

## The Structures of Pyrimidines and Purines. II. A Determination of the Structure of Adenine Hydrochloride by X-ray Methods

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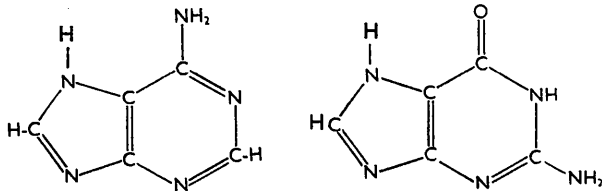
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An X-ray analysis employing two-dimensional Fourier methods has established the crystal structure of adenine hydrochloride. The purine molecule is planar, and the intramolecular bond distances are in general agreement with those found in the pyrimidine molecule. Hydrogen bonds linking a purine molecule to chlorine atoms and to water molecules, and short van der Waals contacts with other purine molecules, lie approximately in the plane of the molecule.

### Introduction

A determination of the crystal structures of the hydrogen chloride salts of two purines, adenine and guanine, was undertaken as a continuation of a programme of investigation of a group of comparatively simple compounds related to nucleic acid (Clews & Cochran, 1948). The formulae of adenine and guanine are written below



It is hoped, eventually, to provide information which may contribute to the understanding of the structures of this group of substances, of which pyrimidines and purines are important constituents. In this paper the structure of adenine hydrochloride is described, but discussion of the possible significance of certain features is deferred until an investigation of the closely related guanine salt has been completed.

Earlier crystallographic measurements on adenine hydrochloride were made by Bernal & Crowfoot (1934). They found the crystals to be monoclinic, with four molecules of adenine hydrochloride and two of water in a unit cell of dimensions  $a = 8.41$ ,  $b = 4.80$ ,  $c = 20.00$  Å.,  $\beta = 62^\circ$  and space group  $P2_1/c$  or  $Pc$ . The latter was included because, although no trace of pyroelectricity could be detected, some crystals were hemihedral. The optical properties of the crystals indicated that the molecules are probably arranged in layers with their lengths along the  $c$  axis and with their planes inclined at  $30$ – $40^\circ$  to the (100) planes, but no attempt was made to determine the positions of the atoms in the unit cell from X-ray intensities.

### Experimental

#### *Determination of cell and space group*

The material was kindly provided by Prof. Todd and Dr Kenner of the Cambridge University Chemical Laboratory, and tabular crystals elongated along the  $b$  axis were obtained by slow evaporation of an aqueous solution. Cell dimensions, determined by the ' $\theta$ -method' of Weisz, Cochran & Cole (1948), are  $a = 8.771 \pm 0.002$ ,  $b = 4.834 \pm 0.002$ ,  $c = 19.46 \pm 0.01$  Å.,  $\beta = 114^\circ 15' \pm 2'$ . (The wave-length of Cu  $K\alpha_1$  radiation has been taken as 1.5405 Å.) Reflexions of indices ( $h0l$ ) are absent when  $l$  is odd, and the space group is  $P2_1/c$  or  $Pc$ . Bernal & Crowfoot (1934) favoured  $P2_1/c$ , owing to the absence of pyroelectricity, and it was decided to proceed on the assumption that this was correct.

#### *Determination of $F(h0l)$ 's*

A tabular crystal elongated along the  $b$  axis with cross-section, perpendicular to the  $b$  axis, approximately 0.5 by 0.1 mm. was used to take a series of  $b$ -axis zero-layer-line Weissenberg photographs with filtered Cu  $K\alpha$  radiation. Exposure times varied between  $\frac{1}{2}$  and 25 hr. Intensities of reflexions were estimated visually, using an intensity scale, but agreement between intensities which should have been identical on space-group considerations was sometimes poor. It has been pointed out by Wells (1937) that for a crystal of this shape reflexions most affected by absorption lie on straight lines on the Weissenberg photograph. In this case the effect of the variation in shape of the reflected beam as recorded on the film must also be taken into account. Of two reflected beams of equal intensity, the one which traverses the crystal in its direction of maximum extension has a minimum breadth and gives rise to a sharp spot on the film, while one reflected at right angles to the above has maximum breadth and is recorded as a broad spot.

