Acta Cryst. (1949). 2, 46

The Structures of Pyrimidines and Purines. III. An X-ray Investigation of Hydrogen Bonding in Aminopyrimidines

By C. J. B. Clews and W. Cochran

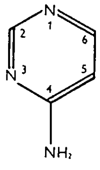
Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 22 *October* 1948)

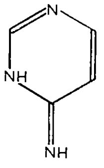
The crystal structures of two aminopyrimidines, 4-amino-2,6-dichloropyrimidine and 5-bromo-4,6-diaminopyrimidine, have been determined by two- and three-dimensional Fourier methods. The electron distribution determined by three-dimensional Fourier synthesis is sufficiently accurate to fix the positions of the hydrogen atoms, and experimental evidence is obtained in support of the view that in hydrogen bonding the hydrogen is covalently bound to one atom but the proton interacts electrostatically with the unshared electron pair on the other. The hydrogen atom and the orbit of the unshared electrons are both directed along the line joining the hydrogen-bonded atoms. Other effects associated with hydrogen bonding in these compounds are pointed out. Bond lengths calculated on the assumption that 'resonance structures' involving a positive formal charge on an amino group make an appreciable contribution to the molecular state are in good agreement with the observed values.

1. Introduction

A knowledge of the structures of a group of comparatively simple compounds, pyrimidines, purines, nucleosides and nucleotides, for example, might be of value in furthering an understanding of the structures of nucleic acids and related substances which are themselves too complex for successful attack by X-ray methods. The structures of 2-amino-4,6-dichloropyrimidine and 2-amino-4-methyl-6-chloropyrimidine have been described in a previous communication (Clews & Cochran, 1948, subsequently referred to as Part I). Many of the properties of amino and hydroxy pyrimidines are determined by the possibility of tautomerization within the ring nucleus. An amino group at position 4 or 6 of the pyrimidine nucleus, for instance, shows greatly reduced amino behaviour, since tautomerization causes (I) in certain circumstances to react mainly in the iminodihydro-pyrimidine form (II).



(I)



(II)

The question as to which of the tautomeric forms of pyrimidine derivatives capable of prototropic change will be most prominent under normal conditions of chemical reaction is of considerable practical importance in the synthesis from substituted pyrimidines of more complex related compounds (Baddiley, Lythgoe & Todd, 1943). The nature of the molecular structure in the solid state is of some interest in this connexion, but greater interest attaches to it because it is undoubtedly closely connected with the formation of intermolecular hydrogen bonds. Indeed, Hunter (1945) has attached such importance to this phenomenon as to suggest that distinction between the tautomeric forms is meaningless and that in solution or in the solid state the true structure of certain molecules which can be written either as $\mathrm{H}—A\wedge\wedge B$ or $A\wedge\wedge B—\mathrm{H}$ is a resonance hybrid of the unperturbed states

$$--\mathrm{H}—A\wedge\wedge B--\mathrm{H}—A\wedge\wedge B--\mathrm{H}—A\wedge\wedge B--$$

and $$—\mathrm{H}--A\wedge\wedge B—\mathrm{H}--A\wedge\wedge B—\mathrm{H}--A\wedge\wedge B—,$$

with properties intermediate between these extreme forms. The view that the hydrogen bond is in any sense a resonance phenomenon has been largely superseded by the view that it is mainly, if not entirely, electrostatic in origin (Wheland, 1944). The presence of links of some kind between the substituent nitrogen of one molecule and ring nitrogens of others was inferred from the crystal structures described in Part I, but the exact points of attachment of the hydrogen atoms remained a matter for speculation. A more thorough investigation of a closely related compound, 4-amino-2,6-dichloropyrimidine, was therefore undertaken in the hope that it would provide further information on this point, which may be of some importance for an understanding of the nature of the hydrogen bond. A less accurate investigation of the compound 5-bromo-4,6-diaminopyrimidine has also been made.

The determination of the position of a hydrogen atom has generally been regarded as beyond the power of the X-ray method because of the small scattering power of its single electron. The work of Brill, Hermann & Peters (1942) has shown that when the structure amplitudes have been measured very carefully direct indication of the positions of hydrogen atoms can be obtained from the electron distribution calculated by Fourier synthesis. In an investigation of the crystal structure of melamine Hughes (1941) found that improved agreement between observed and calculated structure amplitudes was obtained when allowance was made for contributions from hydrogen atoms placed in positions suggested by symmetry considerations and by the occurrence of hydrogen bonds between nitrogen atoms. The former of these methods is to be preferred as it does not require that initial assumptions about the hydrogen positions be made. Calculation shows that conditions are more favourable for the detection of small variations in electron density if a three-dimensional synthesis is resorted to, and it will be shown later that the random error introduced by photographic recording of the reflected X-ray beams and eye-estimation of intensities need not introduce errors greater than 0·2 or 0·3 e.A.$^{-3}$ into the electron density. Investigation of the effect of terminating the Fourier series showed that in a particular case it would introduce a further error of about the same magnitude. As the electron density in the neighbourhood of a hydrogen nucleus may be expected to be about 1 e.A.$^{-3}$ there seemed to be a possibility of deducing the positions of the hydrogen atoms from a three-dimensional Fourier synthesis. It has also been shown by Booth (1946) that the larger number of terms included in a three- as compared with a two-dimensional synthesis results in a more precise determination of atomic parameters.

2. Preliminary investigation of some amino and hydroxy pyrimidines

A number of pyrimidine derivatives were investigated by taking oscillation and Weissenberg photographs. The unit-cell dimensions and space groups of four of these are given in Table 1. The cell dimensions of (1) were measured by the θ-method (Weisz, Cochran & Cole, 1948), and of the others by measurement of layer-line separations on oscillation photographs. Values for (1) obtained by the latter method are given in parentheses; the agreement with the more accurate values, which are correct to $\pm 0{\cdot}005$ A., $\pm 2'$, indicates that the others should be correct to ± 1 %. In the case of 5-bromouracil the strength of the $\bar{2}01$, $\bar{4}02$ and $\bar{6}03$ reflexions indicates a layer structure with the b axis in the plane of the molecule. This, combined with the fact that the length of the b axis is no greater than the diameter of a single molecule, makes it improbable that the space group is other than $P2$. (1) and (2) were selected for more extensive investigation, partly because crystals of suitable dimensions could be obtained, and partly because the presence of a centre of symmetry considerably simplifies the problem of structure analysis. Since the investigations of these two compounds differed in scope and in object, they will be described separately.

3. 4-amino-2,6-dichloropyrimidine

3·1. *Experimental*

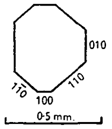


Fig. 1. Cross-section of crystal

Crystals were grown from alcoholic solution in the form of prisms several millimetres long in the direction of the short crystallographic axis and up to 0·5 mm. in diameter. A drawing, approximately to scale, of the cross-section of the crystal from which most of the data were recorded is shown in Fig. 1. This crystal was cut so that its extension along the c axis was only 0·5 mm. Two series of zero-layer-line Weissenberg photographs of different exposure times were taken with the crystal oscillating about the c and b axes respectively. Data from these photographs were used to obtain approximate atomic parameters by two-dimensional Patterson and Fourier methods. The reflexions required for the three-dimensional Fourier synthesis were recorded on a series of 15° oscillation photographs with adjacent ranges of oscillation overlapping by 3°. Although indexing of oscillation photographs is more troublesome than is the case with Weissenberg photographs, the former method has certain advantages in that the photographs can be obtained in a shorter time, and all reflected beams belonging to the same layer line give spots of equal length on the film. This is not true of Weissenberg photographs, other than those of zero layer lines, since the divergence of the X-ray beam together with the motion of the film causes certain reflexions to be recorded on a smaller area than others. It then becomes necessary to use an integrating photometer for intensity measurement. Photographs were taken with the same specimen oscillating about each of the three axes in turn. The crystal was lightly attached to a glass fibre by means of a speck of plasticine so that it could be taken off and remounted in any desired orientation. With widely spaced layer lines (c axis

