 (32)	20 (4)	49 (9)	475 (161)	-8 (11)	-13 (51)	-55 (73)
C(6)	2595 (5)	5352 (9)	3327 (33)	22 (4)	59 (10)	483 (161)	16 (12)	-5 (47)	-38 (77)
O(6)	1912 (3)	5187 (5)	1593 (19)	15 (2)	75 (7)	368 (84)	1 (7)	-70 (26)	-70 (48)
N(7)	3093 (4)	3251 (6)	5023 (25)	25 (4)	44 (7)	250 (115)	-3 (9)	-26 (36)	8 (57)
C(8)	3783 (7)	2917 (8)	6938 (33)	30 (5)	59 (10)	413 (157)	12 (13)	-131 (50)	-111 (74)
N(9)	4284 (4)	3849 (6)	8053 (25)	17 (3)	48 (7)	431 (105)	-3 (9)	-98 (33)	1 (61)
O(10)	5341 (4)	9396 (7)	7668 (32)	39 (4)	202 (13)	3190 (180)	-18 (10)	197 (48)	168 (90)

compounds, the unit-cell dimension parallel to the  $2_1$  axis – the **b** direction – is nearly identical. A prominent feature of the structures of guanosine and inosine is the formation of hydrogen-bonded chains of purine rings running along this  $2_1$  axis; the same arrangement was presumed to exist in guanine. This presumption was corroborated by a strong similarity between a sharpened (001) Patterson projection of guanine and the  $w=0$  section of the sharpened three-dimensional Patterson map of guanosine. Trial  $x$  coordinates were immediately derived. Approximate  $y$  coordinates were obtained by evaluating the  $R$  index for the  $hk0$  reflections while systematically varying the positions of the molecules along **b**; there was a pronounced minimum at  $R=0.45$ . After some least-squares refinement based on the  $hk0$  data, the  $z$  coordinates were assigned so as to place the molecules parallel to and midway between the strongly diffracting ( $\bar{3}01$ ) planes. The water molecule was located in a subsequent difference map. The hydrogen atoms were positioned from geometric considerations.

Refinement was by full-matrix least-squares, carried out on an IBM 7094 computer under the CRYRM system (Duchamp, 1964). The quantity minimized was  $\sum w(F_o^2 - F_c^2)^2$ , with weight  $w$  equal to  $1/\sigma^2(F_o^2)$  and  $F_c^2$

as defined by Larson (1967), equation (3). Atomic scattering factors for the heavier atoms were obtained from *International Tables for X-ray Crystallography* (1962), and those for the hydrogen atoms were from Stewart, Davidson & Simpson (1965). The contributions of the hydrogen atoms were included in the  $F_c^2$ 's, but their parameters were not adjusted.

Table 3. Assumed hydrogen atom parameters

Atoms H(6), H(7), and H(8) are water hydrogen atoms, positions H(7) and H(8) being half populated.

	$x$	$y$	$z$	$B(\text{\AA}^2)$
H(1)	0.437	0.827	0.723	2.5
H(2)	0.350	0.861	0.480	2.5
H(3)	0.254	0.718	0.274	2.5
H(4)	0.393	0.205	0.746	2.5
H(5)	0.483	0.380	0.963	2.5
H(6)	0.590	0.945	0.804	2.5
H(7)	0.510	0.982	0.933	6.0
H(8)	0.510	0.982	0.576	6.0

The final  $R$  index for the 530 reflections with non-zero weight is 0.101. In the last cycle of refinement, no parameter shift exceeded one-fourth of its indicated standard deviation. The goodness of fit,  $[\sum w(F_o^2 -$

Table 4. Observed and calculated structure factors ( $\times 10$ )

Reflections indicated with an asterisk had net counts less than  $1\sigma$  above background, and were given zero weight; reflections indicated with a minus sign were too weak to be observed on the photographs, and were given zero weight whenever  $F_o$  was less than the threshold value of  $F_c$ . Due to an oversight, the contribution of half-weight hydrogen atom H(8) was not included in these  $F_o$  values.

