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The Crystal and Molecular Structure of 4,5-Diamino-2-Chloropyrimidine

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The crystal and molecular structure of 4,5-diamino-2-chloropyrimidine has been determined by two-dimensional Fourier methods. The monoclinic unit cell has dimensions $a = 3{\cdot}73$, $b = 12{\cdot}637$, $c = 12{\cdot}437$ Å, $\beta = 98°\ 6'$, and the space group is $P2_1/c$. The crystal structure has been solved by the 'heavy atom' technique, the position of the chlorine atom being found from a 'modified' Patterson projection. A difference synthesis projected on the (100) plane clearly indicates the positions of the hydrogen atoms, showing that the molecule is in the amino form and that the molecules are held together by a system of hydrogen atoms between the nitrogen atoms of the amino groups and the ring nitrogens of neighbouring atoms.

1. Introduction

Certain of the pyrimidines—cytosine, thymine, uracil—, together with purines and sugars, constitute building units of the nucleic acids and nucleoproteins. Hence a detailed knowledge of their molecular structure and bonding in the crystalline state is of great interest and importance, and some years ago one of us initiated a programme of research into the crystal structures of pyrimidines and purines (Clews & Cochran, 1948, 1949; Broomhead, 1948, 1951; Cochran, 1951) in connexion with the chemical investigations of Todd and his co-workers on the nucleic acids which he has summarized in a recent lecture (Todd, 1955). The 4,5-diamino pyrimidines are intermediates in the synthesis of another important group of biological substances, the pteridines; thus 4,5-diamino-2-chloropyrimidine condenses with polyglyoxal to form 2-chloropteridine (Albert, Brown & Cheeseman, 1951). This pyrimidine also presented an opportunity of obtaining further data on the formation of hydrogen bonds of the type N–H · · · N, which have been discussed in an earlier paper (Clews & Cochran, 1949).

2. Experimental

A sample of 4,5-diamino-2-chloropyrimidine, kindly provided by Prof. A. Albert of the Department of Medical Chemistry of the Australian National University, was crystallized from water in the form of fine needles. As attempts to grow larger crystals were unsuccessful, all photographs were taken using one crystal with an approximately uniform cross-sectional diameter of 0·1 mm. and extension in the direction of the a axis of 1 mm. Owing to the crystal dimensions it was convenient to orient it for rotation about the a axis only. Oscillation and Weissenberg photographs established the space group unequivocally as $P2_1/c$ with 4 molecules in the unit cell. The cell side a was measured from layer-line separations on oscillation photographs, β from Weissenberg photographs, and b and c by the θ-method (Weisz, Cochran & Cole, 1948):

$$a=3{\cdot}73\pm0{\cdot}01,\quad b=12{\cdot}637\pm0{\cdot}005,\quad c=12{\cdot}437\pm0{\cdot}005\ \text{Å},$$
$$\beta = 98^\circ\ 6'\pm5' \quad (\lambda\ (\text{Cu}\ K\alpha) = 1{\cdot}5418\ \text{Å})\ .$$

The $0kl$ and $1kl$ intensity data were estimated visually from multiple-film Weissenberg photographs, and the two sets of data wêre placed approximately on the same relative scale on the basis of a series of oscillation photographs. Using Cu $K\alpha$ radiation, 161 of the possible 201 non-equivalent $(0kl)$ reflexions were recorded and 307 of the possible 390 $(1kl)$ reflexions. The intensities were corrected for Lorentz and polarization factors, but no correction was applied for absorption as this was negligible. The observed structure amplitudes were set on to an absolute scale at a later stage by comparison with the calculated values. Temperature and scaling factors were determined by plotting $\log (\Sigma|F_c|\div\Sigma|F_o|)$ against $\sin^2\theta$, the summations being taken over increments of 0·1 in $\sin^2\theta$.

3. Determination of structure

3·1. *Determination of the y, z parameters*

Since $Z^2_{\text{Cl}}/\Sigma Z^2_L = 0{\cdot}84$, where Z_{Cl} is the atomic number of chlorine and Z_L that of a light atom, it seemed probable that the 'heavy atom' method of phase determination would prove successful, and the Patterson projection on (100) was computed, using relative values of $F(0kl)^2$. From this the y and z parameters of the chlorine atom were deduced, but the y co-ordinate was found to be nearly zero so that the chlorine contribution is small for reflexions with $k+l = 2n+1$. Thus, in order to determine the signs of most $(0kl)$ structure amplitudes it was necessary to deduce an approximate structure.

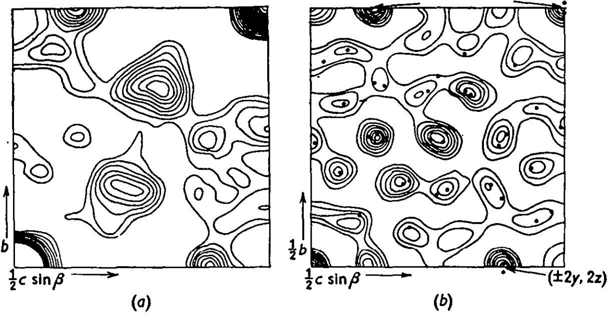


Fig. 1. (*a*) Patterson projection on (100). Contours drawn at equal intervals on an arbitrary scale.