The intensity of the latter is consequently underestimated when the eye-estimation method is used. From Fig. 1 it is clear that the breadth of the reflected beam is a function of  $(2\theta - \psi)$ , where  $\psi$  is the angle which the  $a$  axis of the plate-shaped crystal makes with the primary beam. The absorption of the reflected beam is also a function of  $(2\theta - \psi)$ , while the extent to which the primary beam is absorbed depends only on  $\psi$ . We may therefore write, in an obvious notation,

$$I = I_1 f(2\theta - \psi) g(\psi).$$

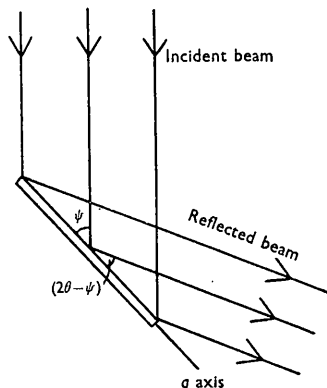


Fig. 1. Cross-section of the crystal in the incident X-ray beam. The width of the reflected beam is  $f(2\theta - \psi)$ .

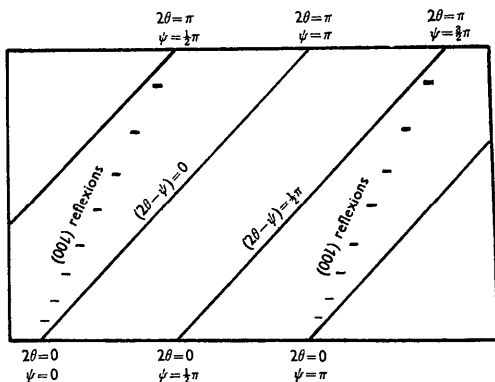


Fig. 2. Drawing of a Weissenberg film showing the position of the lines  $(2\theta - \psi) = 0$  and  $(2\theta - \psi) = \frac{1}{2}\pi$ .

It was found that to a sufficient approximation  $g(\psi)$  could be treated as constant, that is, the effect of 'spot shape' was the over-riding factor. Now in a rotation of the crystal through  $180^\circ$ , certain reflexions, which on symmetry considerations should be identical, occur with widely different values of  $(2\theta - \psi)$ . An empirical correction was therefore applied. The first step was to divide the reflexions into groups, all in one group having approximately the same value of  $(2\theta - \psi)$ . This may readily be done as the rectangular co-ordinates of a point on the Weissenberg film are proportional to  $2\theta$  and  $\psi$  respectively; reflexions having the same value of  $(2\theta - \psi)$  thus lie on a straight line drawn diagonally across the film. Fig. 2 shows how the

lines  $(2\theta - \psi) = 0$  and  $(2\theta - \psi) = \frac{1}{2}\pi$  were constructed. The region between these lines was further divided by drawing the lines  $(2\theta - \psi) = 15^\circ, 30^\circ, \dots, 75^\circ$ , and the interval into which each reflexion fell was listed along with the appropriate indices and intensity. The ratio  $f(2\theta - \psi)_1 / f(2\theta - \psi)_2$  was then found by comparison of identical reflexions in intervals 1 and 2, and the procedure was repeated for all the different intervals. Taking  $f(90^\circ) = 1$  it was found that  $f(2\theta - \psi)$  remained constant between  $(2\theta - \psi) = 90^\circ$  and  $60^\circ$ , after which it fell gradually to 0.74 at  $(2\theta - \psi) = 0$ . The validity of this procedure was confirmed by the good agreement between the intensities of individual reflexions after correction in this way. The intensities were then corrected for polarization and Lorentz factors, and a set of coefficients, proportional to  $F_{h0l}^2$ , was obtained.

In order to record reflexions of indices  $(0kl)$  a crystal similar in shape to that used above was cut so that the cross-section of the crystal perpendicular to the  $a$  axis was almost the same as that of the original crystal perpendicular to the  $b$  axis and the subsequent procedure was similar to that described above.