Table 1. *Cell dimensions and space groups of certain pyrimidine derivatives*

No.	Compound	a (A.)	b (A.)	c (A.)	β	Space group	Molecules per cell
(1)	4-amino-2,6-dichloro.	11·910 (11·85)	13·912 (13·90)	3·789 (3·80)	94° 29′ (94°)	$P2_1/a$	4
(2)	5-bromo-4,6-diamino.	13·40	3·80	12·20	100°	$P2_1/a$	4
(3)	5-bromo-2,4-diamino-6-hydroxy.	16·95	4·95	10·40	120°	$P2_1/a$	4
(4)	5-bromouracil	7·23	6·85	5·63	96°	$P2$ (or Pm)	2

(Wave-length of Cu $K\alpha_1 = 1{\cdot}5405$ A.)

vertical) three exposures of 60, 15 and 6 min. were made on the same film, which between exposures was displaced vertically through a distance sufficient to prevent overlapping. Where successive layer lines were relatively close together, only the 60 and 15 min. exposures were made on the same film, the 15 min. exposure being repeated with the 6 min. exposure on a separate film. In this way a wide range of intensities was brought within the range of the intensity scale used. All films were from the same batch and were developed under identical conditions as far as possible. Indexing was carried out with the help of a Bernal chart and accurate drawings of the reciprocal lattice. Intensities were measured by comparison with an 'intensity scale' as described in Part I. It is obvious that this method does not give the integrated reflexion intensity, but only the X-ray intensity corresponding to the maximum blackening in the spot produced on the recording film. For a given reflected beam these two intensities are proportional, and they are also proportional in the case of two reflected beams which can be recorded at the same position on the film, provided the specimen has a regular shape so that differences due to differential absorption in the crystal do not arise. If the latter is spherical, the absorption factor is the same for all reflexions having the same Bragg angle. In comparing two beams reflected from a regularly shaped crystal, both of which belong to the zero layer line but have different Bragg angles, the following factors should be taken into account: (1) absorption in the specimen (Bradley, 1935); (2) variation of spot breadth with Bragg angle due to the divergence of the incident beam; (3) gradually increasing resolution of $K\alpha$ doublet. These factors depend on 2θ only, provided the specimen is spherical or cylindrical. In comparing reflexions on different layer lines at least two additional factors must be considered; (4) increased area of spots on higher layer lines due to the increased distance from crystal to film and the oblique incidence of X-rays on the film; (5) increased absorption in the film and enhanced photographic action due to oblique incidence (Cox & Shaw, 1930). Factors (4) and (5) depend only on the height of the layer line, i.e. on the ζ-co-ordinate of the corresponding reciprocal-lattice points. We may, therefore, write

$$I = I' . f(\zeta) . g^2(\sin\theta), \tag{3·1}$$

where I is the integrated reflexion intensity and I' that obtained using the intensity scale.

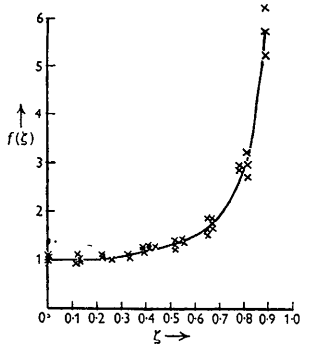


Fig. 2. Layer-line factor *v.* height of layer line.

Although the specimen used in this investigation was not spherical it was thought that it would be sufficiently regular in shape to prevent serious errors due to differential absorption. The measured intensities were corrected for polarization and Lorentz factors, and the function $f(\zeta)$ was determined as follows. Reflexions of indices ($hk0$) are recorded on the zero layer line if the crystal is oscillated about the c axis, but on the hth and kth layer lines when oscillated about the a and b axes respectively. Taking $f(0) = 1$ we therefore have

$$f(\zeta_h) = \frac{\text{sum of intensities allotted to reflexions } (hk0) \text{ on zero layer}}{\text{sum of intensities allotted to identical reflexions on } h\text{th layer}}. \tag{3·2}$$

The effect of random error of measurement is reduced by taking a ratio of sums. When values of this ratio for different layer lines were plotted against ζ they were found to lie on a smooth curve (Fig. 2). After applying this factor as a correction in the way indicated by (3·1) good agreement was obtained between measured intensities of identical reflexions recorded on different layer lines and with the crystal in different orientations, showing that differential absorption effects were not important. This procedure gave a set of numbers proportional to the F^2's, although the factor of proportionality and its variation with $\sin\theta$ was not known.

At a later stage of the analysis it became clear that a few intense reflexions were probably affected by extinction. Weissenberg photographs of a crystal about 0·1 mm. in diameter were therefore taken before and after the crystal had been immersed in liquid air, but within the limits of experimental error (about 5 % in this favourable case) all intensities, including the strongest, remained unchanged.

3·2. *Determination of the approximate crystal structure*

The shortness of the c axis made it probable that all atoms would be resolved in a projection of the structure on (001). The Patterson function

$$P(x, y) = \Sigma\Sigma\, F^2(hk0) \cos 2\pi hx \cos 2\pi ky$$

was computed and from it the x and y co-ordinates of the chlorine atoms were deduced as shown in Fig. 3. A first approximation to the electron density projected on (001) was then calculated, the probable signs of the coefficients being calculated from these chlorine co-ordinates. Successive approximations were then made in the usual manner. The function $P(x, z)$ was next computed in order to find the z co-ordinates of the chlorine atoms, but it proved difficult to interpret this projection because its small area prevented the resolution of individual peaks. At least two sets of possible co-ordinates gave broad agreement between calculated and observed structure amplitudes, so the correct z co-ordinates were finally obtained by calculating line sections through the three-dimensional Patterson function along the lines $x=2x_1$, $y=2y_1$, and $x=2x_2$, $y=2y_2$, where x_1, y_1 and x_2, y_2 are the known co-ordinates of the chlorine atoms. These showed maxima at $z=2z_1$, $z=2z_2$ respectively. Successive approximations to the electron density projected on (010) were then calculated, and a sufficient number of atoms were found to be resolved to enable co-ordinates to be assigned to all atoms on the assumption that the molecule was planar. The signs of all structure amplitudes obtainable with Cu radiation—about 1400 in number—were then calculated using these z co-ordinates and the x and y co-ordinates taken from the projection on (001), corrected for finite termination of the Fourier series as suggested by Booth (1946). Before proceeding further it seemed advisable at this stage to investigate two points—the effect of terminating the Fourier series, and the best method of dealing with extinction.

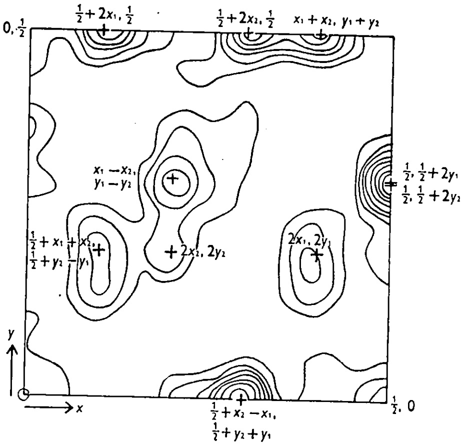


Fig. 3. Patterson projection on (001). Contours are drawn at equal intervals on an arbitrary scale. Crosses denote the sytem of vector peaks arising from chlorine atoms at $x_1, y_1=0{\cdot}20$, $0{\cdot}10$ and $x_2, y_2=0{\cdot}40$, $0{\cdot}40$. x, y is used to denote any one of the equivalent points x, y; $\bar{x}, \bar{y}$; $\bar{x}, y$; $x, \bar{y}$.