$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$
0	0	0	100	100	0	0	0	100	100	0	0	0	100	100	0	0	0	100	100
1	0	0	100	100	1	0	0	100	100	1	0	0	100	100	1	0	0	100	100
2	0	0	100	100	2	0	0	100	100	2	0	0	100	100	2	0	0	100	100
3	0	0	100	100	3	0	0	100	100	3	0	0	100	100	3	0	0	100	100
4	0	0	100	100	4	0	0	100	100	4	0	0	100	100	4	0	0	100	100
5	0	0	100	100	5	0	0	100	100	5	0	0	100	100	5	0	0	100	100
6	0	0	100	100	6	0	0	100	100	6	0	0	100	100	6	0	0	100	100
7	0	0	100	100	7	0	0	100	100	7	0	0	100	100	7	0	0	100	100
8	0	0	100	100	8	0	0	100	100	8	0	0	100	100	8	0	0	100	100
9	0	0	100	100	9	0	0	100	100	9	0	0	100	100	9	0	0	100	100
10	0	0	100	100	10	0	0	100	100	10	0	0	100	100	10	0	0	100	100
11	0	0	100	100	11	0	0	100	100	11	0	0	100	100	11	0	0	100	100
12	0	0	100	100	12	0	0	100	100	12	0	0	100	100	12	0	0	100	100
13	0	0	100	100	13	0	0	100	100	13	0	0	100	100	13	0	0	100	100
14	0	0	100	100	14	0	0	100	100	14	0	0	100	100	14	0	0	100	100
15	0	0	100	100	15	0	0	100	100	15	0	0	100	100	15	0	0	100	100
16	0	0	100	100	16	0	0	100	100	16	0	0	100	100	16	0	0	100	100
17	0	0	100	100	17	0	0	100	100	17	0	0	100	100	17	0	0	100	100
18	0	0	100	100	18	0	0	100	100	18	0	0	100	100	18	0	0	100	100
19	0	0	100	100	19	0	0	100	100	19	0	0	100	100	19	0	0	100	100
20	0	0	100	100	20	0	0	100	100	20	0	0	100	100	20	0	0	100	100
21	0	0	100	100	21	0	0	100	100	21	0	0	100	100	21	0	0	100	100
22	0	0	100	100	22	0	0	100	100	22	0	0	100	100	22	0	0	100	100
23	0	0	100	100	23	0	0	100	100	23	0	0	100	100	23	0	0	100	100
24	0	0	100	100	24	0	0	100	100	24	0	0	100	100	24	0	0	100	100
25	0	0	100	100	25	0	0	100	100	25	0	0	100	100	25	0	0	100	100
26	0	0	100	100	26	0	0	100	100	26	0	0	100	100	26	0	0	100	100
27	0	0	100	100	27	0	0	100	100	27	0	0	100	100	27	0	0	100	100
28	0	0	100	100	28	0	0	100	100	28	0	0	100	100	28	0	0	100	100
29	0	0	100	100	29	0	0	100	100	29	0	0	100	100	29	0	0	100	100
30	0	0	100	100	30	0	0	100	100	30	0	0	100	100	30	0	0	100	100
31	0	0	100	100	31	0	0	100	100	31	0	0	100	100	31	0	0	100	100
32	0	0	100	100	32	0	0	100	100	32	0	0	100	100	32	0	0	100	100
33	0	0	100	100	33	0	0	100	100	33	0	0	100	100	33	0	0	100	100
34	0	0	100	100	34	0	0	100	100	34	0	0	100	100	34	0	0	100	100
35	0	0	100	100	35	0	0	100	100	35	0	0	100	100	35	0	0	100	100
36	0	0	100	100	36	0	0	100	100	36	0	0	100	100	36	0	0	100	100
37	0	0	100	100	37	0	0	100	100	37	0	0	100	100	37	0	0	100	100
38	0	0	100	100	38	0	0	100	100	38	0	0	100	100	38	0	0	100	100
39	0	0	100	100	39	0	0	100	100	39	0	0	100	100	39	0	0	100	100
40	0	0	100	100	40	0	0	100	100	40	0	0	100	100	40	0	0	100	100
41	0	0	100	100	41	0	0	100	100	41	0	0	100	100	41	0	0	100	100
42	0	0	100	100	42	0	0	100	100	42	0	0	100	100	42	0	0	100	100
43	0	0	100	100	43	0	0	100	100	43	0	0	100	100	43	0	0	100	100
44	0	0	100	100	44	0	0	100	100	44	0	0	100	100	44	0	0	100	100
45	0	0	100	100	45	0	0	100	100	45	0	0	100	100	45	0	0	100	100
46	0	0	100	100	46	0	0	100	100	46	0	0	100	100	46	0	0	100	100
47	0	0	100	100	47	0	0	100	100	47	0	0	100	100	47	0	0	100	100
48	0	0	100	100	48	0	0	100	100	48	0	0	100	100	48	0	0	100	100
49	0	0	100	100	49	0	0	100	100	49	0	0	100	100	49	0	0	100	100
50	0	0	100	100	50	0	0	100	100	50	0	0	100	100	50	0	0	100	100
51	0	0	100	100	51	0	0	100	100	51	0	0	100	100	51	0	0	100	100
52	0	0	100	100	52	0	0	100	100	52	0	0	100	100	52	0	0	100	100
53	0	0	100	100	53	0	0	100	100	53	0	0	100	100	53	0	0	100	100
54	0	0	100	100	54	0	0	100	100	54	0	0	100	100	54	0	0	100	100
55	0	0	100	100	55	0	0	100	100	55	0	0	100	100	55	0	0	100	100
56	0	0	100	100	56	0	0	100	100	56	0	0	100	100	56	0	0	100	100
57	0	0	100	100	57	0	0	100	100	57	0	0	100	100	57	0	0	100	100
58	0	0	100	100	58	0	0	100	100	58	0	0	100	100	58	0	0	100	100
59	0	0	100	100	59	0	0	100	100	59	0	0	100	100	59	0	0	100	100
60	0	0	100	100	60	0	0	100	100	60	0	0	100	100	60	0	0	100	100
61	0	0	100	100	61	0	0	100	100	61	0	0	100	100	61	0	0	100	100
62	0	0	100	100	62	0	0	100	100	62	0	0	100	100	62	0	0	100	100

