Acta Cryst. (1961). **14**, 965

The Crystal Structure of Calcium Thymidylate

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(*Received* 9 *June* 1960)

Crystals of the hexahydrate of calcium thymidylate, $C_{10}H_{13}O_8N_2CaP.6\,H_2O$, are monoclinic, with

$$a_0 = 14{\cdot}40 \pm 0{\cdot}02,\ b_0 = 6{\cdot}87 \pm 0{\cdot}01,\ c_0 = 9{\cdot}81 \pm 0{\cdot}01\ \text{Å},\ \beta = 90°58' \pm 3'\ .$$

The space group is $P2_1$, with one formula weight comprising the asymmetric unit. The structure was solved by analysis of a sharpened three-dimensional Patterson function and was refined by Fourier and least squares methods. During the early stages of refinement strong correlations were noted between errors in position parameters and the apparent values of corresponding vibration parameters. After seven least squares cycles, as apparent convergence was being approached, it was discovered that the sign of one of the eighty-four position parameters (for one of the water molecules) was wrong; when it was corrected, changes of as much as three e.s.d. occurred at once in bond distances not involving the wrongly placed atom. Refinement was completed with five more least squares cycles. The final e.s.d.'s of bond distances vary from 0·011 Å for the Ca–O and P–O bonds to an average of 0·023 Å for the C–C distances; for the bond angles, e.s.d.'s vary from 0·7 to 1·4°.

The six atoms of the pyrimidine ring are planar, with the four attached atoms (which occur in adjacent pairs) alternately above and below the plane of the ring by 0·05–0·10 Å. These displacements, and even more the significant distortions of the corresponding extra-ring angles, increase the distances between the atoms in these two pairs by about 0·1 Å. The deoxyribose ring is puckered, with C3′ 0·53 Å from the plane of the other four atoms. The phosphate group has about the expected dimensions; the P–O ester bond is 0·07 Å longer than any of the other P–O bonds. The environment of the calcium ion is much like that in $CaHPO_4$, a distorted pentagonal bipyramid, with two water molecules on the axis and four phosphate oxygens (from three different molecules) and one water molecule in the central plane. The entire structure is held together by the Ca–O bonds and a complex network of hydrogen bonds; all but one of the fourteen hydrogen atoms which might participate in hydrogen bonding appears to do so, although the precision of the determination is not sufficient to permit unambiguous location of all the hydrogen atoms.

The deoxyribose ring makes an angle of 75° with the plane of the thymine nucleus. The conformation of the thymidylate about the glycosidic C–N bond is intermediate between that in the DNA model of Crick & Watson (1954) and that suggested by Langridge *et al.* (1957); the latter two models differ by about 70° in this conformational parameter. The disposition of the C5′–O5′–PO_3 chain is much like that in the model of Langridge *et* al., although it appears that there would not be an appreciable energy barrier to rotation of this group to other positions. The planes of the thymine nuclei in adjacent molecules along the screw axis are about 12° from a parallel orientation, with the average spacing between them 3·4 Å, and the closest approach 3·20 Å.

The general pattern of anisotropic thermal vibrations deduced from the analysis is reasonable in terms of the packing and orientation of the components of the structure, but absorption errors in the data prevented any precise detailed analysis of thermal anisotropies.

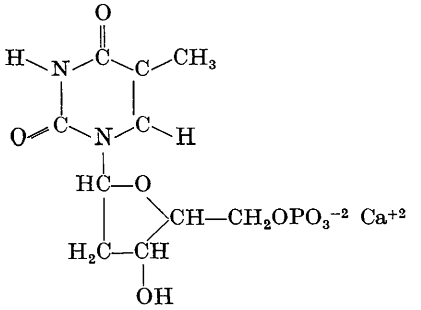
Introduction

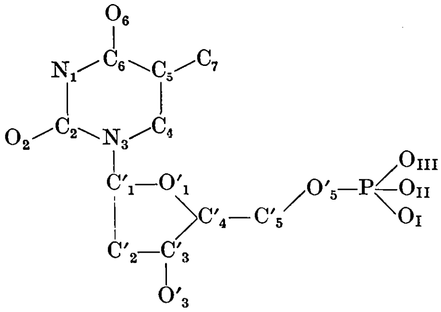
The key role of deoxyribonucleic acid (DNA) in the storage and transport of genetic information has focussed a great deal of effort in recent years on the elucidation of its molecular structure. The complexity of the material and the fact that it gives only fibre diffraction patterns have precluded the use of the usual single-crystal X-ray methods of structure analysis and refinement. Consequently the approach adopted has been that of attempting to construct plausible models which are in accord with the known physical, chemical, and, if possible, biological properties of DNA. Several early suggestions culminated in the ingenious double-helix model proposed by Watson & Crick (1953); Crick & Watson (1954), which not only fitted remarkably well the facts known at that time but which has been supported by almost all the evidence on DNA accumulated since. However, as Crick (1957) and others have stated, further elaboration, modification, and understanding of the model must await the accumulation of additional basic physical chemical information, including precise data on the intra- and inter-molecular geometry to be expected in polynucleotides.