3·3. *The effect of Fourier series termination*

The termination of the Fourier series when its coefficients are still appreciable causes a spherically-symmetric maximum to be surrounded by a series of ripples of gradually diminishing amplitude. The influence of this effect on the accuracy of atomic co-ordinates obtained by the Fourier method has been fully discussed by Booth (1946), who derives an approximate expression for the background undulation on the assumption that the atomic scattering factor of an atom can be represented by the expression

$$f_r=N_r \exp\left[\frac{-\pi^2}{p}\left(\frac{\sigma}{\lambda}\right)^2\right]. \qquad (3{\cdot}3)$$

N_r is the atomic number of the rth atom, $\sigma=2\sin\theta$, and p is a constant. If the atom is centred at the origin, the electron density along the x axis is then given by

$$\rho(x,0,0)=\frac{2Np}{\pi a}\left\{\sum_{h=0}^{H}\left(\exp\left[\frac{-\pi^2h^2}{pa^2}\right]-\exp\left[\frac{-\pi^2\sigma_1^2}{p\lambda^2}\right]\right)\cos 2\pi\frac{hx}{a}\right\}, \qquad (3{\cdot}4)$$

assuming that all coefficients whose σ value is less than some specified value σ_1 are included in the synthesis (Booth, 1946, eq. (8·3), p. 88, with slight change of notation). It follows from (3·4) that this may be written

$$\rho(x,0,0)=\frac{2p}{\pi a}\sum_{0}^{H}(f_{h00}-f_{\text{lim.}})\cos 2\pi\frac{hx}{a}, \qquad (3{\cdot}5)$$

where f_{h00} is the scattering factor corresponding to the reciprocal-lattice point ($h00$) and $f_{\text{lim.}}$ is that corresponding to $\sigma=\sigma_1$. This one-dimensional Fourier series is easily evaluated, and it is found that the form of the peak and of the first few ripples is practically independent of a provided this is large compared with the diameter of the peak. In this case $\sigma_1=1{\cdot}95$; a few reflexions corresponding to greater values were recorded but were not included in the Fourier series. The value of p is to some extent at our disposal, since the method of intensity measurement gave a set of numbers (which we may denote by $G^2(hkl)$) proportional to the $F^2(hkl)$'s, but with the factor of proportionality varying with $\sin\theta$ in an unknown way. We may define the 'effective scattering factor' of a particular atom for the plane (hkl) as

$$f_e=f_0\frac{G(hkl)}{F(hkl)},$$

where f_0 is the atomic scattering factor for that atom at rest, and $F(hkl)$ is also calculated for stationary atoms. In order to find f_e for chlorine the ($h0l$) structure amplitudes were divided into groups, all of one group having approximately the same value of $\sin\theta$. The factor G/F for a particular value of $\sin\theta$ was then evaluated as $\Sigma G(h0l)/\Sigma F(h0l)$, the summation being taken over all members of the corresponding group. It should be clear that this effective scattering factor has no particular significance as its variation with $\sin\theta$ arises not only from the variation of the true scattering factor but also from the way in which the intensities have been measured. We are, therefore, at liberty to multiply the coefficients $G(hkl)$ by any factor $\alpha(\sin\theta)$ which will make $f'_e=(\alpha G/F)f_0$ vary in a reasonable way with $\sin\theta$. For instance, by taking $\alpha=F/G$ we could make $f'_e=f_0$ (α would then be equal to g as defined at (3·1)). This represents too abrupt a termination of the Fourier series, and it was found more convenient to choose α to make f'_e for a chlorine atom fit a Gaussian curve as the background undulation could then be calculated from (3·5). This was done for a number of different values of p, as defined in (3·3), the following considerations being kept in mind: (1) the amplitude of the diffraction ripples should be kept as small as possible compared with the height of the central peak, and (2) the central peak should not be too broad. A spreading of the nitrogen atoms beyond a radius of 1 A. would obscure the region in which a hydrogen atom should be looked for, while a somewhat greater spreading of any atom would directly influence the apparent position of a neighbouring one by overlapping it (Booth, 1946). These requirements are contradictory, as a sharpening of the central peak causes increased background undulation. A value of $p=7{\cdot}6$ corresponding to $f'_e=17\exp[-0{\cdot}55\,(2\sin\theta)^2]$ was chosen as the best compromise. $\rho(x,0,0)$ calculated from (3·5) with this value of f is shown in Fig. 4. a was taken as 11·91 A. This curve will overestimate the background variation around a carbon or nitrogen atom, even when the difference of scale is allowed for, as the scattering factors of these atoms fall off more rapidly than that of chlorine.

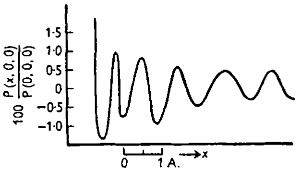


Fig. 4. Variation in background near a chlorine atom expressed as a percentage of the maximum electron density in the atom.

3·4. *Correction for extinction*

It has already been mentioned that an unsuccessful attempt to obtain better agreement between the observed and calculated values of certain strong reflexions was made by recording data from a small crystal which had been dipped in liquid air (Lonsdale, 1947). Powder photographs are of little help in this connexion as few lines are separately resolved.

For the purpose of determining more accurate atomic co-ordinates it can be shown that the effect of replacing a doubtful coefficient by its calculated value is simply to give almost zero weight to this observation (Cochran, 1948*a*). If one wishes to draw conclusions from the electron distribution, the validity of this procedure might seem questionable, but it can be established by the following argument. The mean value of

$$\big|\,|F_{\text{obs.}}(h0l)|-|F_{\text{calc.}}(h0l)|\,\big|$$

is 2·2—for comparison $F(000)=328$. In the case of the intense (040) reflexion, however, $F_{\text{obs.}}=86{\cdot}2$, $F_{\text{calc.}}=104{\cdot}0$, a difference of 17·8. Now the average contribution from the hydrogen atoms, bonding electrons, etc. is less than 2·2, as is the error of measurement since their combined mean value amounts to only 2·2. The discrepancy of 17·8 is thus too great to be reasonably attributed to anything but systematic error, and it appears that $F(040)=104{\cdot}0$, which we may expect to be in error by about 2, is to be preferred to $F(040)=86{\cdot}2$, which we suspect is in error by about 18. In the final synthesis the observed values $F(430)=84{\cdot}0$, $F(040)=86{\cdot}2$, $F(060)=114{\cdot}8$ and $F(\bar{1}21)=124{\cdot}0$ were therefore replaced by the calculated values 102·0, 104·0, 128·5 and 164·0 respectively. Finally, it may be remarked that the effect of replacing a few observed coefficients by corresponding values calculated from a distribution of spherically-symmetric atoms cannot result in atoms which depart more from spherical symmetry than would have been the case if the original coefficients had been used.

3·5. *Calculation of the electron distribution*

The electron distribution is given by the formula

$$\begin{aligned}\rho(x,y,z)=\frac{8}{V}\sum_0^H\sum_0^K\sum_0^L\Big[&\underset{h+k\text{ even}}{\{F(hkl)+F(\bar{h}kl)\}}\cos 2\pi hx\cos 2\pi ky\\ &\times\cos 2\pi lz+\underset{h+k\text{ even}}{\{F(\bar{h}kl)-F(hkl)\}}\sin 2\pi hx\cos 2\pi ky\sin 2\pi lz\\ &-\underset{h+k\text{ odd}}{\{F(hkl)+F(\bar{h}kl)\}}\cos 2\pi hx\sin 2\pi ky\sin 2\pi lz\\ &+\underset{h+k\text{ odd}}{\{F(\bar{h}kl)-F(hkl)\}}\sin 2\pi hx\sin 2\pi ky\cos 2\pi lz\Big].\end{aligned}\qquad(3{\cdot}6)$$

In order to obtain co-ordinates which would be more accurate than those given by the poorly-resolved projection on (010) the electron density along lines passing approximately through the centres of the atoms was calculated by a method similar to that described by Goodwin & Hardy (1938). Using these more accurate co-ordinates the signs of certain small terms were recalculated and a few sign changes were made. The electron density was then calculated at most points in the unit cell where it was greater than 0·5 e.A.$^{-3}$. For this purpose a punched-card method, similar to that described by Cox, Gross & Jeffrey (1947), but modified to resemble more closely the original method of Lipson & Beevers (1936), was used. The general procedure adopted was one which is particularly suitable when one crystallographic axis is much shorter than the others, as is the case here. From (3·6) we may write

$$\rho_3=\frac{8}{V}\sum_0^L[P(x,y,l)\cos 2\pi lz+Q(x,y,l)\sin 2\pi lz],\qquad(3{\cdot}7)$$

where

$$\begin{aligned}P(x,y,l)=\sum_k\sum_k&\underset{h+k\text{ even}}{\{F(hkl)+F(\bar{h}kl)\}}\cos 2\pi hx\cos 2\pi ky\\ &+\underset{h+k\text{ odd}}{\{F(\bar{h}kl)-F(hkl)\}}\sin 2\pi hx\sin 2\pi ky,\ \text{etc.}\end{aligned}$$

The nine functions P and Q for $l=0\ldots4$ were evaluated at 60×15 points, exactly as would be done by the method of Lipson & Beevers. The electron density along a line parallel to the c axis through any one of these points was then given by the one-dimensional summation (3·7). This final synthesis was generally calculated only for those points which were within about 1·5 A. of an atomic centre.