**Determination of the structure**

*b-axis projection*

Because of the shortness of the  $b$  axis it was decided to find first the  $x$  and  $z$  co-ordinates by means of a projection parallel to this axis. There are four molecules of the salt and two molecules of water in each unit cell and, since the space group  $P2/c$  has four general positions  $\pm(x, y, z), \pm(x, \bar{y}, \frac{1}{2} + z)$ , the water molecules must lie either on symmetry centres or on diad axes. The structure amplitude for reflexions of the type  $(h0l)$  is therefore

$$F(h0l) = 2f_O + 4f_{Cl}S_{Cl} + 4\sum_i f_i S_i,$$

where  $f_O, f_{Cl}, f_i$  are the scattering factors for oxygen, chlorine and the rest of the atoms (carbons and nitrogens), and  $S_{Cl}$  and  $S_i$  the structure factors for the chlorine and for the rest of the atoms respectively. Since the  $b$  axis is short, it seemed likely that all the atoms would be resolved in a projection of the electron density on  $(010)$ , and that in general  $(\frac{1}{2}f_O + f_{Cl}S_{Cl})$  would be greater than  $\sum_i f_i S_i$ . If, therefore, the position

of the relatively heavy chlorine atom could be fixed by Patterson methods, probable signs could be given to the observed  $F^2$ 's, and a Fourier synthesis, which might be expected to show the approximate positions of all the atoms, could be computed.

The Patterson function projected on  $(010)$  is of the form

$$P(x, z) = \sum_h \sum_l F_{h0l}^2 \cos 2\pi(hx + lz),$$

and a chlorine atom situated at  $(x, z)$  produces in the Patterson diagram vector peaks Cl-Cl whose co-ordinates for space group  $P2/c$  are  $(2x, 2z), (0, \frac{1}{2}), (1 - 2x, \frac{1}{2} - 2z)$  and whose magnitude should be large

compared with other interatomic vector peaks. An examination of the Patterson diagram (Fig. 3) showed that the peak of greatest magnitude occurred at (0.567, 0.050), expressed as fractions of the appropriate cell edges, and that another peak of about half the size occurred at (0.283, 0.025). It seemed probable that the former would be a Cl-Cl vector peak at  $(2x, 2z)$  and the latter a  $\text{H}_2\text{O}-\text{Cl}$  vector peak at  $(x, z)$ , the positions of both supporting the conclusion that the co-ordinates of the chlorine atom are (0.283, 0.025).

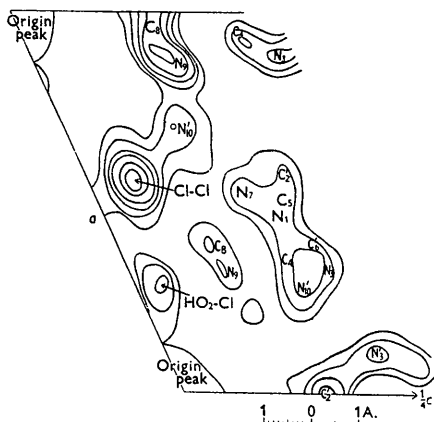


Fig. 3. Patterson projection on (010). Contours drawn at equal intervals on an arbitrary scale. The letters C and N indicate the positions of Cl-C and Cl-N vector peaks respectively.

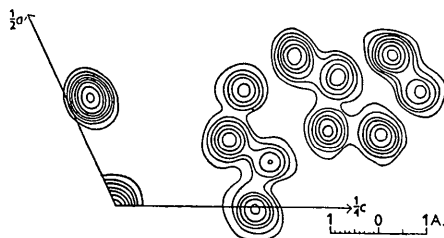


Fig. 4. Electron density projected on (010). Contours at an interval of two electrons per  $\text{Å}^2$ , except enclosing the chlorine atom where the interval is four electrons per  $\text{Å}^2$ . Atoms can be identified with the help of Fig. 8.

Having then determined the probable signs of the observed  $F$ 's, a two-dimensional Fourier synthesis

$$\rho(x, z) = \sum_h \sum_l F(h0l) \cos 2\pi(hx + lz)$$

was computed and the resulting electron-density map showed quite clearly the position of the purine molecule. The Patterson projection, studied initially in order to find the position of the chlorine atom, is also interesting when examined in conjunction with the electron-density map, as the Cl-N and Cl-C vector peaks can all be identified, as shown in Fig. 3.