$F_o^2/k^2(m-s)^{1/2}$ , is 1.6. The average estimated standard deviations in the positional coordinates of the heavy atoms are 0.007–0.012 Å, corresponding to e.s.d.'s of about 0.013 Å for bond lengths. At the conclusion of

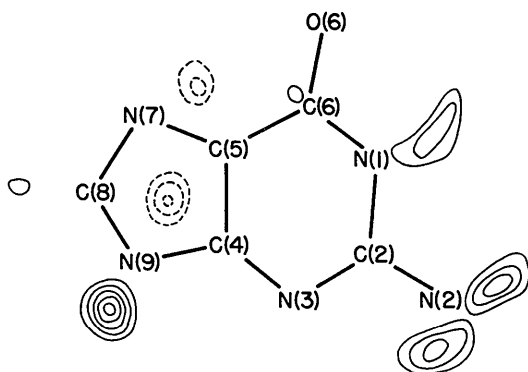


Fig. 1. A composite drawing of the final difference map in the least-squares plane of the molecule. The hydrogen atom contributions were omitted from the  $F_o$  values. The contours are at intervals of 0.1 e.Å<sup>-3</sup>, beginning with the 0.4 e.Å<sup>-3</sup> contour. The dashed lines represent regions of negative electron density.

the refinement, a three-dimensional electron density difference map was calculated; this map showed no peaks or troughs exceeding 0.50 e.Å<sup>-3</sup> in magnitude.

The heavy-atom parameters and their estimated standard deviations are listed in Table 2; the assumed hydrogen atom parameters are listed in Table 3. Observed and calculated structure factors are given in Table 4.

A difference map in the plane of the guanine molecule, for which the contributions of the hydrogen atoms were omitted from the  $F_o$ 's, is shown in Fig. 1. A similar three-dimensional map gave no indication as to the locations of the protons of the water molecule.