3·6. *Accurate determination of atomic co-ordinates*

The z co-ordinates were obtained by examination of the three-dimensional electron distribution, but x and y

co-ordinates were obtained from the two-dimensional distributions $P(x,y,l)$ and $Q(x,y,l)$ with $l=0$, 1 and 2. In order to understand why this was done it is necessary to examine more closely these functions and their relation to the electron distribution. Putting $l=0$ we have $Q(x,y,0)=0$ and $P(x,y,0)=\rho_2$, where ρ_2 represents the electron density projected on (001), shown in Fig. 5 (*a*). The function $Q(x,y,1)$ is shown in Fig. 5 (*b*), it is similar to ρ_2 in that peaks occur at the same points, but the height of a peak now depends on the z co-ordinate of the corresponding atom, and may be positive or negative. In general

$$\rho_3=\frac{1}{V}\sum_h\sum_k\sum_l F(hkl)\,e^{-2\pi i(hx+ky+lz)}, \qquad (3\cdot8)$$

and

$$F(hkl)=\int_V \rho_3 e^{2\pi i(hx+ky+lz)}. \qquad (3\cdot9)$$

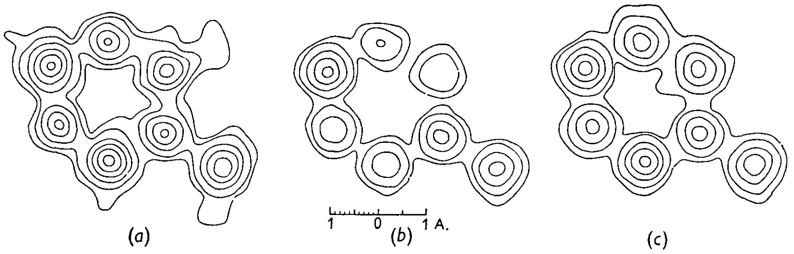


Fig. 5. Plots of the functions (*a*) $Q(x, y, 0)=\rho_2$, (*b*) $Q(x, y, 1)$ and (*c*) $|R(x, y, 1)|$ in the neighbourhood of the pyrimidine ring. The scale is arbitrary, but is the same for all three. Contours are drawn at 50, 100, 200, ... units.

If the atoms are spherically symmetric and the scattering factor of the rth atom is f_r, (3·9) may be written

$$F(hkl)=\sum_r f_r e^{2\pi i(hx_r+ky_r+lz_r)}. \qquad (3\cdot10)$$

Also

$$\rho_2=\frac{1}{A}\sum_h\sum_k F(hk0)\,e^{-2\pi i(hx+ky)},$$

which from (3·10) reduces to

$$\rho_2=\frac{1}{A}\sum_h\sum_k\left[\sum_r f_r e^{2\pi i\{h(x_r-x)+k(y_r-y)\}}\right]. \qquad (3\cdot11)$$

If the atoms are well resolved from one another, we may write, for points close to (x_r,y_r),

$$\rho_2=\frac{1}{A}\sum_h\sum_k f_r e^{2\pi i\{h(x_r-x)+k(y_r-y)\}}. \qquad (3\cdot12)$$

Now consider the function

$$R(x,y,l_1)=\frac{1}{A}\sum_h\sum_k F(hkl_1)\,e^{-2\pi i(hx+ky)},$$

which from (3·10) reduces to

$$R(x,y,l_1)=\frac{1}{A}e^{2\pi i l_1 z_r}\sum_{\substack{h\ \ k\\ l=l_1}}\sum f_r e^{2\pi i\{h(x_r-x)+k(y_r-y)\}} \qquad (3\cdot13)$$

at points close to (x_r,y_r).

The similarity to, and relationship with, ρ_2 is clear from a comparison of (3·13) with (3·11), although it should be remembered that f_r of (3·11) is that appropriate to reciprocal-lattice points for which $l=0$, while f_r of (3·13) corresponds to those for which $l=l_1$. In this case it is most convenient to calculate

$$|R(x,y,l_1)|=\{P^2(x,y,l_1)+Q^2(x,y,l_1)\}^{\frac{1}{2}}.$$

$|R(x,y,1)|$ is shown in Fig. 5 (*c*).

The advantage of this procedure is that it enables one to obtain as many independent determinations of the x and y co-ordinates as there are values of l_1, although actually R was calculated only for $l=0$, 1 and 2, as the small number of terms involved when $l=3$ or 4 did not make it worth while to evaluate the corresponding functions. The determinations are completely independent as regards experimental error since different coefficients appear in the different syntheses. That they do not have identical errors due to the termination of the series follows from the fact that the f_r's are changed and the upper limits of h and k decrease as l_1 increases. The values obtained for the x and y co-ordinates of the atoms by inspection of the functions $R(x,y,0)$, $R(x,y,1)$ and $R(x,y,2)$ are given in Table 2. z co-ordinates obtained from the three-dimensional synthesis are also given. By comparing individual determinations with the mean value, the standard deviation of the mean is found to be 0·0037 A. for chlorine and 0·014 A. for carbon or nitrogen co-ordinates. A further test of the accuracy of the co-ordinates can be obtained by testing

Table 2. *Independently determined atomic co-ordinates*

(All values in A.)

Atom	x_0	x_1	x_2	Mean x	y_0	y_1	y_2	Mean y	z
Cl_2	2·368	2·376	2·372	2·373	1·359	1·357	1·373	1·361	−0·001
Cl_6	4·760	4·756	4·762	4·759	5·489	5·484	5·489	5·487	2·239
N_1	3·714	3·706	3·676	3·700	3·351	3·346	3·337	3·346	1·118
N_3	4·959	4·959	4·947	4·956	1·452	1·445	1·433	1·445	0·486
N_4	7·265	7·237	7·249	7·247	1·377	1·387	1·384	1·384	0·745
C_2	3·887	3·869	3·881	3·877	2·175	2·161	2·159	2·164	0·613
C_4	6·066	6·096	6·130	6·098	2·048	2·024	1·997	2·024	0·922
C_5	6·078	6·080	6·114	6·088	3·295	3·323	3·300	3·312	1·497
C_6	4·883	4·869	4·869	4·873	3·850	3·873	3·931	3·882	1·553

the planarity of the molecule. If all atoms lie in a plane, we may write $z=Ax+By+C$ and find the best values of A, B and C by the method of least squares. When this was done, comparatively large deviations were found unless the observations for N_4 (the extra-ring nitrogen) were excluded from the least-squares solution. Taking all others into consideration, and giving the observations of chlorine co-ordinates four times the weight of others, the result $z=0{\cdot}03439x+0{\cdot}10261y-1{\cdot}0154$ was obtained. In the following table the observed z co-ordinates are compared with those calculated from this equation:

Atom ...	Cl_2	Cl_6	N_1	N_3	N_4
Obs. z (A.)	−0·001	2·239	1·118	0·486	0·745
Calc. z (A.)	−0·002	2·239	1·106	0·477	0·853
Deviation (A.)	+0·001	0	+0·012	+0·009	−0·108