Although there have been about fifteen structure determinations of individual purines and pyrimidines reported, there have been only four of nucleosides (cytidine, Furberg, 1950; 2′:3′-isopropylidene, 3:5′-cycloadenosine, Zussman, 1953; 5′-bromo-3′:5′-dideoxythymidine, Woolfson, 1956; 5′-bromo-5′-deoxythymidine, Huber, 1957), and three of nucleotides (adenylic acid, Brown *et al.*, 1953; cytidylic acid *b*, Alver & Furberg, 1957; vitamin B_{12}, Hodgkin *et al.*, 1956, 1957). Furthermore, of these last seven determinations, only that of vitamin B_{12} was three-dimensional, and its precision was low because of the large number of atoms involved; in addition, it has the α-configuration at the glycosidic linkage, while all nucleic acid derivatives appear to be β. The only precise published study of the phosphate diester linkage, an important grouping in polynucleotides, is the structure analysis of dibenzyl phosphoric acid (Dunitz & Rollett, 1956). Spencer (1959*a*) has critically summarized the available structural information on the components of and atomic groupings in DNA and has underscored the need for precise structural studies which can define better the range of likely variation in the geometrical parameters of a polynucleotide double-helix.

The present study was undertaken with the object of providing the first structural information on the mutual arrangement of the phosphate, the sugar, and the base in a deoxyribonucleotide. Hydrated calcium thymidylate proved to be very amenable to three-dimensional structure analysis; the calcium and phosphorus atoms were easily found in the Patterson function, and were at once sufficiently heavy to make the structure determination fairly straightforward but not so heavy that they greatly limited the precision in the location of the carbon, nitrogen, and oxygen atoms. The structure has been refined to the ultimate precision that the experimental data warrant.

The molecular formula of calcium thymidylate and the atomic numbering[*] which we shall follow here are:





The crystal contains (according to the results of the structure determination) six water molecules in the asymmetric unit; these will be designated W1, . . . , W6.

Experimental data and procedures

All experimental work with the crystals was done at Strasbourg. Calcium thymidylate was obtained from the California Foundation for Biochemical Research and was recrystallized by slow evaporation of aqueous solutions. The thin plates which formed were elongated along **b**; **a***was normal to the principal faces of the plates.

Weissenberg and precession photographs with Ni-filtered Cu $K\alpha$ radiation showed the crystals to be monoclinic. The only systematic extinctions were $(0k0)$ absent with k odd, which indicated that the space group is $P2_1$; the group $P2_1/m$ is incompatible with the optical activity of the thymidylate ion. Unit cell dimensions were measured on equatorial Weissenberg photographs about **b** and **c** which had been superposed on the diffraction pattern of an aluminum wire; they are

$$a_0 = 14{\cdot}40 \pm 0{\cdot}02,\quad b_0 = 6{\cdot}87 \pm 0{\cdot}01,\quad c_0 = 9{\cdot}81 \pm 0{\cdot}01\ \text{Å};$$
$$\beta = 90^\circ\ 58' \pm 3'.$$

The density of the crystals, measured in a mixture of 'Freon 113' and bromoform was between 1·58 and 1·61 g.cm.$^{-3}$; the density calculated for a unit cell containing two molecules of calcium thymidylate and twelve water molecules is 1·60, and thus the asymmetric unit consists of one calcium ion, one thymidylate ion, and six water molecules. (If there were only five water molecules in the asymmetric unit, the density would be 1·54; if there were seven, it would be 1·66.)

The intensities were recorded on two series of equi-inclination Weissenberg photos. For the layers $k=0$ through 5 we used a crystal of dimensions about 1·5 mm. along **b***, 0·2 mm. along **a***, and 0·5 mm. along **c***; for layers $l=0$ through 8 a smaller fragment, about 0·5 by 0·2 by 0·5 mm. was used. Each photograph was taken on four superposed Kodak Kodirex films and in most cases several different exposure times were used for each layer. Intensities were determined with a microdensitometer by measuring the density in the central region of each spot, without

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[*] The numbering which we have adopted for the pyrimidine ring differs from that recommended by Chemical Abstracts but is in common use and, because of its similarity to the scheme used for numbering purines, seems preferable to the C.A. system when comparisons between pyrimidines and purines are to be made. Such comparisons are frequent in consideration of nucleic acid models.

integration but with correction for the error due to the separation of $K\alpha_1$ and $K\alpha_2$. Film factors were measured directly for each series of photographs. After the usual geometrical corrections had been applied, the corrected intensities were brought to a common scale by consideration of the reflections which occurred on both sets of films. An arbitrary limit was set at $\sin\theta = 0{\cdot}91$; of the 1786 possible reflections within this limit, 1575 gave a measurable intensity.