### The crystal packing and hydrogen bonding

Fig. 2 shows the structure projected on the (301) plane (approximately the plane of the guanine molecule); Fig. 3 shows the structure projected down the  $b$  axis. As anticipated, the hydrogen bonding along the two-fold screw axes is similar to that found in the crystal structures of guanosine and inosine (Thewalt, Bugg & Marsh, 1970). In addition, pairs of molecules are

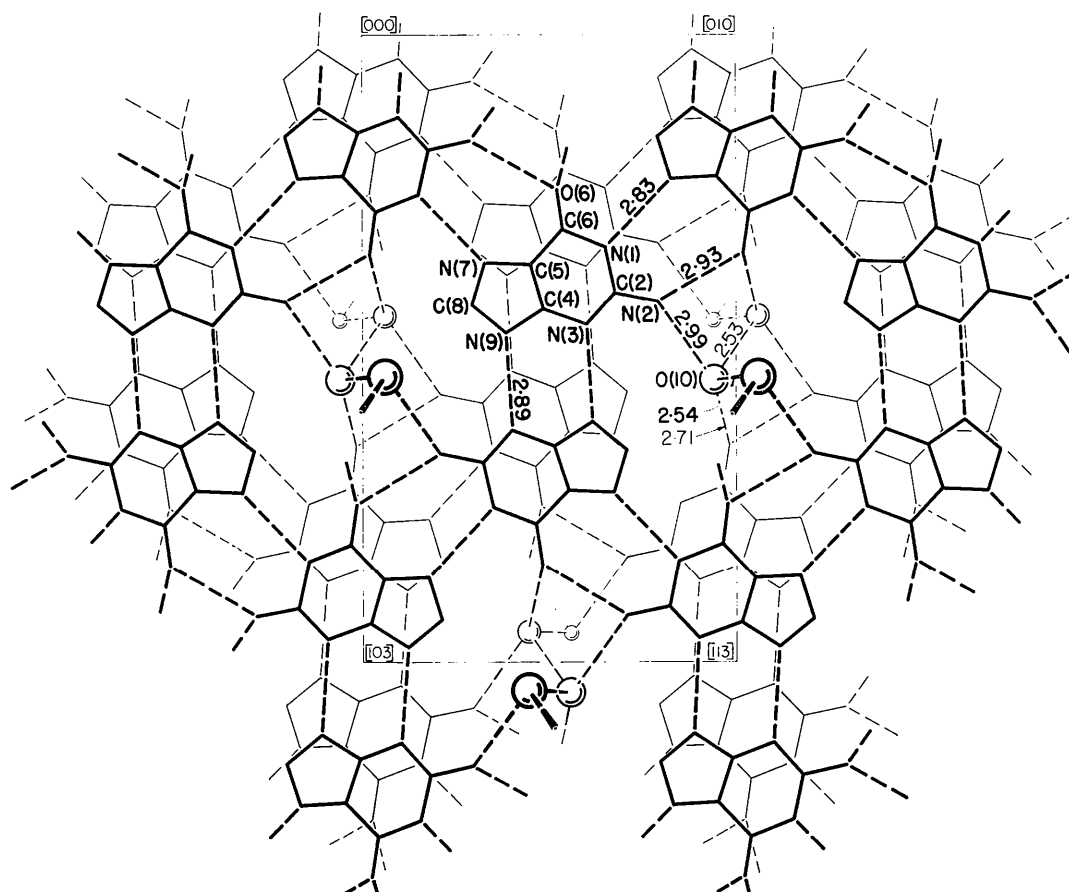


Fig. 2. The structure viewed perpendicular to the (301) crystallographic plane (approximately perpendicular to the plane of the guanine molecule). The dashed lines represent hydrogen bonds.

hydrogen bonded together, *via* N-H...N bonds, across centers of symmetry. The result is a sheet of molecules in a hexagonal, graphite-like array (Fig. 2). Columns of water molecules pass through the interstices of these hexagonal arrays, each water molecule forming an O-H...O hydrogen bond (2.71 Å) to an oxygen atom O(6) of a guanine molecule and accepting a hydrogen bond from an -NH<sub>2</sub> group (2.99 Å).

