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The Crystal Structure of Cytidine

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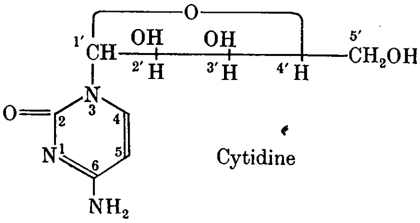
Crystals of cytidine, $C_9H_{13}O_5N_3$, are orthorhombic with $a=13{\cdot}93$, $b=14{\cdot}75$, $c=5{\cdot}10$ A. The space group is $P2_12_12_1$, and the unit cell contains four molecules. Atomic co-ordinates were postulated by extensive use of structure-factor graphs, supported by chemical and physical data, and then refined by two-dimensional Fourier syntheses. Direct confirmation is given that cytidine may be described as cytosine-3-β-D-ribofuranoside. The pyrimidine ring is found to be planar, whereas the D-ribose ring is non-planar with one of its atoms lying about 0·5 A. from the plane containing the four remaining atoms. The central C–N bond lies in the plane of the pyrimidine ring and makes tetrahedral angles with the adjacent ring bonds in the D-ribose. Evidence is found for a weak intramolecular hydrogen bond between the 5′-hydroxyl group in the D-ribose and a (CH) group in the pyrimidine.

The molecules are held together in the crystal by a very comprehensive system of hydrogen bonds, each molecule taking part in ten such external linkages.

Introduction

As a component of the nucleic acids, cytidine is a compound of great biological interest, and a knowledge of its structure would appear to be of value in furthering an understanding of these complex substances. Its chemical formula is well established. The sugar is in the furanose condition, and the configuration at the *N*-glycosidic centre is almost certainly of the β-type (Davoll, Lythgoe & Todd, 1946). Very little is, however, known about the steric relationships in cytidine and the other nucleosides. Astbury (1947) suggested on basis of X-ray studies of fibres of Na-thymonucleate that the pyrimidine ring is parallel to the ribose ring, but no X-ray investigation of the nucleosides themselves is reported in the literature. The precise structure of some pyrimidines is, however, known from X-ray investigations by Pitt (1948) and Clews & Cochran (1949). The carbohydrate D-ribose has not been studied crystallographically, but Beevers & Cochran (1947) have worked out the structure of sucrose sodium bromide dihydrate, which contains a furanose ring (fructofuranoside), and we have thus some stereochemical information about each of the two components of cytidine.



Cytidine

No crystalline derivative containing a heavy atom was available, and the analysis had therefore to be carried out on cytidine itself. This tends to complicate the first stages of the structure determination, but in the end gives probably a more reliable structure than in those cases where a heavy atom is employed.

Preliminary investigation

A sample of cytidine was kindly supplied by Dr D. O. Jordan, University of Nottingham. Several techniques were tried in order to grow crystals big enough for X-ray work, the best results being obtained by letting a solution of cytidine in an alcohol–water mixture evaporate slowly.

The crystals had the shape of prisms, elongated along the c axis, bounded by $\{110\}$ and, more rarely, $\{100\}$. No end-faces were observed, and the crystals were on the whole rather poorly developed.

An optical investigation showed that the crystals are orthorhombic with $\alpha \parallel c$, $\beta \parallel b$ and $\gamma \parallel a$. The birefringence is weakly positive and the optic axial angle about 70°, measured in glycerine.

Oscillation and Weissenberg photographs were taken, and the following cell dimensions were derived:

$$a=13{\cdot}93,\quad b=14{\cdot}75,\quad c=5{\cdot}10\ \text{A}.$$

These values are correct to about 0·5 %. Copper radiation ($\lambda=1{\cdot}54$ A.) was used throughout the investigation.

The molecular weight of cytidine is 243, the cell volume 1048 A.^{3}, and the density $1{\cdot}53_2$ g.cm.$^{-3}$. There are thus four molecules per unit cell (calc. 3·98).

The X-ray photographs show that odd-order reflexions of the types $h00$, $0k0$ and $00l$ are absent. No other systematic absences occur, and the space group

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is therefore $P2_12_12_1$. The asymmetric unit in the crystal consists of one molecule of cytidine, and all atoms occupy general positions in the cell.

Determination of the structure factors $F_{\text{obs.}}$

Weissenberg photographs were taken about the three principal axes. A crystal of length 0·3 mm. and with a cross-section of 0·08 × 0·08 mm. was used for the *c*-axis photograph. For the *a*- and *b*-axis photographs the same crystal was cut in order to get approximately a square cross-section perpendicular to these axes too. Long exposures of about 130 hr. were needed. The important *c*-axis photograph recording the *hk*0 reflexions was good, whereas the *a*- and *b*-axis photographs were rather weak owing to the smallness of the crystals. In all 160 *hk*0, 45 0*kl* and 42 *h*0*l* reflexions were recorded.