The parameters of the atoms were refined by successive approximations and the fourth approximation is shown in Fig. 4. The value of the factor

$$\frac{\sum ||F_{\text{obs.}}| - |F_{\text{calc.}}||}{\sum |F_{\text{obs.}}|}$$

for this approximation is 0.23 but is reduced to 0.20

if the atomic parameters are corrected for Fourier-series termination in the manner suggested by Booth (1946). These  $x$  and  $z$  parameters were taken as the final ones. The  $z$  co-ordinates from the  $a$ -axis projection (discussed below) were considered to be less accurate than those from the  $b$ -axis projection for three reasons: the lack of resolution of some of the atoms, the lower accuracy of the intensity data, and the smaller number of terms inserted in the Fourier series.

#### *a*-axis projection

In this case a knowledge of the  $y$  and  $z$  co-ordinates of the chlorine atom might not be sufficient to determine the signs of the  $F(0kl)$ 's as there is bound to be lack of resolution in this projection and the scattering power of the chlorine atom is not great compared with the effective scattering power of two or more unresolved nitrogen atoms. Thus the condition

$$f_{\text{Cl}} S_{\text{Cl}} > \sum_i f_i S_i$$

might not hold in a sufficient number of cases for a reasonable first approximation to be obtained.

It was decided, therefore, to use Patterson methods to determine the  $y$  co-ordinate of the chlorine atom, and to fix the approximate co-ordinates of the carbon and nitrogen atoms from a model of the purine molecule, assumed planar and having similar bond lengths to those already found in the pyrimidine molecule (Clews & Cochran, 1948). Comparison of calculated and observed structure amplitudes would then indicate whether the chosen co-ordinates were approximately correct and successive Fourier syntheses would refine the parameters.

The Patterson function projected along the  $a$  axis was computed and examined for vector peaks of the type Cl-Cl occurring in positions  $(2y, 2z)$ ,  $(0, \frac{1}{2}-2z)$ ,  $(1-2y, \frac{1}{2})$ . Of these the  $(2y, 2z)$  peak should be the most helpful as the  $z$  co-ordinate of the chlorine atom is already known. An examination of the line  $2z_{\text{Cl}} = \text{constant}$  showed that a small peak occurred at  $y=0.350$  and a larger one at  $y=0$ . The latter may be due to interatomic vector peaks of the type  $(0, \frac{1}{2}-2z)$ , and all that could be deduced was that the  $y$  co-ordinate of the chlorine atom might be 0 or  $\pm 0.175$ .

The relative  $y$  co-ordinates of the carbon and nitrogen atoms were determined by constructing a model of the purine molecule and tilting it until the projected image on the (010) plane resembled as closely as possible the map of electron density on (010). Absolute values of  $y$  were obtained since the position of  $\text{N}_3$  could be fixed by the following reasoning. The nature of the symmetry element at the origin of the Fourier plot shown in Fig. 4 has not been discussed. If it is a centre of symmetry, then the nitrogen atoms  $\text{N}_3$  and  $\text{N}_3'$  are linked by a diad axis and their separation in space will be that shown in the projection, namely 2.1 Å. Now the closest distance of approach between ring nitrogen atoms of neighbouring molecules must

be expected to be at least 3.0 Å., and this can be attained only if the symmetry element is a centre and the nitrogen atoms are separated in the  $b$ -axis direction by the maximum distance possible. The fractional co-ordinates of  $N_3$  and  $N'_3$  must therefore be 0.25 and -0.25 respectively.

Structure amplitude calculations were then made for models with the  $y$  co-ordinates of the carbon and nitrogen atoms fixed as explained above, and the  $y$  co-ordinate of the chlorine atom taken as 0, 0.175, -0.175, in turn. Poor agreement between observed

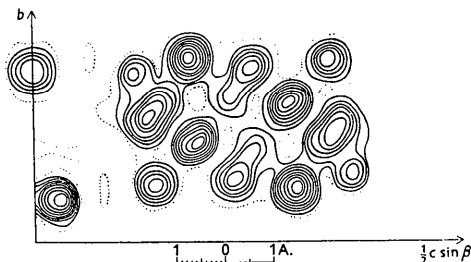


Fig. 5. Electron density projected along the  $a$  axis. Contours at an interval of two electrons per Å.<sup>2</sup>, except enclosing the chlorine atom, where the interval is four electrons per Å.<sup>2</sup> Atoms can be identified with the help of Fig. 6.