Atom ...	C_2	C_4	C_5	C_6
Obs. z (A.)	0·613	0·922	1·497	1·553
Calc. z (A.)	0·613	0·937	1·504	1·547
Deviation (A.)	0	−0·015	−0·007	−0·006

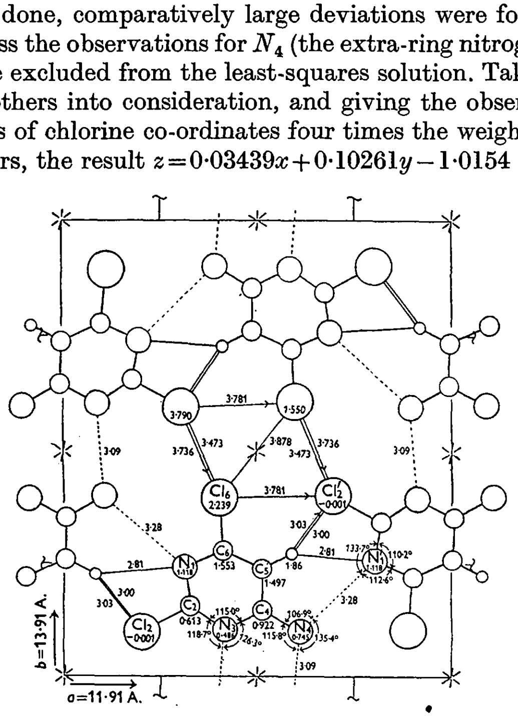


Fig. 6. Structure of 4-amino-2,6-dichloropyrimidine projected on (001). z co-ordinates are given in A. Full lines represent van der Waals contacts, dotted lines hydrogen bonds. Arrow-heads indicate that the bond is to an atom in the unit cell above.

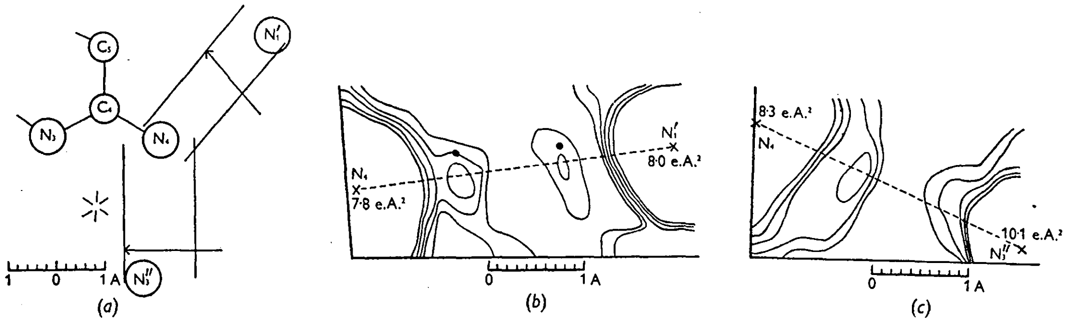


Fig. 8. (a) A section from Fig. 6. The electrons between planes represented by the two sets of lines are projected in the directions of the arrows on to vertical planes. The resulting electron distributions are shown in (b) and (c). Contours are drawn at 2/6, 3/6, ... 6/6 e.A.$^{-2}$.

The molecule is, therefore, planar within the limits of experimental error, apart from N_4, which is definitely displaced from the plane containing the other atoms. Bond lengths and angles calculated from these co-ordinates are shown in Fig. 10 (*b*), and intramolecular bonds are shown in Fig. 6, which is a projection of the structure on (001).

3·7. *The electron distribution*

The electron distribution in the plane of the molecule was obtained by drawing straight lines

$$z=0{\cdot}03439x+0{\cdot}10261y-1{\cdot}0154$$

across the maps on which the three-dimensional distribution was recorded; the electron density in this plane could then be read off by interpolation. This could be done quite accurately as $\rho(x,y,z)$ was evaluated at an interval of 0·063 A. in the c direction. The result is shown in Fig. 7. A correction has been made within circles of radius 1·5 A. drawn about the centres of each of the chlorine atoms by subtracting the background undulation shown in Fig. 4. The effect of this is to change the electron densities in regions midway between chlorine and adjacent carbon atoms from negative to positive values.

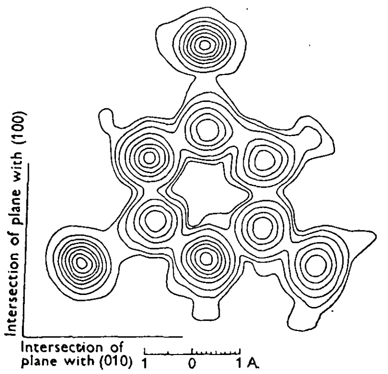


Fig. 7. The electron distribution in the plane of the molecule. Contours are drawn at ½, 1, 2, 4, ... e.A.$^{-3}$ and ½, 5, 10, ... e.A.$^{-3}$ in chlorine atoms.

It will be seen that a definite maximum of height 1·3 e.A.$^{-3}$ occurs in this plane at a distance of 1·06 A.

from C_5 and in a direction from C_5 which approximately bisects the angle $C_4C_5C_6$. This is exactly the position in which one would expect to find a hydrogen atom. Two smaller maxima occur close to N_4 and two others are just over 1 A. distant from N_1 and N_3 respectively. Examination of the complete three-dimensional synthesis shows that the very small peak adjacent to N_1 has a maximum height of 0·8 e.A.$^{-3}$ at a point somewhat below the molecular plane, while the one close to N_4, which has the greater y co-ordinate, reaches a maximum of 1·0 e.A.$^{-3}$, also at a point below the molecular plane. This is shown more clearly in Fig. 8 (b, c), in which the electrons between planes represented by two sets of lines in Fig. 8(a) are projected on to two vertical planes parallel to these lines. The black dots in Fig. 8 (b) are the positions which would be occupied in this projection by 'bulges' on N_4 and N_1' if they were directed from the centres of the atoms in a direction parallel to the planes of their respective molecules. It appears that the observed maxima lie more closely along the line joining N_4 to N_1'.

3·8. *Accuracy of results*

The standard deviations of atomic co-ordinates have already been derived, and correspond to standard deviations in bond length of 0·02 for C–C, C–N or N–N, 0·015 for C–Cl and 0·005 A. for Cl–Cl bonds. For angles involving only C or N atoms the standard deviation is 1·2°, and is somewhat less if a chlorine atom is involved. Greater interest attaches to the question of how far the observed variations of electron density can be relied on, and in particular whether peaks which could be interpreted as hydrogen atoms, etc., might be due to experimental error or to the termination of the Fourier series. It can be shown (Cochran, 1948b) that the random error in the electron density caused by random errors