(*b*) Modified Patterson projection on (100) from which terms having $\sin\theta < 0{\cdot}5$ are omitted. The calculated chlorine–light-atom vectors are indicated by dots.

In addition to the Cl–Cl interactions, the Patterson projection (Fig. 1(*a*)) shows a number of large unresolved peaks resulting from Cl–light-atom interactions together with a background due to light-atom–light-atom vectors. Dr A. McL. Mathieson of the Division of Industrial Chemistry, C.S.I.R.O., Melbourne, pointed out to us that, while the ratio of the atomic scattering factor of chlorine to that of carbon is equal to the ratio of their atomic numbers at $\sin\theta = 0$, it increases to about $\frac{3}{2}$ of that value at larger values of $\sin\theta$. Thus it seemed likely that if terms with $\sin\theta < 0{\cdot}5$ were omitted the Cl–Cl and Cl–light-atom peaks in the resulting Patterson projection would be enhanced.

This procedure proved highly successful and led to a complete trial structure. The modified Patterson is shown in Fig. 1(*b*) and on it the calculated chlorine–light-atom vector set is marked. It has since been found that this method of accentuating heavy-atom–heavy-atom and heavy-atom–light-atom vectors has serious limitations as the omission of low-angle terms introduces a large diffraction ripple (Mathieson, private communication). That it was successful in the present case was probably largely fortuitous, owing to the favourable spacing of the atomic peaks in the particular projection.

The $(0kl)$ structure factors were calculated on the basis of the set of atomic y and z co-ordinates deduced from the Patterson projections, using atomic scattering factors for nitrogen and carbon listed by McWeeny (1951), while for chlorine an unpublished atomic scattering factor curve due to Dr B. Dawson of C.S.I.R.O., Melbourne, was used. The percentage discrepancy, $(100\Sigma|F_o-F_c|\div\Sigma F_o)$, between observed and calculated structure amplitudes was 25·7, and after two successive Fourier refinements this was reduced to 11·7. The electron-density maxima in the Fourier projections were located by the 'semi-analytical' method of Burns & Iball (1955). The final electron-density projection on (100), after further refinement discussed in § 3·3 below, is shown in Fig. 2. It will be noted that the molecule is well resolved and that the peak heights for carbon and nitrogen atoms are significantly different.

3·2. *Determination of x parameters*

As the (010) and (001) projections would be poorly resolved, and further the needle-shaped crystals were unsuitable for collecting reliable $(h0l)$ and $(hk0)$ intensity data, it was most convenient to deduce the x co-ordinates from the $(1kl)$ generalized projection. Since the x parameter of even the Cl atom was unknown, and in any case the Cl contribution to at least half the $(1kl)$ reflections would be small, it was necessary first to obtain approximate x co-ordinates from the first-layer Patterson synthesis (Zussman, 1953;

Dyer, 1951). In the present case the procedure was modified in that two component maps of the first-layer Patterson were computed, i.e.

$$ {}_CP_1 = \frac{1}{A}\sum_k\sum_l |F(1kl)|^2 \cos 2\pi(kv+lw) $$

and

$$ {}_SP_1 = -\frac{1}{A}\sum_k\sum_l |F(1kl)|^2 \sin 2\pi(kv+lw)\,. $$

The Cl x-parameter was deduced by forming $\tan 2\pi(2x_{\text{Cl}})$ from the peak heights of the Cl–Cl interactions in the two component projections. The light-atom parameters could not be found with the same degree of accuracy owing to the fact that most of the Cl–light-atom vectors occur as double unresolved peaks. However, from the *signs* of the peaks in the two component maps the orders of magnitude of $2\pi(x_{\text{Cl}}-x_L)$ could be deduced and the use of this information, together with a structure model, led to an approximate set of parameters.

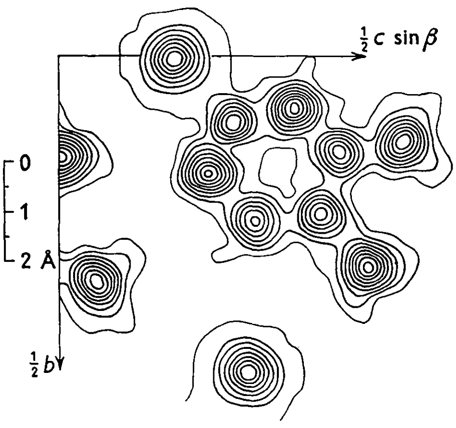


Fig. 2. Electron-density projection on (100). Contour interval 1 e.Å^{-2}, except in chlorine atom where contours are at 1, 2, 4, 8, 12, ... e.Å^{-2}.