No absorption corrections were made. Absorption very likely constitutes the most important source of error in the intensities; the linear absorption coefficient for Cu $K\alpha$ radiation is about 44 cm.$^{-1}$. An approximate calculation indicates that in the most unfavorable cases variations in absorption could introduce variations in the relative values of the recorded intensities of between 2·5 and 3, and thus variations in relative F's up to a factor of 1·7. The average variation due to absorption will of course be considerably smaller but one must expect a systematic effect with $\sin\theta$ which is formally equivalent to a negative temperature factor. Thus the thermal vibration parameters derived from these data are probably smaller than the true values.

Preliminary two-dimensional calculations were done with the von Eller photosummation device and with Beevers–Lipson strips, and corresponding structure factor calculations were made for us by La Compagnie BULL, Paris. All subsequent calculations were made on the computer SWAC (Sparks, Prosen, Kruse & Trueblood, 1956). The form factors used for oxygen, nitrogen, and hydrogen were those of McWeeny (1951), that for carbon was McWeeny's (1954) diamond curve, and that for phosphorus was taken from the *Internationale Tabellen* (1935). The scattering curve for the calcium ion was approximated by using the curve for the neutral calcium atom (Berghuis *et al.*, 1955) above $\sin\theta/\lambda = 0{\cdot}2$ and by extrapolating this curve smoothly to $Z = 18$ below this value.

Determination and refinement of the structure

Consideration of a Patterson projection on (010) and of certain features of the intensity distribution on different layers about **b** led to rather good x and z parameters for the calcium atom and the phosphate group, and indicated approximate positions and orientations for the sugar and the base. However, many attempts to interpret Fourier projections calculated with signs based on positions derived from this Patterson distribution proved fruitless; the usual iterative procedures led nowhere. We believe in retrospect that this failure was due primarily to the absence of the water molecules from these calculations. Fig. 1 shows the relation of this first trial structure to the final structure; the mean error in the position of the calcium atom and the phosphate group was only about 0·14 Å, that for the atoms of the sugar was about 0·5 Å, and that for the thymine residue was considerably more than 1 Å.

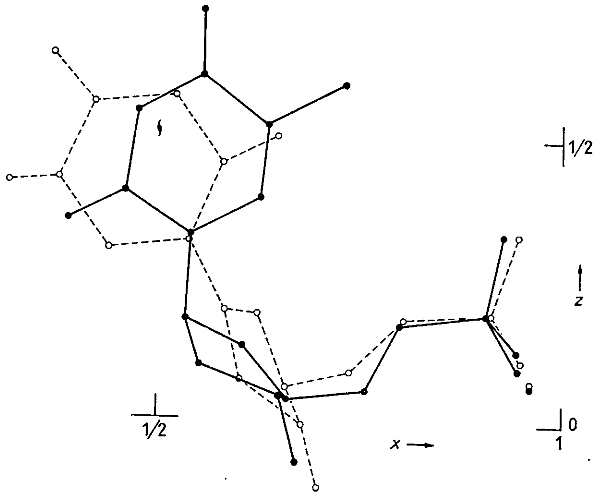


Fig. 1. Comparison of the first trial structure deduced from the Patterson projection on (010) (—○—) with the final refined structure (—•—). Water molecules have been omitted.

A sharpened three-dimensional Patterson function, with the origin peak approximately removed, was then calculated. The sharpening function by which the observed F^2-values were divided was $\Sigma f_i^2 \exp(-5s^2)$, where $s = \sin\theta/\lambda$ and the summation is over all atoms in the unit cell. (Actually the summation included only four water molecules, rather than the twelve actually present in the unit cell, because of doubts about the number; however, this made no significant difference in the effectiveness of the sharpening, although it did affect the absolute scale slightly.) The average sharpened F^2 was then substracted from each sharpened value and all were multiplied by a modification function (Waser, 1944) to insure convergence. The modification function was $s^4 \exp(-19s^2)$, which put maximum weight on the data at $s = 0{\cdot}32$, in the middle of the Cu $K\alpha$ range.