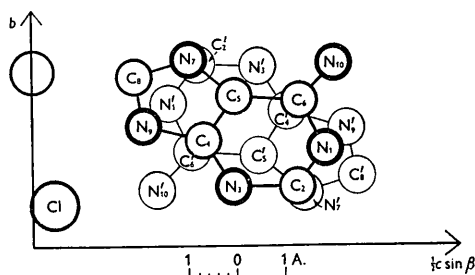


Fig. 6. Structure projected along the  $a$  axis.

and calculated  $F$ 's was obtained with  $y_{Cl}=0$  and  $y_{Cl}=-0.175$ , but fairly good agreement with  $y_{Cl}=0.175$ . A Fourier synthesis was then computed using  $F$ 's with signs calculated on the assumption  $y_{Cl}=0.175$ , and parameters were refined in the usual manner. The fourth approximation is shown in Fig. 5 and it will be seen that in the purine molecule itself four of the nine atoms are well resolved (see Fig. 6). Calculations using the  $x$  and  $z$  co-ordinates of all the atoms and the  $y$  co-ordinates of atoms resolved in the  $a$ -axis projection showed that the molecule is planar to within the limits of experimental error and the  $y$  co-ordinates of the unresolved atoms were calculated on this assumption.

The final value of  $\Sigma ||F_{obs.}|-|F_{calc.}|| \div \Sigma |F_{obs.}|$  for reflexions  $(0kl)$ , calculated from the observed  $z$  co-ordinates and the calculated  $y$  co-ordinates, was 0.24. The atomic co-ordinates are given in Table 1 and the observed and calculated values of the  $F(h0l)$ 's and  $F(0kl)$ 's in Table 2.

Table 1. Atomic co-ordinates expressed as fractions of the corresponding unit-cell dimension

$$a=8.771, b=4.834, c=19.46 \text{ \AA.}, \beta=114^\circ 15'$$

Atom	$x$	$y$	$z$
H <sub>2</sub> O	0	0.745	0
Cl	0.2817	0.178	0.0257
N <sub>1</sub>	0.8200	0.407	0.3450
N <sub>3</sub>	0.6033	0.246	0.2358
N <sub>7</sub>	0.8033	0.788	0.1833
N <sub>9</sub>	0.5967	0.504	0.1300
N <sub>10</sub>	0.0092	0.767	0.3550
C <sub>2</sub>	0.6929	0.237	0.3105
C <sub>4</sub>	0.6550	0.443	0.2000
C <sub>5</sub>	0.7933	0.630	0.2368
C <sub>6</sub>	0.8783	0.605	0.3142
C <sub>8</sub>	0.6883	0.716	0.1200

### Description of the structure

Bond distances within the molecule and interbond angles are given in Fig. 7.

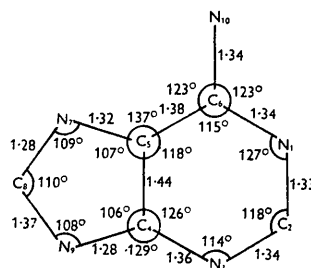


Fig. 7. Bond lengths and bond angles.

The experimental error in any one bond distance may be as great as 0.05 Å., and it is thus impossible to say whether there are any significant differences in the C-N bond distances. They may, however, be compared with the values of  $1.32 \pm 0.02$  Å. found by Clews & Cochran (1948) in the compounds 2-amino-4,6-dichloropyrimidine, 2-amino-4-methyl-6-chloropyrimidine and 4-amino-2,6-dichloropyrimidine. The C<sub>5</sub>-C<sub>6</sub> bond length is in agreement with the C-C bond lengths found in the pyrimidine ring, but the C<sub>4</sub>-C<sub>5</sub> distance seems significantly longer. This difference may be due to experimental error, although it is believed to be outside the probable limits of error. Comparison of this distance with the corresponding distance in the guanine molecule should be interesting.