At this stage the percentage discrepancy for the $(1kl)$ structure factors was 30·0, but it was possible to allocate signs to 280 of the 307 observed reflexions and to compute the components of the generalized Fourier projection from the following expressions (Fridrichsons & Mathieson, 1955):

$$ C_1(y,z) = \frac{2}{A}\sum_0^k\sum_0^l [F(1kl)+F(1kl)] \cos 2\pi ky \cos 2\pi lz\,, \qquad (k+l) = 2n $$

$$ -\frac{2}{A}\sum_0^k\sum_0^l [F(1kl)-F(1kl)] \sin 2\pi ky \sin 2\pi lz\,, \qquad (k+l = 2n+1) $$

$$ S_1(y,z) = -\frac{2}{A}\sum_0^k\sum_0^l [F(1kl)-F(1kl)] \cos 2\pi ky \sin 2\pi lz\,, \qquad (k+l = 2n) $$

$$ -\frac{2}{A}\sum_0^k\sum_0^l [F(1kl)+F(1kl)] \sin 2\pi ky \cos 2\pi lz\,, \qquad (k+l = 2n+1)\,. $$

The x parameters for all atoms could then be determined by the relationship

$$ \frac{2\pi x_r}{a} = \tan^{-1}\frac{S_1(y_r, z_r)}{C_1(y_r, z_r)}\,. $$

Recalculation of the $(1kl)$ structure factors with this new set of atomic parameters reduced the percentage discrepancy to 13·2. $C_1(y,z)$ and $S_1(y,z)$ were computed twice more as phases could be assigned to more of the coefficients, and in the final computation the 'unobserved' terms were included with their calculated values to improve peak heights. The final component maps are shown in Fig. 3(*a*) and (*b*), and percentage discrepancy using the corresponding values of x_r is 9·7.

3·3. *Refinement of y, z parameters*

The modulus projection $\varrho_1(y,z)$, which was used by Clews & Cochran (1949) to refine atomic parameters, may be formed from the components $C_1(y,z)$ and $S_1(y,z)$ referred to in the preceding section, thus

$$ \varrho_1 = [C_1^2+S_1^2]^{\frac{1}{2}}\,. $$

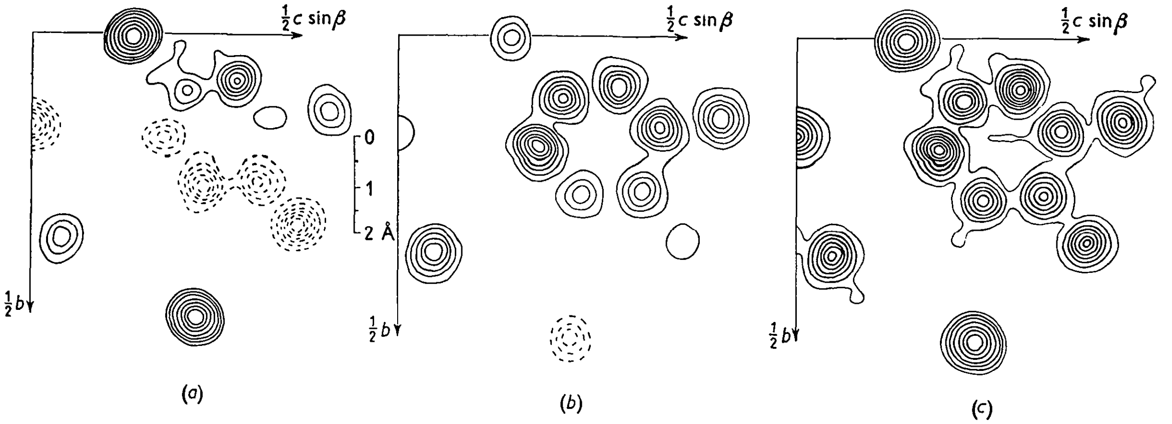


Fig. 3. (*a*) $C_1(y,z)$, (*b*) $S_1(y,z)$. Contour interval 1 e.Å^{-2}. Negative contours broken and zero contour omitted. (*c*) $\varrho_1(y,z)$, the generalized projection obtained by combining $C_1(y,z)$ and $S_1(y,z)$. Contour intervals as in Fig. 2.

The function ϱ_1, calculated from the final values of the two components C_1 and S_1, is shown in Fig. 3(*c*). The *y* and *z* co-ordinates deduced from this map agreed closely with those previously obtained from the Fourier projection on (100). Proceeding from the mean values of these two sets of co-ordinates, further refinement was carried out by means of the Fourier difference synthesis which uses as coefficients values of (F_o-F_c).

The first difference synthesis showed that there were small errors in the atom co-ordinates due to series termination effects, and these were corrected so that the slope of $(\varrho_o-\varrho_c)$ was approximately zero at the atomic centres. That the values of $(\varrho_o-\varrho_c)$ at atomic positions did not differ appreciably from zero justified the use of an average temperature factor ($B=3\cdot35$ Å^2) for all atoms. There was evidence for thermal anisotropy only in the case of the chlorine atom, but as the effect was not large no attempt was made to correct for this.

The final difference synthesis is shown in Fig. 4. Here, apart from the two peaks associated with the chlorine atom which may be attributed to thermal anisotropy, all the other major peaks are clearly due to the presence of hydrogen atoms. Co-ordinates were assigned to the hydrogen atom attached to the one free carbon atom in the pyrimidine ring, and to the four hydrogen atoms of the amino groups. When the hydrogen atoms were taken into account the percentage discrepancy between observed and calculated structure amplitudes was reduced from 9·5 to 7·8. The observed and calculated structure amplitudes are listed in Table 3.