The strongest peaks in the three-dimensional Patterson map were, as expected, those due to Ca–Ca and Ca–P interactions, and it was immediately possible to deduce coordinates not only for the calcium and phosphorus atoms but also for all of the phosphate oxygens. From the heights of the various identified peaks, it was possible to estimate the approximate height expected for a P–C interaction. The vector convergence or superposition method (Beevers & Robertson, 1950) was then applied, using the known positions of the calcium and phosphorus atoms, and admitting overlaps only for regions of Patterson density of at least the height expected for a P–C interaction. The success of this technique was striking; every atom of the calcium thymidylate molecule was located and in addition about ten possible positions were found for the six water molecules believed to be present in the asymmetric unit.

There was one significant source of ambiguity in the analysis of the vector map. The packing of the molecules is such that the calcium and phosphorus atoms have very nearly the same y-parameters. This means that the distribution of these two atoms has the symmetry of $P2_1/m$, not just $P2_1$, and consequently calculations based on this distribution have a false mirror plane perpendicular to **b**. Thus there was an ambiguity in the choice of the sign of y for the other atoms. One sign could be chosen arbitrarily, with the others for atoms within the molecule then dictated by chemical and stereochemical considerations; since in this molecule there is a known absolute configuration, even the arbitrariness of the first choice was eventually removed. However, it was more difficult to decide upon the proper choice of a sign for y for the water molecules, particularly since there were more plausible positions than there were water molecules. On the basis of the Patterson analysis, positions were assigned tentatively to seven water molecules.

While the Patterson superposition diagram was being made, a crude approximation to the electron density, $\varrho_1(xyz)$, was calculated with the observed structure factor amplitudes and phases based on the positions deduced from the Patterson for the calcium atom, the phosphorus atom, and the four phosphate oxygens. This distribution also had a false mirror plane normal to **b** inasmuch as the phosphate group is oriented in such a way that two of the oxygen atoms lie approximately in the plane of the calcium and phosphorus atoms, and the other two are equally displaced above and below this plane and have about the same x and z coordinates. When this false symmetry was taken into account, comparison of this distribution with the results of the Patterson analysis indicated that the positions chosen for all of the atoms in the molecule and for four of the seven water molecules were plausible. However, the density at the positions suggested for each of the other three possible water molecules was very low.

A centrosymmetric Fourier projection, $\varrho_1(xz)$, with signs based on the postulated positions of all twenty-nine atoms, was then calculated. It indicated that two of these three doubtful water molecules were indeed spurious, while the other one, and all of the remaining atoms, looked reasonable. Improved x and z parameters were estimated for about two-thirds of the atoms, those which were resolved in this projection, and a three-dimensional Fourier synthesis, $\varrho_2(xyz)$ was then calculated with phases based on the positions of the twenty-two atoms of the molecule and the five accepted water molecules. No trace of either of the two spurious water molecules remained, but a peak of about one-half the height expected for an atom not included in the phasing appeared at a plausible position for a sixth water molecule; as indicated below, this molecule was later confirmed and included in the calculations.

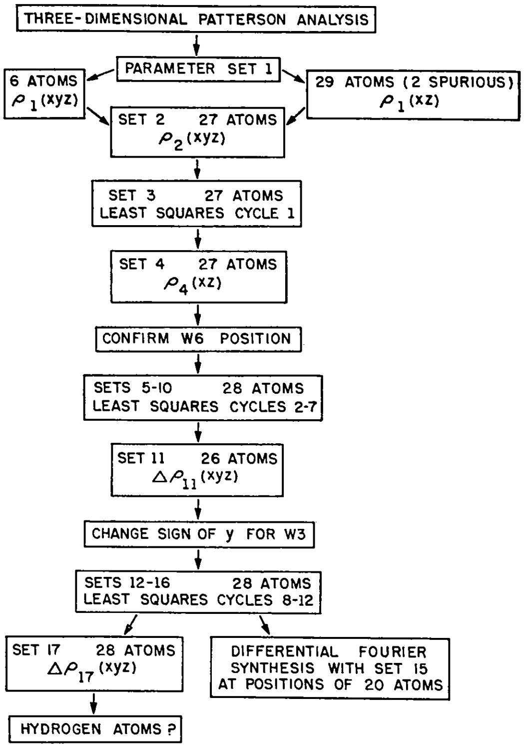


Fig. 2. Outline of the refinement stages and procedures discussed in the text.