Table 3. *Observed and calculated structure amplitudes*

4-amino-2,6-dichloropyrimidine			5-bromo-4,6-diaminopyrimidine		
Indices	$F_{\text{calc.}}$	$F_{\text{obs.}}$	Indices	$F_{\text{calc.}}$	$F_{\text{obs.}}$
000	328	—	000	368	—
200	5·3	7·1	200	−70	58
400	−47·5	50·1	400	90	89
600	−17·3	14·4	600	31	47
800	−19·5	21·7	800	−21	16
10,0,0	77·5	68·7	10,0,0	58	55
12,0,0	6·7	0	12,0,0	−77	65
14,0,0	−8·0	5·1	14,0,0	24	21
110	6·0	3·9	16,0,0	−19	20
210	57·4	51·0	$\overline{16}$,0,1	7	5
310	−42·9	47·4	$\overline{14}$,0,1	2	0
410	32·0	24·6	$\overline{12}$,0,1	64	56
510	13·3	19·3	$\overline{10}$,0,1	−30	27
610	−33·0	30·5	$\bar{8}$01	−84	82
710	−37·0	32·1	$\bar{6}$01	37	35
810	−21·1	18·4	$\bar{4}$01	−31	30
910	18·4	13·9	$\bar{2}$01	32	38
10,1,0	−23·2	24·5	001	55	53
11,1,0	8·7	0	201	−149	108
12,1,0	4·5	0	401	132	116
13,1,0	−13·6	11·3	601	−42	31
14,1,0	4·7	6·6	801	3	0
15,1,0	1·1	6·0	10,0,1	16	18
020	−26·6	30·0	12,0,1	−43	34
120	−31·3	31·1	14,0,1	40	36
220	−17·0	19·0	16,0,1	−30	27
320	90·2	90·9	$\overline{16}$,0,2	26	30
420	−24·8	26·6	$\overline{14}$,0,2	−11	14
520	2·0	0	$\overline{12}$,0,2	−8	16
620	−30·0	31·4	$\overline{10}$,0,2	43	45
720	−75·8	75·0	$\bar{8}$02	−102	99
820	0·0	0	$\bar{6}$02	95	98
920	21·6	30·1	$\bar{4}$02	−124	117
10,2,0	1·3	0	$\bar{2}$02	14	18
11,2,0	6·0	0	002	−53	59
12,2,0	−10·1	8·2	202	−56	59
13,2,0	19·0	13·7	402	95	103
14,2,0	−1·4	0	602	−119	111
15,2,0	3·6	0	802	94	78
			10,0,2	−26	26
			12,0,2	24	20
			14,0,2	23	20
			16,0,2	−17	15

The above sections from the complete sets of calculated and observed values were not specially chosen. For the first compound

$$\Sigma \mid F_{\text{obs.}} - F_{\text{calc.}} \mid / \Sigma \mid F_{\text{obs.}} \mid = 0{\cdot}17,$$

and for the second

$$\Sigma \mid F_{\text{obs.}} - F_{\text{calc.}} \mid / \Sigma \mid F_{\text{obs.}} \mid = 0{\cdot}11.$$

$\beta(hkl)$ in the measured values of $F(hkl)$ can be characterized by a standard deviation

$$\Delta = (32\pi\overline{\beta^2}/3V\lambda^3)^{\frac{1}{2}}. \qquad (3\cdot14)$$

An upper limit to the value of $(\overline{\beta^2})^{\frac{1}{2}}$ is got by taking $(\overline{\beta^2})^{\frac{1}{2}} = (\overline{(F_o - F_c)^2})^{\frac{1}{2}} = 2\cdot75$. This is an upper limit since $F_{\text{obs.}}$ and $F_{\text{calc.}}$ differ not only because of experimental error, but also because in calculating $F_{\text{calc.}}$ the atoms have been taken to be spherically symmetric and the hydrogen contributions have been ignored. A selection from the set of calculated and observed structure amplitudes is given in Table 3. A lower limit to the value of $(\overline{\beta^2})^{\frac{1}{2}}$ is got by comparing the intensities given to identical reflexions which can be produced by oscillating the specimen about more than one crystallographic axis. This gave $(\overline{\beta^2})^{\frac{1}{2}} = 1\cdot18$, which is probably too low as it takes no account of possible systematic errors. On substitution in (3·14) we obtain $0\cdot33 > \Delta > 0\cdot14$ e.A.$^{-3}$. In addition to this, variations in the electron density due to finite termination must be considered. It appears from Fig. 4 that the amplitude of the ripple in the neighbourhood of a chlorine atom is at most 1·5 % of the height of the peak, decreasing to 0·5 % at a distance of 3 A. The observed heights of the chlorine peaks are 36·9 and 36·8 e.A.$^{-3}$. We may therefore assume that at a distance of more than 3 A. from a chlorine atom the background undulation will not exceed 0·19 e.A.$^{-3}$, and will not exceed 0·37 e.A.$^{-3}$ at any point. The ripples around carbon or nitrogen atoms, which have an amplitude of less than one-third of those around chlorine, will make smaller contributions to the variation in background. When the independent systems of ripples from all the atoms are combined, and the effect of experimental error is taken into account, a reasonable estimate of the standard deviation is 0·5 e.A.$^{-3}$. Confirmation is provided by the fact that the deepest minimum observed in the electron density was −0·5 e.A.$^{-3}$, points within 1·5 A. of the chlorine centres being excluded. A further indication is obtained by comparing the maximum densities in the atoms. Although chemical binding results in a redistribution of charge, this does not affect the electron density near the nucleus. Maximum electron densities in chemically similar atoms may differ, however, if they have different amplitudes of thermal vibration, but we may expect all atoms in the ring to have the same temperature factor. The values given below were obtained by extrapolation from Fig. 7, assuming a parabolic distribution near the atomic centre:

Atom ...	Cl_2	Cl_6	N_1	N_3	N_4
Maximum density (e.A.$^{-3}$)	36·9	36·8	12·8	12·9	9·3

Atom ...	C_2	C_4	C_5	C_6
Maximum density (e.A.$^{-3}$)	9·4	9·4	9·2	9·6

The closeness of the agreement suggests that the figure 0·5 e.A.$^{-3}$ is an overestimate of the standard deviation.

4. The structure of 5-bromo-4,6-diaminopyrimidine

The structure of this compound was determined by two-dimensional Patterson and Fourier methods, similar to those described in Part I and in the earlier part of this paper. In the projection on (010) all atoms are separately resolved, while a sufficient number are resolved in the (001) projection to give the orientation of the molecule on the assumption that it is planar. Atomic co-ordinates are given in Table 4 and a selection from the set of calculated and observed structure amplitudes in Table 3. Fig. 9 shows the structure projected on (010), while Fig. 10(*c*) shows intramolecular bond lengths and angles calculated from the co-ordinates given above. The value of $\sum | F_{\text{obs.}} - F_{\text{calc.}} | / \sum | F_{\text{obs.}} |$ is 0·11, compared with the value 0·17 for the structure already described. This does not mean that the former is more accurate, but is due to the fact that errors in the measured *F*'s tend to be absolute rather than proportional. We may take the standard deviation of atomic co-ordinates to be 0·03 A., the same as that of the co-ordinates of 4-amino-2,6-dichloropyrimidine taken from the projection on (001). The standard deviation of bond lengths between light atoms is then about 0·04 A., but we may expect the Br–Br distance of 3·352 A. to have a standard deviation of less than 0·01 A. The comparatively large variations in the background of the Fourier projection on (010) show that no reliable conclusions can be drawn from the electron distribution in this case. It may be assumed, however, that the hydrogen on C_2 is at a distance of 1·06 A. from C_2 and in a direction from the latter which bisects the angle $N_1C_2N_3$.

Table 4. *Atomic co-ordinates*

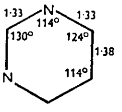
Atom	*x* (A.)	*y* (A.)	*z* (A.)
Br	6·15	0·12	1·49
N_1	5·01	1·59	4·98
C_2	3·64	1·51	4·55
N_3	2·95	1·03	3·38
C_4	3·73	0·63	2·51
C_5	5·12	0·69	2·80
C_6	5·73	1·16	4·03
N_4	2·98	0·17	1·29
N_6	7·06	1·20	4·40

5. Discussion

The following abbreviations are used in describing the compounds discussed in this section:

A—2-amino-4,6-dichloropyrimidine (Part I),
B—4-amino-2,6-dichloropyrimidine,
C—5-bromo-4,6-diaminopyrimidine.