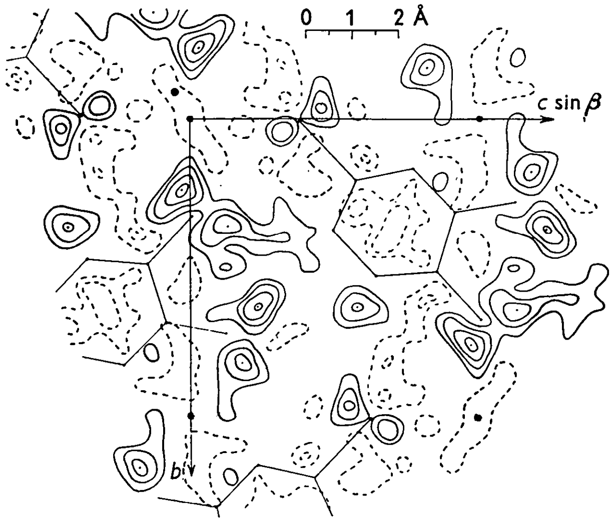


Fig. 4. Difference synthesis projection on (100). Contour interval 0·2 e.Å^{-2}. Negative contours broken and zero contour omitted.

The (1*kl*) structure amplitudes have, for reasons of space, not been included but they show about the same order of agreement.

Table 1. *Atomic co-ordinates*

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*x*′ (Å)	*y* (Å)	*z*′ (Å)
Cl	0·023	0·0052	0·1892	−0·246	0·066	2·330
C_2	0·175	0·103	0·285	0·154	1·302	3·509
C_4	0·210	0·156	0·458	−0·020	1·971	5·639
C_5	0·358	0·255	0·427	0·587	3·222	5·258
C_6	0·408	0·264	0·321	0·959	3·336	3·952
N_1	0·319	0·187	0·245	0·761	2·363	3·017
N_3	0·121	0·083	0·384	−0·222	1·049	4·728
N_4	0·166	0·139	0·562	−0·366	1·757	6·920
N_5	0·462	0·337	0·503	0·842	4·259	6·193
H_4	—	0·183	0·616	—	2·313	7·585
H_4'	—	0·088	0·586	—	1·112	7·215
H_5	—	0·380	0·487	—	4·802	5·996
H_5'	—	0·320	0·566	—	4·044	6·969
H_6	—	0·317	0·297	—	4·006	3·657

Table 2. *Deviations from calculated mean planes*

		Plane *A*			Plane *B*		
Atom	$x'_{\text{obs.}}$	$x'_{\text{calc.}}$	*Δ*	*D*	$x'_{\text{calc.}}$	*Δ*	*D*
Cl	−0·246	−0·095	0·151	0·135	−0·288	0·018	0·016
C_2	0·154	0·170	0·016	0·015	0·107	−0·047	−0·042
C_4	−0·020	−0·033	−0·013	−0·012	−0·020	0·000	0·000
C_5	0·587	0·602	0·015	0·013	0·646	0·059	0·052
C_6	0·959	0·956	−0·003	−0·003	0·970	0·011	0·010
N_1	0·761	0·748	−0·013	−0·011	0·707	−0·054	−0·048
N_3	−0·222	−0·224	−0·002	−0·002	−0·264	−0·042	−0·037
N_4	−0·366	−0·425	−0·059	−0·053	−0·385	−0·019	−0·017
N_5	0·842	0·837	−0·005	−0·004	0·939	0·097	0·086

3·4. *Co-ordinates, molecular dimensions and accuracy*

The final atomic co-ordinates are shown in Table 1, where fractional co-ordinates are referred to the monoclinic crystal axes, and co-ordinates x', y and z' are referred to orthogonal axes a', b and c', such that a' is collinear with a and c' normal to a. Thus

$$z' = z \sin \beta \quad \text{and} \quad x' = x + z \cos \beta \; .$$

No reliable determination of the x co-ordinates of hydrogen atoms could be made, so only the y and z parameters, deduced from difference syntheses, are shown in Table 1.

The bond lengths and angles calculated on the basis of these co-ordinates are shown in Fig. 5.

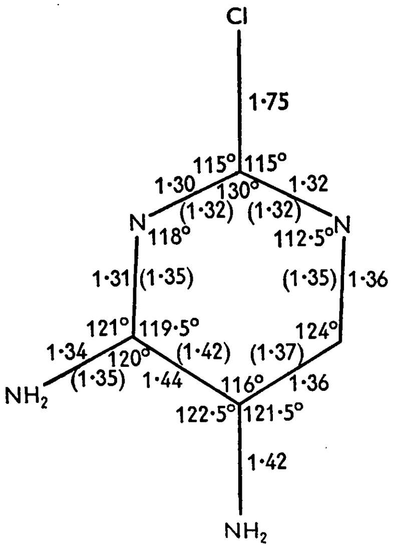


Fig. 5. Molecular dimensions of 4,5-diamino-2-chloropyrimidine.