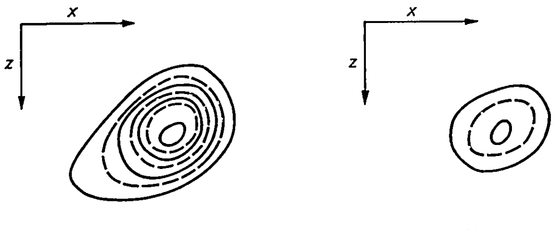
The various stages in the refinement of the structure are outlined in Fig. 2. Least squares refinement was begun with the atomic positions estimated from ϱ_2 for the entire molecule of calcium thymidylate and the five water molecules accepted at that stage (W1 to W5). Because it was known that many of these atomic positions were very crude, no attempt was made to refine temperature factors in the first two least squares cycles. The initial temperature factors were chosen after a comparison of the early calculated structure factor amplitudes with those observed, and were 1·5 Å^2 for Ca and P, and 2·0 Å^2 for all other atoms. The weighting scheme used throughout the least squares procedure was (with $\bar{F}_{\text{min.}}=4{\cdot}8$):

$$F_o \geq 4\bar{F}_{\text{min.}},\quad \sqrt{w}=4\bar{F}_{\text{min.}}/F_o;\quad F_o \leq 4\bar{F}_{\text{min.}},\quad \sqrt{w}=1\ .$$

In the early least squares cycles, the unobserved reflections were included with $F_o=0{\cdot}71F_{\text{min.}}$ (Hamilton, 1955) and $F_{\text{min.}}$ varying significantly in different regions of reciprocal space. In the final five refinement cycles, they were omitted because the corresponding residuals were then comparable in magnitude to those of the observed reflections (rather than appreciably smaller), and because it was not convenient to weight them appropriately (Hamilton, 1955). However, the structure factors for these reflections were calculated at each stage, as also were the terms in the matrix of the normal equations. Even though the latter were not included in the later cycles, their effect was usually calculated; at most they would have changed bond distances and angles by less than 0·01 Å and 1° in any cycle, which is less than the e.s.d. of these quantities, although of course cumulative effects might have been slightly larger. It was also noted that inclusion of the unobserved reflections would not have significantly affected the error estimates.

The presence of so many independent atoms in the structure made it impractical to calculate and solve the full matrix of the least squares normal equations. Instead individual 3×3 and 6×6 matrices, corresponding respectively to the position parameters and anisotropic temperature parameters, were calculated and solved for each atom (Sparks, Prosen, Kruse & Trueblood, 1956). The scale factor was changed only in the first few cycles, when the temperature factors were held constant at about their average values. The shifts called for in the scale factor in later cycles were generally less than 2%; thus the scale factor appeared to be approximately correct and since no cross-terms between it and the temperature factors were calculated, it was held constant thereafter. Because interatomic cross-terms were ignored, the full shifts called for in the position and temperature factors were seldom applied; the position parameters were usually shifted by $\frac{2}{3}$ or $\frac{3}{4}$ of the indicated amount, the temperature factors by $\frac{1}{3}$ or $\frac{3}{8}$ of that calculated. Convergence was slow for various reasons—because the interatomic cross-terms were ignored, because there were so many atoms present, and because the initial structure was rather crude, nine of the atoms being displaced more than 0·2 Å from their correct positions even after one least squares cycle.

After the first cycle of least squares, calculation of a Fourier projection ($\varrho_4(xz)$) strongly confirmed the existence of the sixth water molecule, W6, which had first appeared as a weak peak in ϱ_2. Six successive least squares cycles (cycles 2 through 7) were then calculated with all 28 atoms included. A careful check on the changes in various direct and derived parameters of the structure was made at each stage—the position and vibration parameters, interatomic distances, individual values of $\Delta|F|$, R, and the sum of the weighted squares of the residuals. After cycles 6 and 7 (parameter sets 10 and 11 respectively) we became very suspicious of the position of one of the water oxygen atoms, W3; not only did it have two very short apparent intermolecular contacts with other oxygen atoms (2·35 and 2·39 Å) but its apparent temperature factors continued to increase steadily, although the average value at this stage (about 8 Å^2) was not impossibly large. Rossmann, Jacobson, Hirshfeld & Lipscomb (1959) have pointed out that when atoms are incorrectly placed in a structure and an attempt is made to refine their temperature factors, the latter will tend to increase to very large values. Hand calculation of the effect of atom W3 on $\Delta|F|$ for a few of the reflections showing the greatest discrepancies between $|F_o|$ and $|F_c|$ added credence to the suspicions. Hence a difference map ($\Delta\varrho_{11}$) was calculated, with the contribution of W3, and also of W2, omitted from the phasing and from the calculation of F_c. W2 was omitted partly as a control and partly because its temperature factors had also shown fairly regular increases, although the average value had reached only about 5·4 Å^2.