It is clear from Fig. 10 that the ring nucleus of these compounds preserves certain features almost unchanged. For instance, C–N bond lengths within the ring have a mean deviation of only 0·015 A. from the average value, 1·328 A.; the angle $N_1C_2N_3$ does not vary by more than 2° from 130° and the angles $C_6N_1C_2$ and $C_2N_3C_4$ do not vary greatly from their mean value of 113°. *A* and *C* are symmetrical within the limits of experimental error, but the unsymmetrical arrangement of substituents in *B* causes the ring to depart from a symmetrical arrangement. For instance, $N_3C_4C_5 = 119{\cdot}5°$, but $C_5C_6N_1 = 127{\cdot}4°$, while the mean value of these angles is 124°, taking observations on all three compounds into consideration. In general, a chlorine in the 2, 4 or 6 position causes the corresponding angle to be increased by 2 or 3° from the values 130° for the 2 position and 124° for the 4 and 6 positions, while the attachment of an amino group causes a decrease of about the same amount. We may, therefore, with some justification predict that pyrimidine itself, in which all substituents are hydrogens, will have the dimensions shown here:



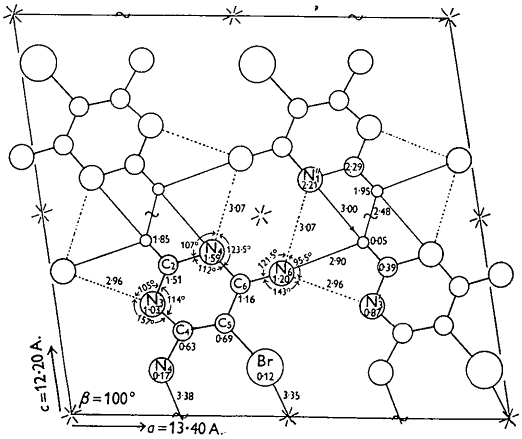


Fig. 9. Structure of 5-bromo-4,6-diaminopyrimidine projected on (010). Notation as in Fig. 6.

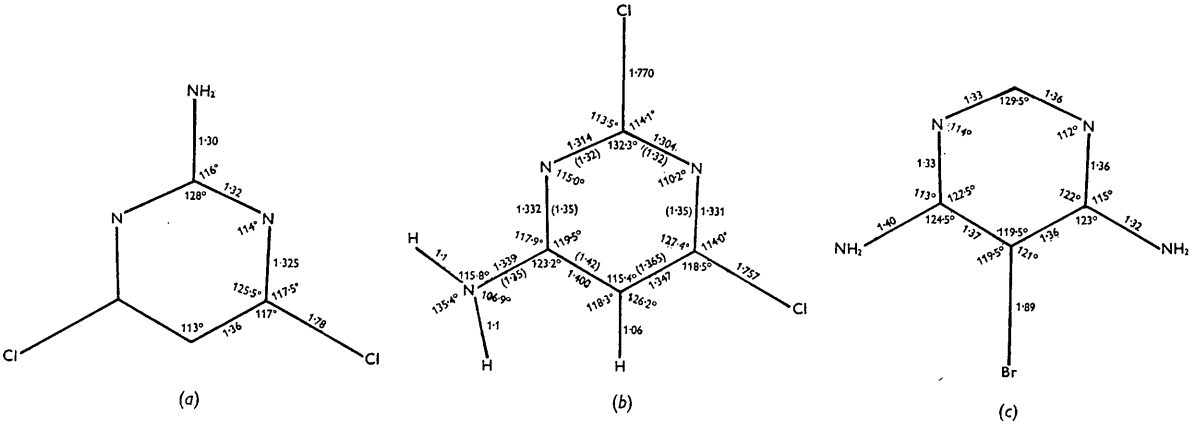


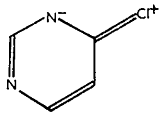
Fig. 10. Dimensions of the molecules of (*a*) 2-amino-4,6-dichloro-, (*b*) 4-amino-2,6-dichloro-, and (*c*) 5-bromo-4,6-diaminopyrimidine. Values in parentheses in (*b*) are calculated (see p. 56).

The similarity of the crystal structures of these compounds is apparent from Fig. 5 (Part I) and Figs. 6 and 9 (this paper). In every case the molecules are held together by hydrogen bonds between an amino group and a ring nitrogen of each of two adjacent molecules, the separation of the nitrogen atoms being $3{\cdot}2 \pm 0{\cdot}2$ A. These hydrogen bonds are close to the plane of the molecule to which the substituent nitrogen belongs, as is one of the other molecules involved. For example, in Fig. 6 the plane of one molecule passes within 0·02 A. of the centre of symmetry at $(\frac{1}{2}, 0, 0)$, and is therefore also the plane of the molecule which is related to the first by the operation of this centre of symmetry. The second hydrogen bond from the amino group, however, generally meets the ring nitrogen of the third molecule involved so as to make a comparatively large angle with the plane of this molecule—at N_3 in Fig. 9 for instance. In the structure of *C* only one amino group is involved in this type of intermolecular bonding, while the other makes two contacts, each of length 3·38 A., with identical amino groups related to the first by the operation of a screw axis. The large difference between the corresponding $C\text{–}NH_2$ distances (1·32 and 1·40 A.) may be connected with this difference in environment of the two amino groups.

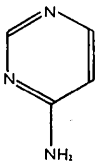
Turning to the problem of the nature of the hydrogen bond in these compounds three interpretations of the observed electron distribution seem to be possible. The small peaks adjacent to an amino nitrogen which have heights of 1·0 e.A.$^{-3}$, and those which are close to ring nitrogens and have heights of 0·8 e.A.$^{-3}$, might all be due to the two hydrogens normally associated with the amino group. Since the observed electron distribution is an average over a long period of time and over the whole crystal, this leaves open the question whether the hydrogens can be exchanged over a distance of about 1·0 A., or whether the structure contains different kinds of molecules, some in the aminopyrimidine form and some in each of the two iminodihydropyrimidine forms. In other words, we cannot distinguish between a static and a dynamic randomness in the positions of the hydrogen atoms. In the structures of *B* and *C* the 'normal' hydrogens attached to C_5 and C_2 respectively make van der Waals contacts of 3·00 and 3·03 with chlorine atoms, 2·81, 2·90 and 3·00 with nitrogen atoms and 2·48 A. with each of two other hydrogen atoms. These all point to hydrogen having a van der Waals radius of 1·2 A. It follows that two nitrogen atoms separated by just over 3 A. cannot both have an attached hydrogen atom directed along the line joining them, as would be bound to happen sometimes if the different kinds of molecules occurred randomly throughout the structure. The arrangement of the hydrogens in any sort of super-lattice seems intuitively somewhat improbable. The other view, that the hydrogens can change position, would appear to receive support from Hunter's results on 'mesohydric tautomerism' (1945). However, although it is thought possible that, for instance, in ice (Owston & Lonsdale, 1948) under normal conditions of thermal vibration protons can jump from one position of minimum potential energy to an equivalent position a few tenths of an angstrom away, the potential maximum which they would have to cross in this case is bound to be larger since the distance is about 1 A.

Neither of these views is in complete accord with the experimental results, for the following reason. The 'normal' hydrogen at position 5 has been found to have a maximum electron density of 1·3 e.A.$^{-3}$, while that in each of the peaks close to N_4 is 1·0 e.A.$^{-3}$. However, the latter atom has a greater amplitude of thermal vibration than the nitrogens in the ring since its maximum density is 9·3 compared with 12·9 e.A.$^{-3}$ in both ring nitrogens. As the attached hydrogen atoms will be spread out by this increased thermal motion we should expect their maximum density to be reduced in about the same ratio, giving the observed value of 1·0 e.A.$^{-3}$ and accounting for the peaks adjacent to N_4 without having to assume that they are fractional. It might appear that a better way of settling this point would be to make an electron count rather than to rely on maximum densities, but this is not practicable because of the merging of these peaks with the adjacent large nitrogen peaks. This leaves unexplained the peaks of maximum density 0·8 e.A.$^{-3}$ close to the ring nitrogens and directed along the lines joining them to an adjacent amino group. Pauling (1945, p. 289) has, however, emphasized the importance for hydrogen bond formation of an unshared electron pair on the atom more distant from the proton, and if these electrons were in a hybrid orbit which carried them well out from the nitrogen atom in a direction giving maximum interaction with the proton of an amino group this would be an explanation of the observed electron distribution.