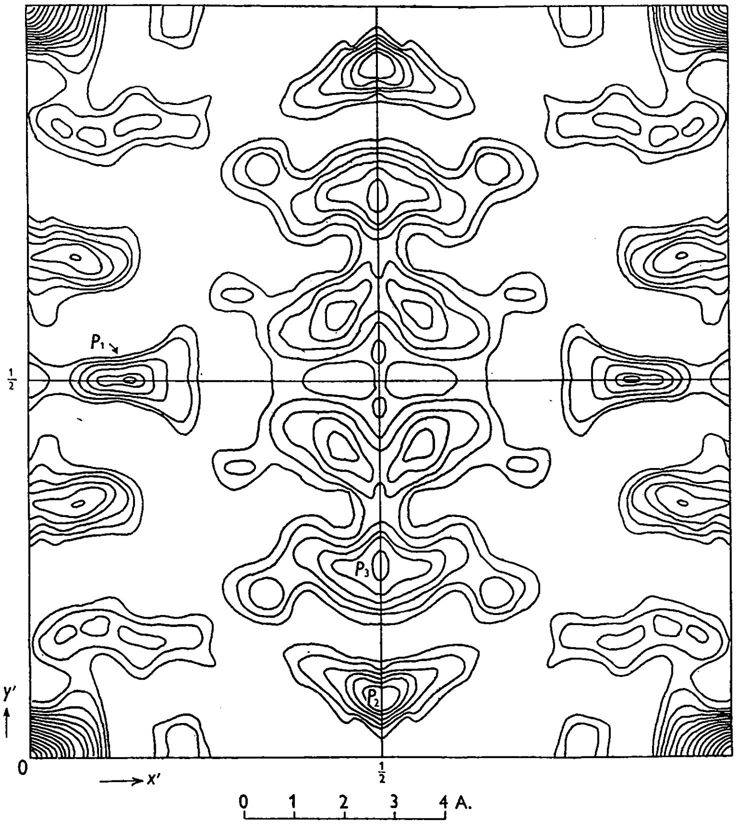

Fig. 1. Patterson projection in direction of *c* axis. Calculated at $\frac{1}{60}$th of *a* and *b* axes.

The usual multiple-film technique and eye estimation of the intensities were applied. The relative values for $I_{\text{obs.}}$ were then corrected for the Lorentz polarization factor, but not for absorption or extinction. They were converted to an absolute scale later by comparison of observed and calculated structure factors.

Determination of the *c* projection of the structure

Because of the shortness of the *c* axis it was decided to find first the *x* and *y* co-ordinates by means of a projection parallel to this axis. In order to determine the phase angles it was essential to postulate an approximately correct structure before the Fourier refinements could be carried out. This was by far the most difficult stage in the structure analysis of cytidine. Its formula, $C_9O_5N_3H_{13}$, shows that thirty-four parameters have to be determined, excluding hydrogen atoms. Not many structure determinations of this type are reported in the literature, and we thought therefore that it might be of value to describe in some detail the reasoning and the methods employed to arrive at the approximate structure.

Evidence from many different sources was collected and correlated, as summarized below:

(*a*) The chemical formula of cytidine is established. The precise stereochemistry is unknown, but we know how the atoms are linked together.

(*b*) The bond lengths and bond angles are known approximately from X-ray work on pyrimidines and sugars, and a tentative model can therefore be made. The freedom of rotation about the central bond greatly increases the number of possible configurations, although steric hindrances make several positions unlikely.

(*c*) The *c* axis is only 5·10 A., and the molecules are therefore likely to lie roughly parallel to the *c* plane, without overlapping each other seriously.

(*d*) The optical investigation confirms this, as α is parallel to the c axis. The positive birefringence indicates, however, a considerable tilt in the pyrimidine rings in relation to each other. The γ vibration direction is parallel to the x axis, suggesting that the molecule is more stretched out in this direction than in the direction of the y axis.

(*e*) In organic structures of this type with active groups (OH, NH_2, N, CO) the molecules are always found to be linked together by hydrogen bonds of length 2·6–3·0 A. Any postulated structure must have the possibility of hydrogen-bond formation.

(*f*) Consideration of the available space and the packing of the molecules is important, and was done by models. Many positions could be ruled out in this way.

(*g*) The Patterson projection is shown in Fig. 1 for one unit cell. The peaks at $x'=\frac{1}{2}$ (P_2 and P_3) and at $y'=\frac{1}{2}$ (P_1) are of special importance, as they are likely to be due mainly to vectors between equivalent atoms, and indicate at which distances from the screw axes most atoms are situated. The elongated peak P_1 stretching from $x'=0$ to $x'=c.\ 0{\cdot}25$ shows thus that most of the atoms must lie round about the screw axes parallel to the y axis, whereas the peaks P_2 ($y'=0{\cdot}08$) and P_3 ($y'=0{\cdot}25$) point towards concentrations of atoms at distances 0·04 and 0·125 from the screw axes parallel to the x axis. A more detailed interpretation of a vector map of such a complex structure is very difficult, but the information obtained, scanty as it may seem, proved to be valuable.

(*h*) The most important and direct approach is, however, the consideration of the structure factors. If the origin is chosen at one of the apparent centres of symmetry, the structure factors are given by

$$F=\Sigma 4f\cos 2\pi hx\cos 2\pi ky \qquad \text{for } h+k \text{ even,}$$

$$F=-\Sigma 4f\sin 2\pi hx\sin 2\pi ky \qquad \text{for } h+k \text{ odd.}$$

The low-order reflexions with large spacings determine the position of the molecule, whereas the high-order ones are related to details within the molecule.

The seven reflexions of lowest order, namely, 110, 200, 210, 310, 020, 120 and 130, were studied first. As only rough values of $F_{\text{calc.}}$ are needed at this stage, the calculations were carried out by means of structure-factor graphs and 'master keys' (Bragg & Lipson, 1936; compare also Bunn, 1948), the difference in scattering power between C, N and O being ignored. The graphs were not made square, but matched to the unit cell, and could therefore be used directly in conjunction with molecular models. Rough 'master keys' of any shape and size were constructed rapidly by a graphical method. Very comprehensive trials were carried out in this way, considering only the seven above-mentioned planes. The trials lead to the conclusion that the molecule was likely to be situated roughly in the area outlined in Fig. 3, a result which also is consistent with the Patterson analysis, the optics, and space considerations.