Table 3. *Comparison of observed and calculated structure factors*

hkℓ	Fo	Fc
000	-	296·0
020	7·6	-7·5
040	15·5	11·4
060	37·3	35·9
080	29·8	29·0
0,10,0	10·8	9·6
0,12,0	27·7	26·0
0,14,0	4·1	5·6
0,16,0	5·8	4·7
011	7·7	-8·0
021	43·1	-42·1
031	25·7	27·7
041	10·3	-12·2
051	43·5	42·4
061	6·5	-6·2
071	5·8	5·9
081	< 1·8	-0·3
091	7·7	7·4
0,10,1	5·0	6·4
0,11,1	4·4	5·7
0,12,1	15·8	-15·3
0,13,1	< 2·0	2·7
0,14,1	2·6	-3·0
0,15,1	< 1·5	-1·2
0,16,1	4·7	-3·8
002	20·6	-18·4
012	37·0	40·2
022	47·7	-46·5
032	6·7	-8·1
042	58·0	-56·4
052	25·0	25·2
062	5·5	-5·1
072	24·1	-22·0
082	10·5	-9·1
092	6·2	-7·1
0,10,2	31·8	-30·9
0,11,2	11·0	-10·5
0,12,2	3·4	-3·7
0,13,2	< 2·0	4·0
0,14,2	< 1·8	-1·1
0,15,2	2·1	-2·2
0,16,2	6·5	-6·7
013	33·5	-31·6
023	20·7	22·2
033	44·1	-44·8
043	17·1	-15·8
053	49·7	-46·7
063	< 1·6	-1·1
073	28·6	-27·3
083	< 1·9	2·4
093	20·3	-20·8
0,10,3	7·3	7·9
0,11,3	4·3	-3·6
0,12,3	5·4	6·4
0,13,3	11·5	-10·4
0,14,3	1·7	-2·8
0,15,3	7·6	-7·4
004	32·7	31·0
014	8·1	-10·5
024	20·4	-20·3
034	7·6	-7·9
044	15·9	-15·3
054	12·1	12·4
064	32·8	31·6
074	12·9	12·8
084	4·2	-4·7
094	4·1	3·6
0,10,4	< 2·1	0·5
0,11,4	< 2·2	-0·2
0,12,4	< 2·1	0·5
0,13,4	6·1	6·9
0,14,4	2·4	-2·7
0,15,4	4·1	3·3
015	58·8	56·9
025	4·7	-7·1
035	16·2	16·7
045	24·0	22·1
055	34·0	32·3
065	7·8	-6·4
075	19·1	20·1
085	2·8	0·1
095	9·3	9·4
0,10,5	7·1	6·3
0,11,5	12·2	11·9
0,12,5	< 2·0	-2·5
0,13,5	13·9	13·3
0,14,5	< 1·6	0·1
0,15,5	6·8	5·4
006	3·0	6·0
016	6·6	6·2
026	23·1	24·3
036	12·8	-13·5
046	22·7	22·3
056	2·5	-2·5
066	19·9	19·0
076	5·6	-7·1
086	12·4	12·4
096	< 2·1	1·2
0,10,6	4·8	5·1
0,11,6	2·1	-3·6
0,12,6	6·8	7·9
0,13,6	< 1·7	0·7
0,14,6	5·7	5·3
0,15,6	3·4	-4·0
017	1·6	1·3
027	10·3	10·7
037	29·9	-28·8
047	< 1·8	2·1
057	17·1	-16·6
067	< 2·0	2·9
077	< 2·1	4·2
087	13·6	-13·5
097	6·1	-8·3
0,10,7	4·2	-4·2
0,11,7	5·4	-5·9
0,12,7	2·6	-2·0
0,13,7	3·8	-2·7
0,14,7	4·1	-2·9
008	26·3	-26·2
018	< 1·8	-0·4
028	15·1	-15·8
038	7·3	-6·9
048	28·9	-28·2
058	5·7	-5·1
068	11·3	-10·5
078	6·4	8·4
088	32·1	-30·6
098	< 2·1	3·2
0,10,8	2·1	-2·6
0,11,8	3·9	-1·7
0,12,8	7·1	-5·9
0,13,8	3·3	-1·8
0,14,8	4·3	-6·2
019	4·4	-5·9
029	8·4	-10·1
039	17·1	-18·4
049	10·8	12·2
059	2·1	3·3
069	< 2·1	-0·6
079	8·7	10·1
089	< 2·1	1·4
099	11·2	-12·5
0,10,9	4·7	4·6
0,11,9	5·2	-5·3
0,12,9	4·4	4·8
0,13,9	< 1·0	-1·4
0,0,10	10·6	13·1
0,1,10	< 2·1	-1·3
0,2,10	17·8	18·2
0,3,10	19·8	18·4
0,4,10	10·9	12·4
0,5,10	5·3	-7·0
0,6,10	2·6	3·8
0,7,10	< 2·1	2·1
0,8,10	8·1	8·9
0,9,10	< 2·1	-2·2
0,10,10	9·5	8·5
0,11,10	4·5	3·8
0,12,10	7·3	7·2
0,1,11	20·3	20·9
0,2,11	6·4	-8·8
0,3,11	3·0	3·1
0,4,11	5·2	-6·5
0,5,11	9·0	10·5
0,6,11	4·3	4·6
0,7,11	10·6	12·5
0,8,11	< 1·9	0·9
0,9,11	7·2	6·7
0,10,11	2·1	-2·7
0,11,11	4·1	3·8
0,0,12	< 2·1	0·4
0,1,12	2·6	-3·1
0,2,12	8·4	-10·0
0,3,12	< 2·1	0·5
0,4,12	4·1	5·5
0,5,12	3·4	-3·2
0,6,12	< 2·0	1·4
0,7,12	< 1·8	1·7
0,8,12	< 1·6	-1·4
0,9,12	< 1·4	-2·0
0,10,12	2·7	-3·0
0,1,13	4·8	-6·0
0,2,13	< 1·9	-1·7
0,3,13	14·7	-14·7
0,4,13	< 1·8	3·6
0,5,13	7·1	-7·8
0,6,13	1·6	-0·8
0,7,13	7·2	-7·0
0,8,13	4·9	-4·0
0,9,13	10·4	-9·4
0,0,14	4·8	-4·9
0,1,14	< 1·7	-1·3
0,2,14	4·1	-4·6
0,3,14	< 1·6	-0·1
0,4,14	6·9	-6·8
0,5,14	< 1·4	0·8
0,6,14	4·7	-4·4
0,1,15	3·8	3·8
0,2,15	< 1·3	1·3
0,3,15	3·0	3·0
0,4,15	< 1·1	0·1
0,5,15	3·3	4·0