The arrangement of the molecules in the structure is illustrated in Fig. 8. The molecule  $A$  is tilted out of the (010) plane so that the line joining C<sub>6</sub> and N<sub>3</sub> and the line joining C<sub>8</sub> and N<sub>1</sub> make angles of about 37 and 19° respectively with this plane. The perpendicular distance between the planes of corresponding purine molecules in adjacent unit cells is about 3.2 Å. Apart from the hydrogen bonds and short van der Waals contacts discussed below, all intermolecular bond distances exceed 3.6 Å.

There is a zig-zag stacking of N<sub>3</sub> atoms parallel to the  $y$  axis, for N<sub>3</sub> is at a distance of 3.22 Å. from N<sub>3</sub>' and of 3.18 Å. from N<sub>3</sub>' in an adjacent unit cell. These are probably short van der Waals contacts similar to

Table 2. Comparison of observed and calculated structure amplitudes

<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>
002	10	14	3̄.0.10	8	9	704	0	3	016	3	1
004	6	4	3̄.0.12	9	-9	706	11	-9	017	3	-2
006	19	-20	3̄.0.14	2	4	708	7	4	018	3	-1
008	11	8	3̄.0.16	6	-6				019	0	1
0.0.10	2	1	3̄.0.18	7	7	7̄02	8	-10	0.1.10	0	-1
0.0.12	3	-3	3̄.0.20	0	0	7̄04	0	2	0.1.11	9	8
0.0.14	5	5	3̄.0.22	6	2	706	5	-6	0.1.12	3	1
0.0.16	0	2	3̄.0.24	4	4	708	6	6	0.1.13	0	0
0.0.18	13	11				7̄.0.10	0	0			
0.0.20	9	-5	400	3	4	7̄.0.12	9	-10	0.1.14	4	3
0.0.22	4	3	402	10	-10	7̄.0.14	3	-2	0.1.15	8	6
			404	6	5	7̄.0.16	3	-5	0.1.16	5	-5
100	2	0	406	5	6	7̄.0.18	8	8	0.1.17	12	-11
102	4	-3	408	2	1	7̄.0.20	5	-7	0.1.18	0	1
104	11	-11	4.0.10	7	6	7̄.0.22	0	2	0.1.19	7	6
106	4	0	4.0.12	8	-6	7̄.0.24	6	-5	0.1.20	4	-4
108	19	-18	4.0.14	6	4				0.1.21	2	-5
1.0.10	3	2	4.0.16	8	-6				0.1.22	2	2
1.0.12	4	11				800	3	-2			
1.0.14	7	5	4̄02	15	-16	802	0	0	020	17	-18
1.0.16	11	-7	4̄04	6	7	804	0	0	021	10	10
1.0.18	6	-6	4̄06	18	-21	806	10	10	022	3	3
1.0.20	5	3	4̄08	8	8	808	4	-4	023	9	-8
			4.0.10	4	-4	8̄02	4	-5	024	10	-10
1̄02	0	0	4.0.12	9	11	8̄04	4	5	025	2	0
1̄04	5	6	4.0.14	6	-5	8̄06	8	-11	026	6	6
1̄06	18	-21	4.0.16	8	-8	8̄08	6	8	027	9	-9