Two very strong high-order planes, 14,0,0 and 160, were then considered. The spacing of 14,0,0 is 0·99 A., and this repeat distance is found in the pyrimidine ring, the dimensions of which are known, if the ring is placed with one pair of edges parallel to the y direction and slightly tilted. A study of the structure-factor graph for 160 helped to fix the y co-ordinates. The structure-factor graphs for 14,0,0 and 160 are drawn out in Fig. 2. In order to show their relationship to intramolecular distances, the correct c projection of the molecule is included in the same figure.

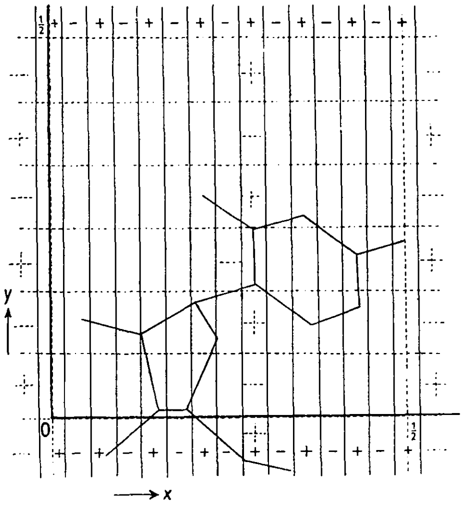

Fig. 2. The structure-factor graphs for 14,0,0 (full lines and signs) and 160 (broken lines and signs), and their relation to intramolecular distances. Notice that nearly all atoms lie on positive 14,0,0 and 160 areas.

On the basis of a careful consideration of all the factors mentioned above ((*a*) to (*h*)), the structure shown in Fig. 3 was postulated. The agreement between $F_{\text{obs.}}$ and $F_{\text{calc.}}$ was poor, but the corresponding electron-density map (Fig. 3) was nevertheless calculated. The map does not look encouraging, as several atoms appear to lie in regions of low electron density, whereas there are areas of high density where no atoms are placed. This holds particularly for the area A. A new structure was therefore postulated by rotating the D-ribose ring about the central bond N_3–C_1', bringing the CH_2OH group, the 'tail' of the molecule, on to the area A. These shifts were supported by extensive use of structure-factor graphs. With the new set of coordinates there was some measure of agreement between $F_{\text{obs.}}$ and $F_{\text{calc.}}$, and the corresponding Fourier map gave a good picture of the molecule. From now on the ordinary refining process was followed, and after fifteen successive approximations the final electron-density map shown in Fig. 4 was obtained. During the refinement the value of the reliability factor

$$R=(\Sigma\,\|F_{\text{obs.}}|-|F_{\text{calc.}}\|)/\Sigma\,|F_{\text{obs.}}|$$

remained very high for a long while. In the second approximation R was about 0·60, and after the seventh refinement had dropped only to 0·53. From now on the process became speedier, and the value of R decreased in the successive refinements in the following way: 0·48, 0·43, 0·35, 0·29, 0·24, 0·21, 0·19, 0·17. In Table 3 $F_{\text{obs.}}$ and $F_{\text{calc.}}$ are compared for 225 $hk0$ reflexions. The contribution from the hydrogen atoms is ignored.

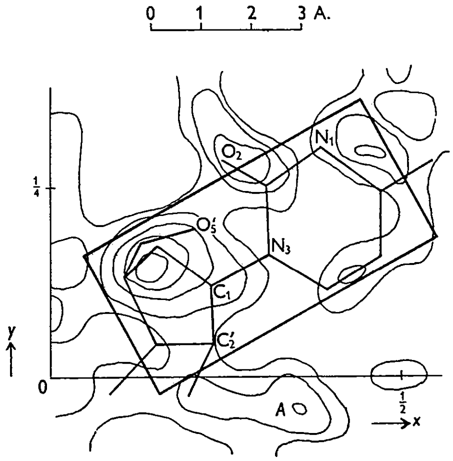

Fig. 3. The first postulated structure and the corresponding electron-density map.

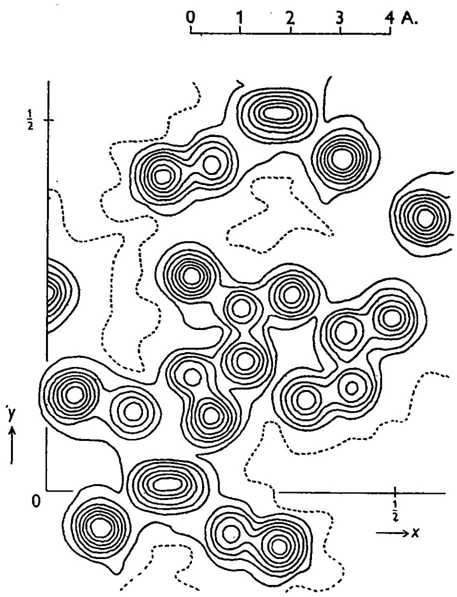

Fig. 4. Final projection in direction of c axis. Contours at intervals of 1 e.A.$^{-2}$, the unit contour line being dotted. The electron density is calculated at $\frac{1}{60}$th of a and b axes.