To test the planarity of the molecule an equation of the form $x' = A + By + Cz'$ can be found which best fits the atomic co-ordinates, the coefficients A, B and C being calculated by the least-squares method. When this was carried out for the ring atoms only, the resulting equation was

$$x' = 0{\cdot}4186 + 0{\cdot}4368y - 0{\cdot}2328z' \quad \text{(Plane } A\text{)} \; .$$

Table 2 shows the deviation, Δ, between the observed x' co-ordinates and those calculated from this equation and the perpendicular displacements, D, of the atoms from the plane. The average deviation Δ for the ring atoms is 0·010 Å, corresponding to an average displacement of 0·009 Å. However, one of the amino nitrogen atoms, N_4, is displaced from this plane by 0·059 Å, while the chlorine atom is 0·135 Å off this plane. These would appear to be significant departures from the plane. In the case of N_4 the departure is in a direction such that the distance between N_4 and the ring nitrogen atoms of neighbouring molecules is shortened, but in the case of the chlorine atom the apparent departure from the plane is unexpected (Clews & Cochran, 1949).

Recalculation of the coefficients A, B and C with the inclusion of the chlorine co-ordinates, and giving them four times the weight of those of the ring atoms, gave a plane with equation

$$x' = 0{\cdot}2232 + 0{\cdot}4690y' - 0{\cdot}2070z' \quad \text{(Plane } B\text{)} \; .$$

The deviations in x' coordinates and displacements from this plane are also shown in Table 2 under the heading Plane B. The average displacement of the ring atoms has here increased to 0·032 Å while, as is to be expected from the weighting of observations, the departure of the chlorine atom can no longer be regarded as significant. Also, the maximum displacement from the plane now occurs for N_5 (D = 0·086 Å) whereas N_4 does not depart significantly from this plane.

To determine which of the above possibilities was correct it was necessary to obtain an estimate of the accuracy of the x co-ordinates. Since these parameters are deduced from the peak heights in C_1 and S_1 from the relation given in § 3·2 their accuracy may be determined by estimating the standard deviations of C_1 and S_1 and calculating the corresponding deviation in x_r/a for each atom. Values for $\sigma(C_1)$ and $\sigma(S_1)$ were obtained by considering the average values of C_1^2 and S_1^2 in regions away from atoms, and also by applying the expression for standard deviation of electron density

$$\sigma(\varrho) = \frac{1}{A}[\Sigma(F_o-F_c)^2]^{\frac{1}{2}}$$

to the $(1kl)$ data. The first method gave $\sigma(C_1) = 0{\cdot}34$ e.Å^{-2} and $\sigma(S_1) = 0{\cdot}26$ e.Å^{-2}, while the second gave an average value of 0·28 e.Å^{-2}. When the corresponding standard deviations of x co-ordinates were calculated, $\sigma(x)$ for chlorine was found to be 0·014 Å while for the carbon and nitrogen atoms $\sigma(x)$ ranged from 0·05 Å to 0·07 Å depending on the value of the x parameter. While these values should represent a lower limit to the accuracy of the x parameters it is obvious that, without further refinement, preferably by three-dimensional synthesis, any further speculation as to the planarity of the molecule as a whole is unjustified, although it is certain that the ring is itself planar in view of other work.

The standard deviations of the y and z atomic co-ordinates $\sigma(y)$ and $\sigma(z)$ were estimated by the method of Cruickshank (Cruickshank, 1949; Ahmed & Cruickshank, 1953) using the following expression:

$$\sigma(y) = \frac{1}{A}\frac{2\pi}{b}(\Sigma k^2(\Delta F)^2)^{\frac{1}{2}}\Big/\left|\frac{\partial^2\varrho}{\partial y^2}\right| .$$

In calculating this expression ΔF was given the value F_o-F_c so that estimated standard deviations include residual finite-series errors in addition to random errors. A value was obtained for the curvature by assuming that the electron density near the centre of an atom can be expressed as

$$\varrho(r) = \varrho(0)\exp[-pr^2] ,$$

so that

$$\partial^2\varrho/\partial y^2 = -2p\varrho(0) .$$

The constant p was evaluated from graphical plots of log ϱ against r^2 for each atom. In this way the following standard deviations of atomic co-ordinates were obtained:

$\sigma(y) = \sigma(z) = 0{\cdot}002$ Å for chlorine ,
$\sigma(y) = \sigma(z) = 0{\cdot}009$ Å for nitrogen ,
$\sigma(y) = \sigma(z) = 0{\cdot}010$ Å for carbon .