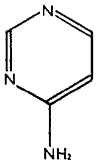
If this interpretation is correct, the molecule is in the aminopyrimidine form, and the measured bond lengths must be accounted for on this assumption. To begin with, the C–Cl bond lengths are all 1·77 ± 0·01 A., in good agreement with the value 1·76 A. for a pure single bond. It follows that resonance structures such as



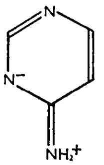
make no appreciable contribution to the state of the molecule. This is an unexpected result, as accepted theories predict the conjugation of an 'unshared' electron pair on the chlorine atom with the aromatic nucleus. The extra-ring C–N bond is much shorter than the single-bond distance of 1·47 A., however, and we may expect the main contributions to come from the structures



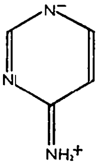
(III)



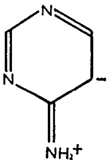
(IV)



(V)



(VI)



(VII)

The Kekulé structures (III) and (IV) must make equal contributions, as will (V) and (VI). (VII) may be expected to make a smaller contribution than (V) or (VI) because of the decreased electronegativity of carbon compared with nitrogen. Satisfactory agreement with the observed bond lengths is in fact got by ignoring (VII) and assuming that (III), (IV), (V) and (VI) contribute in the ratio 2 : 2 : 1 : 1. Bond lengths calculated on this assumption with the help of Pauling's (1945, p. 174) curve relating bond length and double-bond character are shown in parentheses in Fig. 10 (*b*). These are consistently 0·01 or 0·02 A. greater than the observed values (also shown in Fig. 10 (*b*)), but are otherwise in excellent agreement. Better agreement would not be obtained by altering the ratio in which (III)... (VI) contributed, since all involve three double bonds, while the observed bond lengths correspond to 3·6 double bonds distributed over the molecule, but this difference may simply be due to experimental error. The charge distribution associated with (V) and (VI) will have the effect of increasing the strength of the hydrogen bonds.

In Part I it was suggested that the unusually close distance of approach of chlorine atoms in adjacent molecules might be due to strong interactions between these molecules through the hydrogen bonds. Another example of this occurs in the structure of *C*, where the Br–Br separation is 3·352 A., about 0·5 A. less than the normal van der Waals diameter; also in spite of its considerable amount of double-bond character the bond C_4–N_4 in *B* is deflected from the plane of the ring by 4°, a deflexion which is clearly due to forces acting on N_4 in the directions of the hydrogen bonds.

Our best thanks are due to Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their continued interest and encouragement, to Prof. A. R. Todd, Dr J. Baddiley and Dr G. Kenner for the preparation of the specimens and for advice on chemical matters, and to Mrs Coslett and Mrs Musgrave for assistance with the computation. We also wish to thank Dr M. V. Wilkes for placing the facilities of the University Mathematical Laboratory at our disposal. One of us (W. C.) is indebted to the Department of Scientific and Industrial Research for financial aid and the other (C. J. B. C.) to the managers of the I.C.I. Fellowship Fund of the University of Cambridge for the award of a fellowship.

References

Baddiley, J., Lythgoe, B. & Todd, A. R. (1943). *J. Chem. Soc.* p. 571.

Booth, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.

Bradley, A. J. (1935). *Proc. Phys. Soc., Lond.*, **47**, 879.

Brill, R., Hermann, C. & Peters, C. (1942). *Ann. Phys., Lpz.*, **42**, 357.

Clews, C. J. B. & Cochran, W. (1948). *Acta Cryst.* **1**, 4.

Cochran, W. (1948*a*). *Nature, Lond.*, **161**, 765.

Cochran, W. (1948*b*). *Acta Cryst.* **1**, 54.

Cox, E. G., Gross, L. & Jeffrey, G. A. (1947). *Proc. Leeds Phil. Lit. Soc.* **5**, 1.

Cox, E. G. & Shaw, W. F. B. (1930). *Proc. Roy. Soc.* A, **127**, 71.

Goodwin, T. H. & Hardy, R. (1938). *Phil. Mag.* **25**, 1096.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

Hunter, L. (1945). *J. Chem. Soc.* p. 806.

Lipson, H. & Beevers, C. A. (1936). *Proc. Phys. Soc., Lond.*, **48**, 772.

Lonsdale, K. (1947). *Miner. Mag.* **28**, 14.

Owston, P. G. & Lonsdale, K. (1948). *J. Glaciol.* **1**, 118.

Pauling, L. (1945). *The Nature of the Chemical Bond.* Cornell: University Press.

Weisz, O., Cochran, W. & Cole, W. F. (1948). *Acta Cryst.* **1**, 83.

Wheland, G. W. (1944). *Theory of Resonance.* New York: Wiley.

Acta Cryst. (1949). **2**, 57

Crystal Chemical Studies of the 5*f*-Series of Elements. VI. The Ce_2S_3–Ce_3S_4 Type of Structure

By W. H. Zachariasen

Argonne National Laboratory and the Department of Physics, University of Chicago, Illinois, U.S.A.

(*Received* 28 *October* 1948)

The compounds Ce_2S_3, La_2S_3, Pu_2S_3, Ac_2S_3 and Am_2S_3 are shown to be iso-structural. The structure is cubic with sixteen sulfur atoms and $10\frac{2}{3}$ metal atoms per unit cube. The unit-cell constant for the prototypic compound Ce_2S_3 is $a=8{\cdot}6173\pm0{\cdot}0005$ kX.

The metal atoms are randomly distributed over twelve-fold positions such that on the average every ninth site is vacant. The space group is $I\bar{4}3d$–T_d^6 and the atomic positions are:

$$(0,\ 0,\ 0),\ (\tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2})+;\quad 10\tfrac{2}{3}\ \mathrm{Ce\ in}\ (\tfrac{1}{4},\ \tfrac{3}{8},\ 0)\circlearrowleft;\quad (\tfrac{3}{4},\ \tfrac{1}{8},\ 0)\circlearrowleft.$$

$$16\ \mathrm{S\ in}\ (x,\ x,\ x);\quad (x+\tfrac{1}{2},\ \tfrac{1}{2}-x,\ \bar{x})\circlearrowleft;\quad (x+\tfrac{1}{4},\ x+\tfrac{1}{4},\ x+\tfrac{1}{4});\quad (\tfrac{3}{4}+x,\ \tfrac{1}{4}-x,\ \tfrac{3}{4}-x)\circlearrowleft;$$

$$\text{with } x=0{\cdot}083\pm0{\cdot}015.$$

For Ce_2S_3 the homogeneity range of the phase extends to the composition Ce_3S_4 corresponding to all metal sites being filled.

The X-ray diffraction studies of micro-preparations of plutonium compounds showed at an early stage that plutonium in crystal chemical respect was closely related to the lighter elements of the lanthanide group. In order to facilitate the task of chemically identifying plutonium compounds available only in microgram amounts by means of their X-ray diffraction patterns it became of importance to investigate the crystal structure of lanthanum and cerium compounds. Ce_2S_3 was one of the first compounds to be studied as part of this program.

A preparation of Ce_2S_3 was obtained through the courtesy of the late Prof. E. D. Eastman. Prof. L. Brewer of the University of California had made the preparation and checked the composition by direct chemical analysis. The sample was in the form of finely divided red-brown powder. Dr A. Novick carried out a direct density determination and found

$$\rho=5{\cdot}25\pm0{\cdot}10\,\mathrm{g.cm.}^{-3}$$

The crystal structure of Ce_2S_3

Single crystals not being available, the crystal structure investigation had to be carried out with the aid of data from powder diffraction patterns. The observations were taken with Cu *K* radiation filtered through nickel foil.

Table 1 gives a complete list of the diffraction lines as observed in the original powder photograph. The cylindrical specimen was at the center of a cylindrical film camera. In Table 2 are given a series of recent measurements obtained with the Norelco Spectrometer using a specimen of the briquet type.

The tables show that the observed sine squares correspond to a cubic body-centered translation lattice. The unit-cell constant, as determined from the back-reflection region for a Ce_2S_3 sample which had been made with cerium of very high purity, is

$$a=8{\cdot}6173\pm0{\cdot}0005\,\mathrm{kX}.$$