For the atomic scattering factor f the values given by Robertson (1935) are used.

The interpretation of the electron-density map in Fig. 4 is obvious from a comparison with Fig. 7, which shows the corresponding projection of the molecule. All the atoms, except C_3' and C_4', are resolved, and the three kinds of atoms can be distinguished by their different peak heights, which have the following values for the resolved atoms:

Oxygen: 450, 440, 435, 450 and 440.
Nitrogen: 365, 385 and 395.
Carbon: 325, 335, 340, 310, 355, 315 and 325.

The x and y co-ordinates of all the resolved atoms, as well as the y co-ordinates of C_3' and C_4', can be found directly from the map. The x co-ordinates of C_3' and C_4' were determined in the following way: A section parallel to the $(x\,z)$ plane at $y = 0{\cdot}011$ shows the shape of the composite peak of C_3' and C_4', as their y co-ordinates happen to be the same (0·011). This section was compared with the curves obtained by compounding two theoretical Fourier peaks for different distances between the atomic centres. It was convenient to use the standard shape of a Fourier peak as given in a paper by Booth (1946). In this way it was found that C_3' and C_4' lie about 0·5 A. apart. Their co-ordinates are, however, less reliable than those of the other fifteen atoms.

The atomic co-ordinates are collected in Table 1.

Table 1. *Atomic co-ordinates as fractions of the corresponding cell edge*

Atom	x	y	z
C_6	0·431	0·214	0·05
C_2	0·281	0·246	0·21
C_4	0·368	0·122	0·375
C_5	0·438	0·140	0·21
C_1'	0·203	0·153	0·55
C_4'	0·189	0·011	0·75
C_3'	0·150	0·011	0·47
C_2'	0·124	0·109	0·42
C_5'	0·265	0·941	0·83
O_2	0·205	0·291	0·21
O_1'	0·235	0·103	0·77
O_5'	0·332	0·926	0·645
O_3'	0·075	0·948	0·45
O_2'	0·035	0·129	0·54
N_1	0·352	0·266	0·04
N_3	0·285	0·175	0·38
N_6	0·499	0·232	0·88

Determination of the z co-ordinates

Figs. 5 and 6 show the Fourier projections in the direction of the a and b axes respectively, and their interpretation. The origin is shifted compared with Fig. 4, so as to make it fall at an apparent centre of symmetry in all projections.

The a projection was worked out first. The knowledge of the y co-ordinates and the great strength of the reflexions 051 and 0,12,3 facilitated the task very much. As shown on Fig. 5, eight out of seventeen atoms are at least partly resolved (N_3, C_5, O_1', C_4', O_3', C_5', O_5', C_3'), and z co-ordinates are indicated for three more atoms, namely, O_2, C_1' and O_2'. In the b projection very bad molecular overlap occurs, but it gives nevertheless values for the z co-ordinates of C_4 and O_5', and, with less accuracy, those for the atoms C_6, N_6, C_1' and O_3'. The position of C_2, N_1 and C_2' cannot be derived from either of the two projections, and was determined by trials on the a projection. In view of the small number of reflexions available and the high degree of overlap, the z co-ordinates are on the whole less reliable than the x and y co-ordinates, and can only be given to two-figure accuracy (see Table 1). The reliability factor R has the value 0·19 in both the a and b projections.

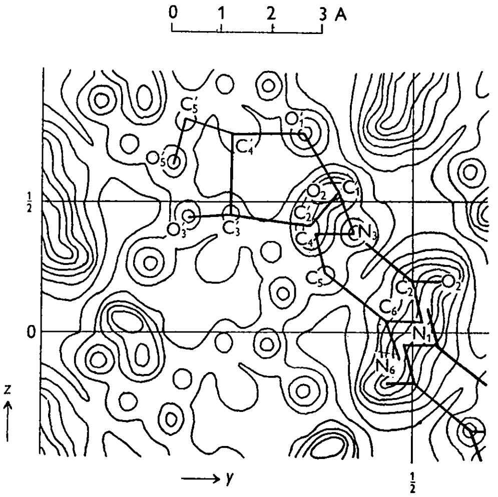

Fig. 5. Fourier projection in direction of a axis. Contours at intervals of 2 e.A.$^{-2}$, the first one being omitted. Calculated at $\frac{1}{60}$th of b axis and $\frac{1}{30}$th of c axis.

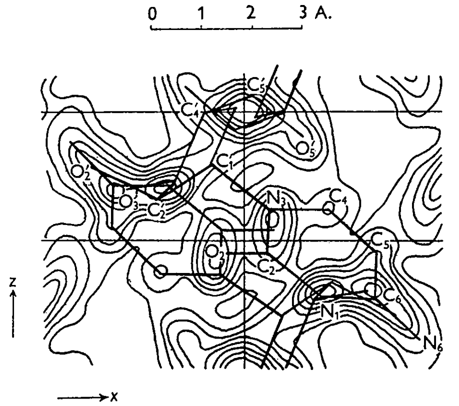

Fig. 6. Fourier projection in direction of b axis. Contours at intervals of 2 e.A.$^{-2}$, the first one being omitted.

Description and discussion of the structure

The bond lengths and bond angles calculated from the co-ordinates in Table 1 are given in Fig. 7. The bond lengths are also collected in Table 2. It is hard to estimate the limits of error, but the error in the bond lengths is probably about 0·04 A., and the maximum possible error less than about 0·1 A.