The deviations of bond lengths depend mainly on the deviations of the y and z atomic co-ordinates, so that the lower accuracy of the x parameters was not so important in this respect. The standard deviation of bond length between any two atoms whose positions are independently determined is given by

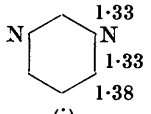
$$\sigma^2L = \{\sigma^2(x_1)+\sigma^2(x_2)\}\cos^2\alpha+\{\sigma^2(y_1)+\sigma^2(y_2)\}\cos^2\beta + \{\sigma^2(z_1)+\sigma^2(z_2)\}\cos^2\gamma .$$

Here $\sigma(x_1)$, $\sigma(y_1)$ are the standard deviations of the co-ordinates of the first atom and cos α, cos β, cos γ are the direction cosines of the line joining the atoms.

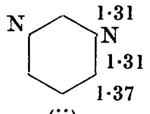
Application of this expression gave $\sigma(L) = 0{\cdot}018$ Å for the Cl–C bond, while the average value of $\sigma(L)$ for C–N and C–C bonds was 0·028 Å with a maximum value 0·043 Å for the C_4–C_5 bond.

4. Discussion

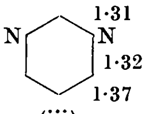
A comparison of the bond lengths and angles within the pyrimidine ring with those observed for other pyrimidine derivatives (Clews & Cochran, 1948, 1949; Pitt, 1948; Furberg, 1950; Parry, 1954) shows that in the present case the ring assumes a shape most closely resembling that in 4-amino-2,6-dichloropyrimidine. From a study of pyrimidine derivatives, Clews & Cochran (1949) predicted dimensions for the pyrimidine ring as shown in (i) below. In (ii) are shown the bond lengths calculated by Chalvet & Sandorfy (1949) by the molecular orbital method. The results of similar calculations, but using different values of the Coulomb integrals, are shown in (iii). From the close agreement between (ii) and (iii) it is apparent that the calculated values of bond length are relatively insensitive to the absolute values of Coulomb integrals.



(i)



(ii)



(iii)

In the present work on 4,5-diamino-2-chloropyrimidine the average length of C–N bonds is 1·33 Å, but the bonds N_3–C_4 and N_1–C_6 differ by 0·05 Å, which is possibly significant. The two C–C bonds are also significantly different in length. The longer C_4–C_5 bond occurs also in the case of 4-amino-2,6-dichloropyrimidine and is associated with the substitution of an amino-group in the 4-position.

Chemical evidence indicates that the substitution of an amino- or other electron-releasing group in the 5-position tends to render a substituent in the 2-position more like a group on an ordinary aromatic nucleus (Brown, 1953). For example, a chlorine atom in the 2-position is then less susceptible to nucleophilic replacement. The C–Cl distance of 1·75 Å corresponds closely to the single-bond length of 1·76 Å, so that the conjugation of an unshared electron pair on the chlorine with the ring, which would be expected for a chlorine substituent on an aromatic nucleus, does not appear to occur. In fact, this bond length is almost the same as that found for other chloropyrimidines without substituents in the 5-position. This effect and the difference in the C–C bonds in the ring might well be the result of some localization of resonance interactions.

The extra-annular C–N bond C_4–N_4 is much shorter than the single-bond distance of 0·47 Å, while C_5–N_5 approximates more closely to a single bond. It is to be expected, then, that the resonance structures contributing to the molecular structure will be principally those proposed for 4-amino-2,6-dichloropyrimidine (Clews & Cochran, 1949). The bond lengths calculated in this way are shown in parentheses in Fig. 5, where it is seen that, except for the bond N_3–C_4, which is smaller by 0·04 Å, the agreement between observed and calculated values is very good.

The standard deviation of electron density for the (100) projection, calculated from the expression

$$\sigma(\varrho_0) = \frac{1}{A}\,[\Sigma(F_o-F_c)^2]^{\frac{1}{2}}\;,$$

was found to be 0·18 e.Å^{-2}. Thus the appearance of peaks due to hydrogen atoms can be expected in the final difference synthesis. That the hydrogen atoms could be located has already been mentioned, and reference to Fig. 4 shows that there are two peaks associated with each of the extra-ring nitrogen atoms. This, together with the fact that there are no similar peaks in the region of the ring nitrogen atoms, confirms that the molecule occurs in the amino form. An amino form was suggested for 4-amino-2,6-dichloropyrimidine and was inferred from crystallographic evidence in the case of cytidine. The complete analysis of adenine hydrochloride (Cochran, 1951) showed this molecule also to be in an amino form.

Fig. 6 shows the structure projected on to (100). The four molecules are numbered for reference purposes. The broken contacts between adjacent molecules represent the most probable system of hydrogen bonds. The distance $(N_1)_1$–$(N_4)_4$ is 3·16 Å while $(N_4)_4$ to $(N_3)_3$ in the unit cell below is 3·11 Å, corresponding to normal N–H · · · N hydrogen bonds. Furthermore, reference to Fig. 4 shows that, at least in projection, the hydrogen atoms associated with $(N_4)_4$ are directed along the lines joining this atom to $(N_1)_1$ and $(N_3)_3$. Bonds of this type between a 4-amino group and the ring nitrogens of adjacent molecules make up a helical system of hydrogen bonds throughout the crystal structure, with the axis of the helix parallel to the *a* axis. In addition to these, the distance from $(N_5)_1$ to $(N_1)_4$ is 3·15 Å, which is of approximately the same magnitude as the N–H · · · N bonds already referred to, and there is clearly a hydrogen atom lying along the line joining $(N_5)_1$ to $(N_1)_4$. Also the electron density is spread out along this line forming a bridge between the two atoms, although too much significance should not be attached to this as the maximum density is not very much greater than the standard deviation of electron density. It is not clear how the atom $(N_1)_4$ can be associated with two hydrogen bonds to two amino-nitrogens of the same molecule.