$y = -0{\cdot}30$ $y = +0{\cdot}30$

Fig. 3. Sections of $\Delta\varrho_{11}$ near x and z of atom W3; y had been believed to be about 0·30. Contours start at 1 e.Å^{-3}; the interval is $\frac{1}{2}$ e.A^{-3}.

In this acentric structure, a real atom omitted from the phasing should appear at about half its normal height (Luzzati, 1953; Hodgkin *et al.*, 1959) and W3 did so appear in $\Delta\varrho_{11}$ at about x, $-y$, z, where x, y, and z represent the coordinates assigned to the atom previously. Pertinent regions of the map are illustrated in Fig. 3. Because the values of x and z had been approximately correct, the projections on (010) calculated earlier had been correct. It will be recalled that there had been some ambiguities about the assignment of signs to y-coordinates at the start of the analysis so that this incorrect sign for y of W3 was not surprising. Inspection of the difference map indicated that the position of W2 was correct; a peak of about the expected height (3·6 e.Å^{-3}) occurred at the expected position, although there was also a small ghost peak (1·6 e.Å^{-3}) at the position with the sign of y reversed. That the latter peak and the corresponding ghost of W3 were not due to disorder of W2 and W3 was shown by the fact that they were completely absent from the final difference map, $\Delta\varrho_{17}$, calculated after further refinement.

Least squares cycle 8 was then calculated. The change in the sign of y for atom W3 led to distinct improvements in R, in the sum of the weighted squares of the residuals, and in a number of the bond distances within the molecule. These are apparent as the discontinuities in the curves of Figs. 4 and 5. These figures illustrate the dangers of this sort of systematic error: a number of the bond distances, none of them involving W3, changed by appreciable amounts (as much as 3σ) when this change was made in the sign of one of the eighty-four position parameters. Furthermore the changes were usually dramatically larger than the changes in the last few cycles before the correction. It is clear that if this correction had never been made,

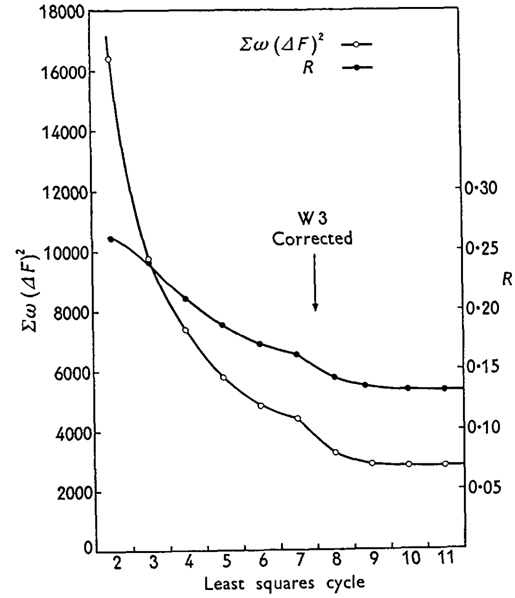


Fig. 4. Values of R (solid circles) and the sum of the weighted squares of the residuals (open circles) at successive least-squares refinement stages.

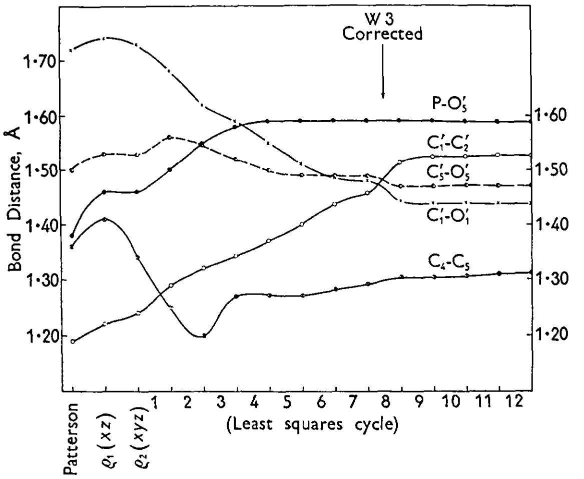


Fig. 5. Apparent values of representative bond distances at different refinement stages.