The molecular structure

The c projection of the molecule (Fig. 7) establishes directly the nature of the N-glycosidic linkage, as the bonds C_1'–N_3 and C_2'–O_2' are in the *trans* position. Cytidine may thus be described as cytosine-3-β-D-ribofuranoside.

The six atoms of the pyrimidine ring, as well as N_6, O_2 and C_1', all lie in the same plane within the experimental error. The bond lengths in the ring vary from 1·32 to 1·39 A., and the bond angles are all near 120°. Similar values are also found by the investigators mentioned in the introduction. The C_2–O_2 distance is 1·25 A., not far from the accepted value for a double bond C=O (1·21 A.). The bond from the ring to the amino group, C_6–N_6, is also short, 1·31 A., whereas the third bond from the ring, N_3–C_1', is shown to be a single bond of length 1·47 A.

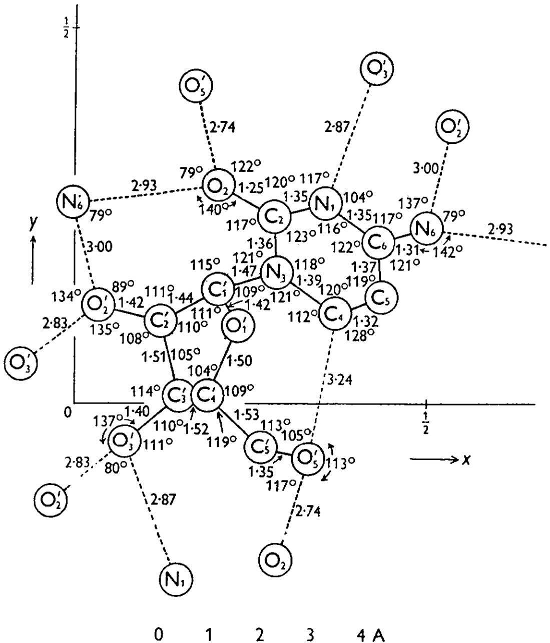

Fig. 7. The c projection of one molecule of cytidine and its nearby contacts, with bond lengths (in Ångström units) and bond angles. Hydrogen bonds are shown as broken lines.

Table 2. *Bond lengths in cytidine*

(Values in Ångström units)

C–C bonds		C–N bonds	
C_4–C_5	1·32	C_6–N_1	1·35
C_5–C_6	1·37	N_1–C_2	1·35
C_1'–C_2'	1·44	C_2–N_3	1·36
C_2'–C_3'	1·51	N_3–C_4	1·39
C_3'–C_4'	1·52	C_6–N_6	1·31
C_4'–C_5'	1·53	N_3–C_1'	1·47

C–O bonds	
C_2–O_2	1·25
C_1'–O_1'	1·42
C_4'–O_1'	1·50
C_2'–O_2'	1·42
C_3'–O_3'	1·40
C_5'–O_5'	1·35

Four of the atoms of the D-ribose ring lie nearly in one plane, namely, C_1', O_1', C_2' and C_4', but the fifth member of the ring, C_3', is out of this plane by about 0·5 A., and this makes the hydroxyl group $(OH)_3'$ fall rather accurately on to the plane. The same feature was found by Beevers & Cochran (1947) in the case of fructofuranoside. All the angles of the D-ribose are found to be near the tetrahedral angle; the only considerable deviation (119°) occurs between the bonds C_3'–C_4' and C_4'–C_5'. This angle is, however, very sensitive to errors in the x co-ordinates of C_3' and C_4', which are rather unreliable (see above).

The three C–OH distances are found to be 1·42, 1·40 and 1·35 A.

The central bond N_3–C_1' lies in the plane of the pyrimidine ring, and forms angles of 109° and 115° with the adjacent ring bonds in the D-ribose. Contrary to Astbury's suggestion of the two rings being parallel, they are oriented in such a way that they are nearly *perpendicular* to each other. This would seem to be a point of considerable importance for the understanding of the structure of the nucleic acids.

The distance between the atom C_4 in the pyrimidine and O_5' in the D-ribose is only 3·24 A., which is considered by the author to be significantly less than the normal van der Waals approach of 3·4–3·5 A. This would seem to indicate some kind of attraction between the two atoms, possibly of the hydrogen-bond type. The relative position of C_4 and O_5' is also what we should expect in the case of bond formation, as a line joining them makes an angle of 105° with the bond C_5'–O_5' and only about 10° with the plane of the pyrimidine ring, a deviation probably due to the influence of the keto group of a neighbouring molecule, which is only 2·74 A. away. The hydroxyl group $(OH)_5'$ takes part in only one intermolecular hydrogen bond, whereas $(OH)_2'$ and $(OH)_3'$ both are engaged in *two* such bonds. All the hydroxyl groups of sucrose also make two external bonds (Beevers & Cochran, 1947). The proposed intramolecular bond thus gives $(OH)_5'$, the 'normal' number of hydrogen bonds.

The reason for the formation of the bond may be sought in a possible polarization of the group $(CH)_4$ by the electronegative substituents in the pyrimidine ring.

The intermolecular bonding scheme

As was to be expected, the molecules are held together in the crystal by an extensive system of hydrogen bonds. All the active groups—$(NH_2)_6$, N_1, O_2, $(OH)_2'$, $(OH)_3'$ and $(OH)_5'$—are engaged in the formation of these bonds. This is illustrated in Fig. 7 for one molecule, and in Fig. 8 for a greater part of the structure. The bond lengths and bond angles are found in Fig. 7.