The columns of water molecules warrant special note. Within these columns, adjacent oxygen atoms are related to one another by two structurally distinct centers of symmetry; the formal O...O distances across these centers are 2.53 and 2.54 Å. Although we could not locate the hydrogen atoms on difference maps, it seems clear that these O...O interactions represent hydrogen bonds. It is tempting to infer that these are symmetric hydrogen bonds, with the hydrogen atoms lying on the centers of symmetry; the observed O...O distances are appreciably shorter than usual, and indeed approach the value of 2.4–2.5 Å expected for a symmetric hydrogen bond (see, for example, Pimentel & McClellan, 1960; Hamilton & Ibers, 1968). We suspect, however, that the hydrogen bonds are *not* symmetric. The oxygen atom of the water molecule has extremely large temperature factors, and the major axis of the thermal ellipsoid is oriented nearly parallel to *c*—the axis of the columns. Accordingly, we suspect that the occupancy factor of the water sites is something less than 1.0, and that these sites cover a fairly large range of *z* values. We envisage a situation completely analogous to that proposed for thymine monohydrate (Gerdil, 1961) and caffeine (Gerdil & Marsh, 1960), with the water molecules forming relatively short chains—perhaps 7 or 8 molecules per chain. Within each chain, the *z* parameter of the oxygen site varies continuously, so that the actual O...O distance is appreciably longer than 2.5 Å—presumably about 2.8 Å; at the ends of these chains the water molecules lose register with the guanine molecules to which they are hydrogen bonded, and the chain terminates with a vacant site. Thus, the coordinates we have assumed for the hydrogen atoms H(7) and H(8) (Table 3) represent a disordered arrangement rather than a symmetric hydrogen bond.

It is unfortunate that the crystals we obtained were too small to allow us either to collect more and better data, or to measure a reliable density. We predict that better data (preferably neutron diffraction data), if and when they are obtained, will indicate that the hydrogen atoms do not lie at the centers of symmetry and that the oxygen sites are not completely occupied; and that the density of the crystals corresponds to appreciably less than one molecule of water per asymmetric unit.

Surprisingly, the crystal structure of guanine monohydrate is essentially identical with that of 8-azaguanine monohydrate (Macintyre, Singh & Werkema, 1965; Sletten, Sletten & Jensen, 1968), in spite of the fact that 8-azaguanine has an additional hydrogen bond

acceptor [N(8)].\* The only major difference between the structures is in the position of the water molecule, which in 8-azaguanine donates a hydrogen bond to N(8) and shows a different type of disorder.

As can be seen from Fig. 3, parallel guanine mole-

\* Unfortunately, we did not notice the close similarity in cell dimensions until after we had completed the solution of the structure.

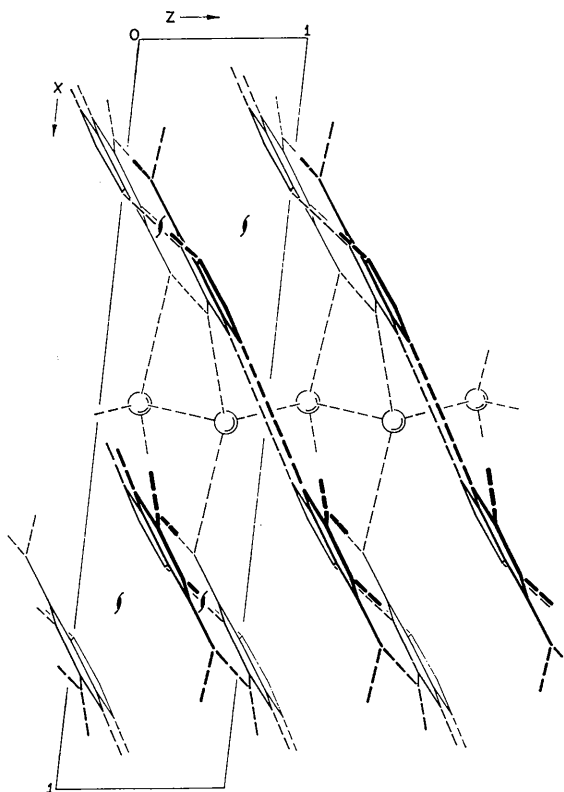


Fig. 3. The structure viewed down the *b* axis. The dashed lines represent hydrogen bonds.