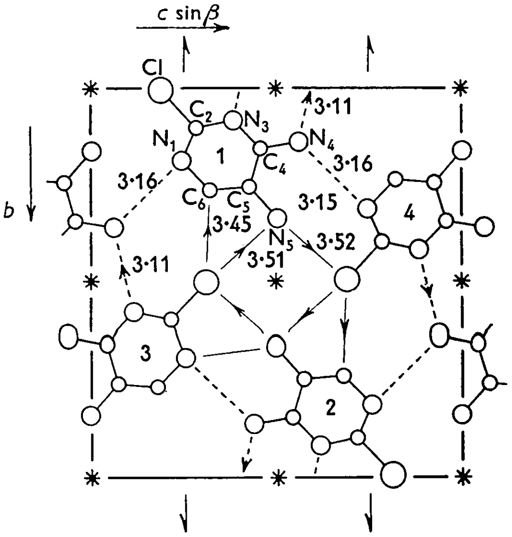


Fig. 6. Structure of 4,5-diamino-2-chloropyrimidine projected on (100). Interatomic distances indicated by broken and full lines, as explained in text. Arrow-heads indicate that the bond is to an atom in the unit cell above.

The following contacts

$(C_6)_1$ to $(Cl)_3$ in the cell below—3·45 Å ,
$(N_5)_1$ to $(Cl)_3$ in the cell below—3·51 Å ,
$(N_5)_1$ to $(Cl)_4$ in the cell above—3·52 Å

are of some interest. In the first of these there is a hydrogen atom attached to the carbon atom, and if it is assumed, as is reasonable, that the hydrogen atom is in the plane of the ring, the Cl–H distance is 3·06 Å, a normal van der Waals contact. In the case of the other two contacts, the N_5 atom has two hydrogen atoms attached to it, but, as in the projection neither of these lie along the directions $(N_5)_1$–$(Cl)_3$ or $(N_5)_1$–$(Cl)_4$, it may be inferred that these represent normal van der Waals contacts between chlorine and nitrogen atoms.

To sum up, from the present investigation and from previous work on amino-pyrimidines and purines it may be concluded, first, that these compounds occur in the *amino* and not in the *imino* forms whatever the position of the substituent NH_2 group and, secondly, that they are held together in the crystalline state by systems of hydrogen bonds between the nitrogen atoms of the amino-groups and the ring nitrogen atoms of neighbouring molecules. Hydrogen bonds of this type have been shown to exist in the present pyrimidine and in adenine hydrochloride, and it has been inferred from the occurrence of short intermolecular N–N contacts that there are hydrogen bonds in a number of other pyrimidines and purines. Hydrogen bonds of the types N–H–O, O–H–O have been deduced for other pyrimidines (Pitt, 1948; Parry, 1954), purines (Broomhead, 1948, 1951) and nucleosides (Zussman, 1953; Furberg, 1950).

That such bonding occurs in a large group of related compounds, which are in turn related to the nucleic acids and nucleo-proteins, is of considerable interest and importance since it is usually assumed that these latter compounds are held together in biological systems by hydrogen bonding between the neighbouring groups. Indeed, Watson & Crick (1953) have suggested that the macromolecule of deoxyribonucleic acids consists of a double helix, in which two helical chains are coiled round the same axis into the pyrimidine and purine bases on the inside of the helix. The two helical chains are held together by hydrogen bonds between the pyrimidine and purine bases. These hydrogen bonds must be of the type found in the simpler compounds.

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On Order–Disorder Structures (OD-Structures)

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Certain features common to structures with one-dimensional position disorder and to related ordered layer structures (OD-structures) are discussed, the corresponding concepts are introduced by examples and the corresponding features of Fourier transforms are deduced. OD-structures are systematized and a glossary of terms is added. In an Appendix a nomenclature for plane space groups in three dimensions, which corresponds to the international nomenclature for three-dimensional space groups, is suggested.

Introduction

In the course of investigating the disorder phenomena exhibited by β-wollastonite (Jeffery, 1953) and Maddrell's salt (Dornberger-Schiff, Liebau & Thilo, 1955), it became evident that an adequate description of these and kindred structures cannot be expressed simply in terms of the current language of 'classical' crystallography, which, by its very nature, can be applied to fully ordered structures only. I have thus been led to attempt a generalization of these classical concepts wide enough to cover what I propose to call 'OD-structures' (order–disorder structures).

This term should—according to my proposal—embrace structures with stacking disorder (1-*dimensionale Lagefehlordnung*) if the lack of order in the stacking results (as usual) from the fact that there are two or more geometrically—and hence energetically—equivalent ways in which neighbouring layers may be placed with respect to one another. It should embrace also such structures which differ from these disordered structures only by the regularity of their stacking.

Before an attempt at the development of a general theory is made I propose to discuss in the present