The main stabilizing force in the z direction is an alternating zigzag chain of O–H...O bonds of length 2·83 A. between groups $(OH)_2'$ and $(OH)_3'$. In each molecule there is a bond from $(OH)_2'$ upwards to $(OH)_3'$ in a neighbouring molecule, and from $(OH)_3'$ downwards to $(OH)_2'$ in the molecule immediately below the neighbouring molecule. Each of these two hydroxyl groups is also engaged in a bond of the type N–H...O.

The keto group is linked to the $(OH)_5'$ group and the amino group in different neighbouring molecules. The bond to $(OH)_5'$ is the shortest intermolecular bond in the structure (2·74 A.), and lies nearly in the plane of the pyrimidine ring, whereas the bond to the amino group makes an angle of about 35° with this plane.

The configuration at the amino group is interesting, as it is found to be planar within the experimental error, and nearly symmetrical. Two hydrogen bonds of length 2·93 and 3·00 A. form linkages to O_2 and $(OH)_2'$ in another molecule, and both lie in the plane of the pyrimidine ring.

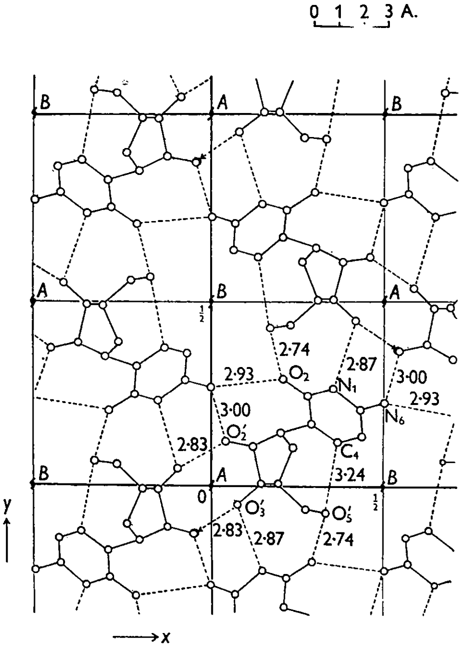

Fig. 8. The c projection of the structure. Hydrogen bonds are shown as broken lines. ⇢o One atom with another directly below (slightly displaced to show where the linkages end).

The ring atom N_1 is at a distance of 2·87 A. from an $(OH)_3'$ group. The bond lies, however, not in the plane of the ring, but forms an angle of about 35° with it. Such deviations are only to be expected in a complicated system like the one we are dealing with.

In general the molecule has one 'active' side extending in a wide half-circle from $(OH)_5'$ to N_6, and one short 'neutral' side from $(OH)_5'$ to C_6 (see Figs. 7, 8). In each molecule ten external bonds are attached to the active side, forming relatively short zigzag chains, starting at each group $(OH)_5'$ and finishing at the atom N_1 in another molecule, as shown schematically in Fig. 9.

The active groups create a very close packing around every alternate one of the screw axes parallel to the z axis, whereas there are 'holes' in the structure around the others, where the 'neutral' sides of the molecules are lying opposite to each other. This feature is clearly illustrated in Fig. 8, where the shortest distance between corresponding atoms across the apparent centres of symmetry is only 2·5 A. in the 'active' case (marked *A*), and as much as 4·5 A. in the 'neutral' case (marked *B*).

There is no evidence from the Fourier maps with regard to the positions of the hydrogen atoms in the structure. Pauling (1940) has, however, pointed out that in a hydrogen bond X–H. . . Y the rules of stereochemistry apply with smaller force to the atom Y than to the atom X. The hydrogen atom is, in other words, likely to be found about 1 A. from the atom where the bond angles are least distorted. If this rule is applied to the crystal structure of cytidine, we get the picture given in Fig. 9. It is interesting to notice that there are two hydrogen atoms bonded to N_6, but none either to N_1 or O_2. We have thus crystallographically, though admittedly in a very indirect way, obtained evidence in favour of the amino form for the molecule in the crystal.

In the present structure hydrogen bonds occur between quite a variety of electronegative groups. It would therefore appear to be of interest to compare the lengths of the different types of hydrogen bonds:

	Type of bond		Bond length (A.)
(1)	O (hydroxyl)–O (keto)		2·74
(2)	O (hydroxyl)–O (hydroxyl)		2·83
(3)	O (hydroxyl)–N (ring)		2·87
(4)	O (hydroxyl)–N (amino)		3·00
(5)	N (amino)–O (keto)		2·93
(6)	O (hydroxyl)–C_4	(intramolecular)	3·24

It should be noted that the bonds to the keto group, (1) and (5), are shorter than the corresponding bonds, (2) and (4), to a hydroxyl group.

No intermolecular distance in the structure, other than the hydrogen bonds mentioned above, is shorter than 3·45 A.

The chemical aspects of the structure will be discussed more fully elsewhere.

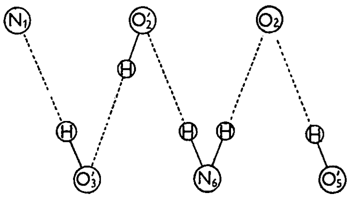

Fig. 9. The chains of hydrogen bonds in the crystal structure of cytidine, with the supposed position of the hydrogen atoms (schematically).