1̄08	16	15	4.0.18	8	-7	8̄.0.10	3	-3	028	4	-4
1̄.0.10	2	-1	4.0.20	11	-11	8̄.0.12	7	11	029	3	3
1̄.0.12	18	16	4.0.22	2	3	8̄.0.14	7	-10	0.2.10	0	1
1̄.0.14	14	-12	4.0.24	4	-4	8̄.0.16	3	4	0.2.11	8	8
1̄.0.16	10	7				8̄.0.18	0	1	0.2.12	3	-2
1̄.0.18	4	2	500	3	4	8̄.0.20	3	3	0.2.13	4	4
1̄.0.20	10	7	502	9	10	8̄.0.22	4	-3	0.2.14	4	-6
1̄.0.22	7	-2	504	8	-8				0.2.15	9	6
			506	9	8	900	3	-4	0.2.16	0	0
200	18	-20	508	4	4	902	9	7	0.2.17	5	-5
202	11	11	5.0.10	13	13	904	3	-4	0.2.18	4	-4
204	5	-2	5.0.12	0	1				0.2.19	4	3
206	4	-2	5.0.14	8	-6	9̄02	5	6	0.2.20	4	4
208	8	8				9̄04	3	-5	0.2.21	7	-6
2.0.10	6	3	5̄02	10	12	9̄06	3	4			
2.0.12	11	8	5̄04	0	-1	9̄08	6	-8	030	12	-11
2.0.14	14	-15	5̄06	4	-5	9̄.0.10	6	-5	031	0	0
2.0.16	6	4	5̄08	8	9	9̄.0.12	0	0	032	7	7
2.0.18	10	-6	5̄.0.10	5	3	9̄.0.14	0	-2	033	0	2
2.0.20	9	7	5̄.0.12	11	15	9̄.0.16	0	3	034	4	-3
			5̄.0.14	7	-10	9̄.0.18	8	-12	035	6	5
2̄02	11	-12	5̄.0.16	6	7	9̄.0.20	3	7	036	8	8
2̄04	18	-18	5̄.0.18	7	-7				037	5	5
2̄06	14	15	5̄.0.20	8	9	10.0.0	10	12	038	0	-1
2̄08	0	2	5̄.0.22	7	-6				039	0	0
2̄.0.10	2	-2				10̄.0.2	5	5	0.3.10	0	1
2̄.0.12	4	-3	600	5	4	10̄.0.4	0	-1	0.3.11	9	-11
2̄.0.14	7	-7	602	3	-4	10̄.0.6	0	0	0.3.12	4	5
2̄.0.16	4	3	604	7	-7	10̄.0.8	0	0	0.3.13	11	-11
2̄.0.18	8	-7	606	13	-16	10̄.0.10	8	12	0.3.14	0	-2
2̄.0.20	10	9	608	0	1	10̄.0.12	0	-2	0.3.15	7	-7
2̄.0.22	9	-9	6.0.10	9	-7	10̄.0.14	7	7	0.3.16	3	5
2̄.0.24	5	4	6.0.12	10	9	10̄.0.16	0	-3	0.3.17	4	5
						10̄.0.18	0	2	0.3.18	9	-8
300	14	12	6̄02	10	12	10̄.0.20	0	-5	0.3.19	0	0
302	14	-15	6̄04	0	-2				0.3.20	4	7
304	9	9	6̄06	6	7						
306	7	-7	6̄08	8	-9	11.0.6	8	-13	040	4	6
308	13	-14	6̄.0.10	4	4	11.0.8	0	3	041	5	-8
3.0.10	15	-14	6̄.0.12	6	-7	11.0.10	0	2	042	4	2
3.0.12	4	-4	6̄.0.14	0	0	11.0.12	8	11	043	6	7
3.0.14	9	-6	6̄.0.16	0	0	11.0.14	0	1	044	4	4
3.0.16	7	5	6̄.0.18	8	6				045	4	-5
3.0.18	4	4	6̄.0.20	17	18	010	14	-14	046	0	-2
			6̄.0.22	5	3	011	6	6	047	4	2
3̄02	4	4	6̄.0.24	4	4	012	15	-14	048	4	3
3̄04	2	-1				013	13	-13	049	4	-5
3̄06	2	-1	700	8	10	014	11	9	0.4.10	0	-1
3̄08	0	0	702	10	-11	015	5	4	0.4.11	0	-2

Table 2 (cont.).