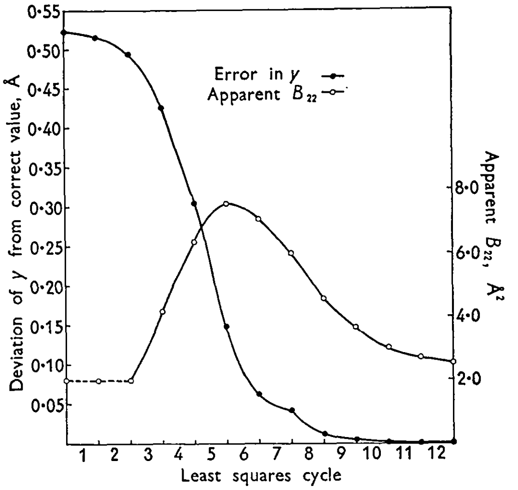


Fig. 6. Correlation between apparent temperature factor B_{22} and deviation of y from true value for atom O_{III} at successive least-squares refinement stages.

the sum of the weighted squares of the residuals would have levelled off at a value only about 20–30% higher than that finally reached, and thus the estimates of 'random errors' would have been only 10–15% higher than those we accept. Yet three of the eighteen bond distances involving C, N and O atoms would have been in error by more than 2σ *from this cause alone.*

Fig. 6 illustrates the overshifting of the temperature factor parameter for an atom when the position parameter for that atom is grossly in error. The sign of y for atom O_{III} was incorrectly chosen at first, but the value of y is sufficiently close to zero for this atom that the refinement moved the atom the needed distance (about 0·55 Å) to the correct position. The apparent vibration parameter parallel to **b** increased markedly as long as y was far from its correct value, then decreased again to a value not far from that originally assumed to be correct. This effect has also been cited by Rossmann *et al.* (1959), who pointed out that it can be used to accelerate refinement. The difficulty with this suggestion is, of course, that it is hard in the early stages to know whether the atom is a real one far from its correct position or is entirely spurious. In any event, it is clear from the examples of W3 and O_{III} that in analyses of complex structures by least squares it is imperative to follow closely the details of the changes of parameters and apparent molecular geometry and packing at every stage.

The conclusion of the refinement was straightforward. Four more cycles of least squares refinement (9 through 12) led to parameter set 17, which was used in the calculation of a final three-dimensional difference map, $\Delta\varrho_{17}$. The largest shift in position in the last squares cycle was 0·009 Å for W2; within the molecule itself, the largest shift was 0·004 Å, the average only 0·002 Å. The final difference map showed no trace of the ghost peaks of atoms W2 and W3 which had been present in $\Delta\varrho_{11}$. It was possible to find peaks, or at least regions of positive density, at positions corresponding to plausible positions for all twenty-five hydrogen atoms of the asymmetric unit, thirteen in the molecule of calcium thymidylate and twelve on the six water-oxygens, W1 through W6. However, the location of these hydrogens was by no means unambiguous; there were several peaks in $\Delta\varrho_{17}$ of height up to 0·7 e.Å^{-3} which, from geometrical considerations, could not possibly be identified as hydrogen atoms. This suggested strongly that the background fluctuations of the electron density caused by inadequacies of the experimental data were so great that location of the hydrogen atoms from peak height evidence alone would be very uncertain. An estimate of the e.s.d. of the electron density from a consideration of these fluctuations gave a value of $\sigma(\varrho)$ of about 0·24 e.Å^{-3}; an independent calculation using the approximation $\sigma(\varrho)=(1/V)[\Sigma(\Delta|F|)^2]^{\frac{1}{2}}$ (Cruickshank, 1949) gave $\sigma(\varrho)=0{\cdot}26$ e.Å^{-3}. Since in this asymmetric structure hydrogen atoms omitted from the phasing are expected at peak heights of only about 0·3–0·4 e.Å^{-3}, it is not surprising that many of them are partially obscured by the background.

Our selection of hydrogen positions was based upon a detailed examination of the difference map and consideration of the molecular geometry expected for both covalent and hydrogen bonding. The average density at the sites chosen is 0·33 e.Å^{-3}, with sixteen of the twenty-five supposed hydrogen atoms having densities between 0·3 and 0·4 e.Å^{-3}. The others range from 0·15 to 0·6 e.Å^{-3} (Table 2). The average X–H distance is 1·07 ± 0·04 Å, and the average Y–X–H bond angle 111 ± 6°. Thus the positions are plausible geometrically and are consistent with the difference map. Furthermore their inclusion improves the agreement between observed and calculated structure factor amplitudes: for the 316 observed reflections with $\sin\theta \le 0{\cdot}500$, R is 14·9% without inclusion of the hydrogen atoms and 14·1% when they are included. (In this calculation, $B=5$ Å^2 for each of the H-atoms on a water molecule and 3 Å^2 for the other hydrogens.) It seems clear that many of the suggested hydrogen atom positions correspond to the approximate sites of hydrogen atoms in the structure, but some of the positions certainly may be specious, particularly on some of the water molecules.