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

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
200	55	−67	120	38	−49	11,3,0	5	+4
400	26	+23	220	14	−11	12,3,0	6	+7
600	9	+4	320	17	−15	13,3,0	4	+6
800	8	−8	420	32	−30	14,3,0	10	−10
10,0,0	3	−5	520	29	−24	15,3,0	10	+12
12,0,0	4	−6	620	8	−4	16,3,0	5	+8
14,0,0	15	+16	720	4	+3			
16,0,0	<2	+1	820	<2	−3	040	3	−0
			920	17	−14	140	25	+27
110	40	+29	10,2,0	14	−13	240	10	−10
210	17	+21	11,2,0	12	−12	340	12	+12
310	<1	−2	12,2,0	9	+10	440	5	+0
410	28	+27	13,2,0	13	+12	540	24	+25
510	6	−4	14,2,0	13	−12	640	23	+20
610	17	−12	15,2,0	<3	+2	740	8	+6
710	6	−2	16,2,0	<2	+2	840	9	−6
810	3	−1				940	14	−12
910	<3	+0	130	37	+35	10,4,0	9	+10
10,1,0	5	−7	230	38	−41	11,4,0	9	−10
11,1,0	<3	−1	330	27	−21	12,4,0	10	+11
12,1,0	13	−16	430	31	+33	13,4,0	<3	+1
13,1,0	<3	−3	530	6	+2	14,4,0	10	+11
14,1,0	<3	+2	630	9	−12	15,4,0	<3	+3
15,1,0	<3	+2	730	19	−16	16,4,0	<2	−2
16,1,0	4	+5	830	14	−7			
			930	3	−4	150	11	−13
020	17	−26	10,3,0	14	−14	250	9	+8

Table 3 (*cont.*)

hkl	$F_{obs.}$	$F_{calc.}$
350	30	−28
450	27	+21
550	9	−11
650	7	+6
750	29	+25
850	<3	−1
950	23	−22
10,5,0	3	+2
11,5,0	4	+6
12,5,0	<3	+1
13,5,0	<3	+0
14,5,0	3	+1
15,5,0	<2	−1
16,5,0	5	+6
060	31	−26
160	55	+50
260	<2	−0
360	12	+8
460	<2	−3
560	14	+11
660	<2	+2
760	<3	−1
860	22	−19
960	12	+9
10,6,0	8	+8
11,6,0	<3	+2
12,6,0	11	−11
13,6,0	4	−5
14,6,0	<3	−0
170	20	+21
270	<2	−3
370	18	−17
470	18	+20
570	37	+39
670	6	+6
770	5	−5
870	5	−7
970	<3	+3
10,7,0	<3	+1
11,7,0	<3	+5
12,7,0	<3	−1
13,7,0	<3	−4
080	22	+26
180	17	−17
280	12	+12
380	12	+11
480	3	−6
580	14	+15
680	14	+15
780	21	−21
880	12	+13
980	6	+7
10,8,0	5	−5
11,8,0	5	−6
12,8,0	6	−8
13,8,0	<3	+4
190	4	−3
290	13	+12
390	20	−21
490	9	−7
590	8	+8
690	<3	−3
790	12	+8
890	<3	−3
990	<3	+0
10,9,0	<3	−0
11,9,0	10	−11
12,9,0	6	−7
13,9,0	<2	−0
14,9,0	<2	+2
15,9,0	8	−11
0,10,0	<3	−4
1,10,0	8	−13
2,10,0	13	−11
3,10,0	16	−16
4,10,0	6	−7
5,10,0	<3	−2
6,10,0	5	+5
7,10,0	4	−5
8,10,0	4	+4
9,10,0	5	−6
10,10,0	<3	+0
11,10,0	6	+5
12,10,0	<3	−3
1,11,0	<3	+2
2,11,0	8	−8
3,11,0	<3	+0
4,11,0	5	+4
5,11,0	<3	+2
6,11,0	6	−7
7,11,0	<3	+1
8,11,0	3	+5
9,11,0	4	+5
10,11,0	7	−8
11,11,0	<3	+0
0,12,0	<3	−3
1,12,0	18	−21
2,12,0	17	−17
3,12,0	4	+6
4,12,0	4	+2
5,12,0	8	+8
6,12,0	8	+11
7,12,0	4	+6
8,12,0	<3	+1
9,12,0	6	−7
10,12,0	3	+3
11,12,0	4	+5
1,13,0	3	−6
2,13,0	6	−6
3,13,0	10	−12
4,13,0	10	−12
5,13,0	<3	+0
6,13,0	7	+9
7,13,0	<3	+1
8,13,0	<3	−1
9,13,0	<3	−1
10,13,0	9	+10
11,13,0	<2	−3
0,14,0	4	+6
1,14,0	10	−8
2,14,0	4	+4
3,14,0	11	+9
4,14,0	<3	−2
5,14,0	6	−6
6,14,0	5	+5
7,14,0	<3	+2
8,14,0	11	−12
9,14,0	9	+9
10,14,0	<2	−1
1,15,0	<3	−0
2,15,0	9	−8
3,15,0	9	+10
4,15,0	12	+13
5,15,0	<3	+4
6,15,0	6	−4
7,15,0	<2	+2
8,15,0	4	+3
9,15,0	<2	+2
0,16,0	4	+6
1,16,0	<3	+3
2,16,0	<3	−0
3,16,0	10	−9
4,16,0	<2	−1
1,17,0	4	+4
2,17,0	<2	−3
3,17,0	<2	−3
0,18,0	5	+7
011	10	−13
021	14	+19
031	46	−52
041	15	−14
051	63	−67
061	22	−13
071	6	−6
081	14	−13
091	8	+8
0,10,1	16	−15
0,11,1	7	−10
0,12,1	5	+7
0,13,1	6	+6
0,14,1	<4	−5
0,15,1	<4	+3
0,16,1	<4	−1
002	<3	+4
012	21	+21
022	<3	+2
032	4	+5
042	<3	−1
052	15	+10
062	10	−8
072	8	+9
082	<4	+2
092	8	+8
0,10,2	10	+9
0,11,2	<4	+2
0,12,2	<4	−5
0,13,2	7	−6
0,14,2	<4	−1
0,15,2	6	+7
0,16,2	<3	−0
0,17,2	11	+10
0,18,2	3	−3
013	14	+12
023	12	+10
033	<4	−2
043	<4	−1
053	4	−6
063	<4	+1
073	10	+11
083	14	+13
093	<4	+5
0,10,3	<4	−2
0,11,3	<4	−1
0,12,3	20	−19
0,13,3	<4	+2
0,14,3	<3	+1
0,15,3	6	−8
004	7	+7
014	<4	+3
024	<4	−3
034	9	−11
044	<4	+8
054	<4	−2
064	<4	−5
074	<3	−1
084	11	+10
094	<3	−1
015	10	−10