<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>hkl</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>
0.4.12	0	- 3	050	8	9	057	4	5	060	3	- 2
0.4.13	3	5	051	4	- 6	058	3	- 4	061	6	4
0.4.14	3	- 2	052	0	- 1	059	0	1	062	1	- 9
0.4.15	0	- 2	053	4	6	0.5.10	0	- 2	063	1	- 3
0.4.16	6	6	054	5	6	0.5.11	3	5	064	1	3
0.4.17	5	6	055	0	- 3	0.5.12	3	2	065	0	- 2
			056	5	- 7	0.5.13	5	6	066	0	1

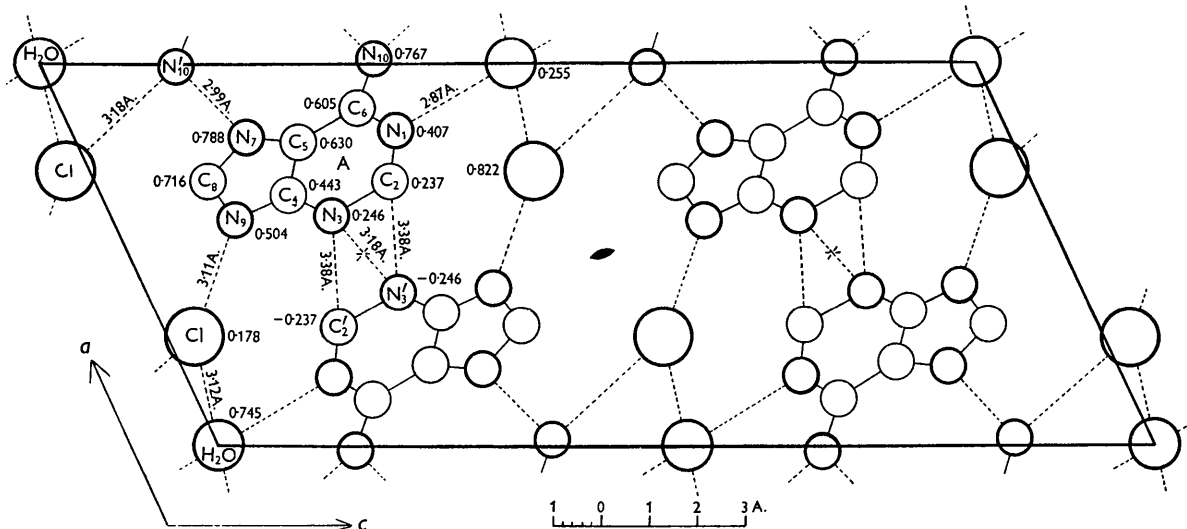


Fig. 8. Structure projected on (010). *y* co-ordinates indicated. Hydrogen bonds and short van der Waals contacts are shown dotted.

those found by Hughes (1941) in the structure of melamine. Another short van der Waals contact of length 3.38 Å. exists between the atoms  $N_3$  and  $C'_2$ .  $N_1$  is linked to a water molecule by a hydrogen bond of length 2.87 Å. and this distance is consistent with those reported by Pitt (1948) in the structure of 2-hydroxy-4,6-dimethyl-pyrimidine.  $N_9$  is separated from the chlorine atom by a distance of 3.11 Å. and  $N_7$  from  $N_{10}$  of a neighbouring molecule by a distance of 2.99 Å.; these bonds are almost coplanar with the molecule.  $N_{10}$  is also linked to a chlorine atom by a bond of length 3.18 Å.  $N_{10}$  has, therefore, two external contacts of about 3 Å. and a longer van der Waals contact of length 3.38 Å. to  $N_7$  in an adjacent unit cell.

Two of the contacts of a chlorine atom are mentioned above; there is a third of length 3.12 Å. to a water molecule and these three lie approximately in a plane. The N-Cl distances may be compared with the distances of 3.17 and 3.24 Å. for N-Cl bonds in the geranylamine hydrochloride structure investigated by Jeffrey (1945) and the Cl-O distance with those of length 2.99 and 3.05 Å. found by Jerslev (1948) in the structure of hydroxylammonium chloride.

The water molecule is bonded to two nitrogen atoms and to two chlorine atoms which form a distorted tetrahedron about it.

It is clear that, as in the structures of amino pyrimidines, hydrogen bonds involving probably all the nitrogen atoms as well as the chlorine atom and the water molecule are the main feature of the structure,

providing the major part of the forces holding the molecules together as well as determining which of the possible molecular structures actually exists in the solid state. Unfortunately the results reported above are not sufficiently accurate for reliable conclusions to be drawn about the hydrogen positions. Possible further refinement of the structure and a full discussion of the chemical significance of its principal features are postponed pending the completion of the investigation of guanine to which reference has already been made.

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