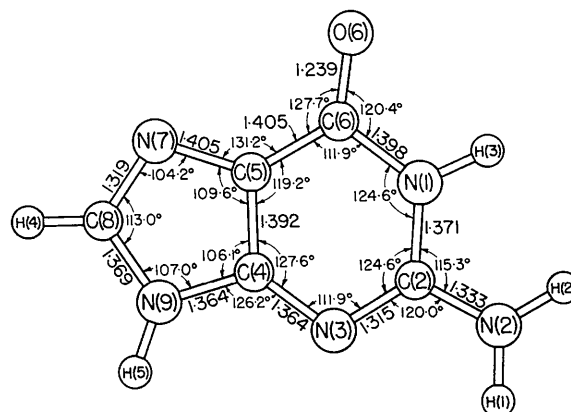


Fig. 4. Bond distances and angles. The estimated standard deviations are in the range 0.010–0.015 Å and 1–1.5°.

cles related by the  $c$  crystallographic translation form a stacked array; the interplanar spacing is 3.30 Å. As in the crystal structures of other nucleic acid constituents (Sundaralingam, Rao & Bugg, 1969; Bugg, Thomas, Sundaralingam & Rao, 1970), the stacking involves only partial overlap of bases and is adjusted so that polar regions of the base [in this case, the carbonyl group and the ring nitrogen atoms N(7) and N(3)] are in close contact with adjacent molecules. The interplanar spacing in crystals of 8-azaguanine is 3.25 Å; and whereas Macintyre *et al.* (1965) interpret this close packing as indicating charge-transfer interactions, Sletten *et al.* (1968) point out that it is not an unusually close spacing for nucleic acid bases.

### Molecular structure

The bond distances and angles are shown in Fig. 4; standard deviations in these distances are in the range 0.01–0.015 Å. Within these standard deviations, the values are in agreement with those found in guanosine (Thewalt, Bugg & Marsh, 1970). The distances and angles confirm the indications of the difference map (Fig. 1) that the only tautomer formed in the crystals is that shown in Fig. 4.

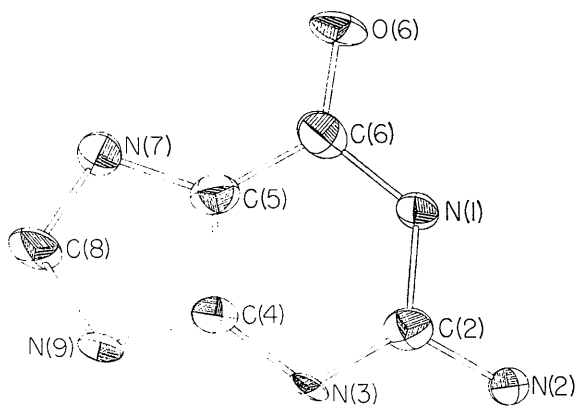


Fig. 5. The thermal ellipsoids.

The guanine molecule is essentially planar. The direction cosines of the least-squares plane, calculated with all atoms weighted equally, are (relative to  $a$ ,  $b$ , and  $c$ ) 0.5214,  $-0.0644$ , and  $-0.8508$ ; the origin-to-plane distance is 0.748 Å. The maximum deviations from this plane are 0.034 Å for N(2),  $-0.025$  Å for N(3), and 0.018 Å for N(7); no other atom deviates by more than 0.01 Å.

The ellipsoids of thermal motion for the atoms of the guanine molecule are shown in Fig. 5. Because of the small size of the crystal and the paucity of high-angle data, the uncertainties in the temperature parameters are relatively high. Nevertheless, the general pattern of thermal anisotropy appears to be reasonable for all atoms except N(3).

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