Table 3 (*cont.*)

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$
025	13	−15	12,0,1	6	+ 8	503	5	+ 9
035	<4	− 0	13,0,1	21	−19	603	6	− 3
045	<4	+ 7	14,0,1	<4	+ 0	703	16	−15
055	<4	+ 4				803	7	+ 8
			102	7	+ 4	903	<4	− 5
006	4	− 4	202	49	+48			
016	<3	+ 1	302	20	+15	104	7	− 5
026	<3	− 1	402	40	+36	204	<4	+ 5
036	7	−10	502	30	−30	304	6	− 9
046	<3	+ 1	602	15	+11	404	6	+ 3
			702	<3	− 1	504	12	+12
101	5	+ 8	802	<4	− 2	604	<4	+ 7
201	51	+60	902	20	−24	704	7	+ 3
301	39	−36	10,0,2	10	− 9			
401	40	−32	11,0,2	<4	− 3	105	<4	+ 3
501	<3	− 0	12,0,2	<4	− 1	205	5	+ 5
601	12	+ 8	13,0,2	6	+ 5	305	11	− 9
701	<3	+ 4				405	<4	− 0
801	9	− 8	103	20	−19	505	<4	− 5
901	13	− 8	203	29	−33			
10,0,1	<4	− 1	303	11	+ 9	106	4	+ 8
11,0,1	8	− 7	403	14	−12	206	<3	+ 0

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The Covalent Bond in Diamond and the X-ray Scattering Factor of Covalent-Bonded Carbon

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By Fourier synthesis it was found that the change which a carbon atom undergoes forming a covalent bond consists in concentrating about one-half to three-quarters of one electron of the outer shell in every chemical bond. An X-ray atomic scattering curve is given for the covalent-bonded carbon atom.

Precision measurements of the X-ray diffraction patterns of diamond show appreciable deviations from the theoretical values for the atomic scattering power of carbon as given by both Hartree and Pauling (Brill, Grimm, Hermann & Peters, 1939). Fig. 1 shows the Hartree (H) and Pauling (P) scattering curves and the measured values. These deviations may be caused by lack of spherical symmetry of the carbon atom in the diamond lattice or by the inaccuracy of the theoretical curves even for the spherical atom.

Because the knowledge of the scattering curve for the carbon atom is important for the determination of atomic arrangements in organic compounds, it seemed worth while to investigate the significance of the differences between the experimental and the theoretical values. This was tried by means of a two-dimensional Fourier synthesis of the projection on the 110 plane of the diamond lattice, using these differences as amplitudes according to

$$\begin{aligned}\Delta\rho(x, z) &= \rho(x, z)_{\text{exp.}} - \rho(x, z)_{\text{theor.}} \\ &= \frac{1}{f}\sum_{h}\sum_{l} \Delta F_{h0l} \exp\left[2\pi i(xh+zl)\right].\end{aligned}$$

The indices in this formula are referred to a tetragonal cell with $a_1 = a\sqrt{2}$ and $c_1 = a$, where a means the length of the cubic elementary cell of diamond. (The indices

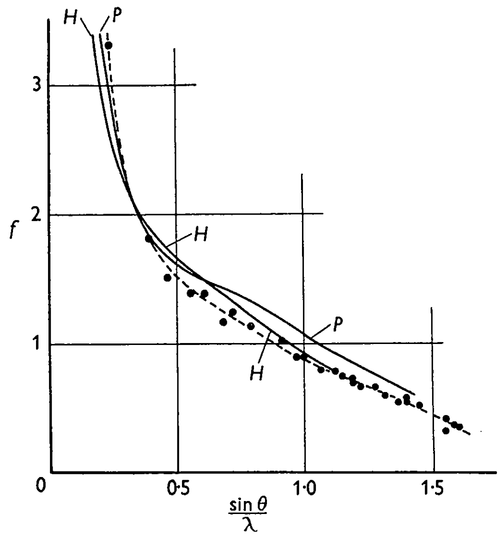

Fig. 1. Comparison of measured atomic scattering factors (dots) and the Hartree (H) and Pauling (P) scattering curves.

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