Table 1. *Final atomic parameters**

					$\varrho_{\max.}$ (e.Å^{-3})	
Atom	x	y	z	$\bar{B}$ (Å^2)	Obs.	Calc.
N1	5287	1630	4664	2·3*b*	11·7	11·0
C2	5386	1436	6056	1·8*b*	10·1	9·7
N3	4580	1346	6766	1·8*b*	12·6	12·0
C4	3734	1517	6126	2·0*b*	9·6	9·1
C5	3629	1701	4803	1·8	10·0	9·5
C6	4435	1790	3936	1·5*a,b*	10·4	9·9
O2	6171	1458	6614	3·6*b*	12·0	11·3
O6	4463	1873	2697	2·7*b*	13·0	12·2
C7	2694	1923	4063	3·0*b*	8·2	7·9
C1′	4654	1065	8245	1·4*b*	9·8	9·4
C2′	4480	2886	9094	2·1*b*	8·8	8·6
C3′	3474	2593	9594	1·4*b*	10·2	10·0
C4′	3417	0431	9701	1·1*a,c*	10·9	10·7
C5′	2453	−0482	9586	1·9	9·0	8·7
O1′	3966	−0349	8613	1·6*a,c*	15·2	14·7
O3′	3274	3570	0817	2·7	13·1	12·6
O5′	2015	0088	8280	2·0	13·5	12·8
P	0915	0079	8150	1·0*a,c*	—	—
O_I	0580	−1787	8731	1·4*a,c*	14·9	14·8
O_{II}	0553	1667	9071	1·6*a,c*	14·8	14·6
O_{III}	0762	0441	6683	2·0*a,b*	14·0	13·7
Ca	0383	4953	9340	1·0*a,c*	—	—
W1	1326	4563	7154	2·9	—	—
W2	3104	6505	6867	7·4	—	—
W3	0538	−3013	5244	5·4	—	—
W4	0852	0285	2252	3·5	—	—
W5	1567	4982	1034	4·0*b,c*	—	—
W6	1934	−2748	3333	4·6	—	—

* The position parameters are those of Set 17. The 'temperature factors' are average values; the letters after them represent approximate directions of maximum vibration when the individual B's varied by more than a factor of 2, i.e., when the apparent vibration amplitudes varied by about 1·4. The electron densities are those evaluated in the differential Fourier synthesis with parameter Set 15; no calculations were made at that stage for the calcium, phosphorus, or water oxygen atoms. Each x, y and z has been multiplied by 10^4.

Table 2. *Suggested hydrogen positions**

Atom to which H is attached		x	y	z	$\Delta\varrho 17$ (e.Å^{-3})
N1	**	590	178	407	0·15
C4		317	133	683	0·3
C7	(*a*)	267	067	340	0·35
	(*b*)	275	315	340	0·4
	(*c*)	217	200	475	0·2
C1′		533	033	867	0·2
C2′	(*a*)	488	321	994	0·3
	(*b*)	450	433	873	0·35
C3′		293	316	887	0·4
C4′		383	020	067	0·6
C5′	(*a*)	245	−200	983	0·35
	(*b*)	195	009	024	0·2
O_3′	**	367	300	160	0·3
W1	(*a*)	120	550	620	0·4
	(*b*)**	117	315	700	0·4
W2	(*a*)**	240	630	700	0·3
	(*b*)	317	800	700	0·4
W3	(*a*)	063	−190	590	0·2
	(*b*)	000	−300	450	0·4
W4	(*a*)**	050	167	267	0·4
	(*b*)	142	−030	267	0·35
W5	(*a*)**	230	500	067	0·2
	(*b*)	167	540	217	0·5
W6	(*a*)	267	−300	333	0·2
	(*b*)	150	−295	405	0·4

* These positions have been chosen to be consistent with the final difference map and with a plausible molecular geometry. They cannot be considered definitely established; those marked with ** are the most ambiguous. The electron density listed is that at the suggested position in the final difference map; this was not always the maximum density of the peak. Each x, y and z has been multiplied by 10^3.

The final position parameters (Set 17) for all the non-hydrogen atoms in the structure are given in Table 1, and those suggested for the hydrogen atoms are in Table 2. Because of the appreciable uncorrected absorption errors, the final values of the anisotropic temperature factors resulting from the least squares procedure were somewhat erratic, and we do not feel that the detailed anisotropies indicated by them are of much significance. Consequently we have merely indicated average values of B for each atom in Table 1, except that when the individual B_{ii} varied by more than a factor of 2 we have given the approximate direction(s) of maximum apparent vibration. These average values can be plausibly interpreted in terms of the structure and packing of the molecules and will be discussed later.

One cycle of differential Fourier synthesis was calculated, as indicated in Fig. 2, with parameter Set 15, just before the last two least squares cycles. Because the routine is limited to calculations at the positions of 20 atoms, the observed and calculated electron densities and their slopes and curvatures were evaluated only at the positions of the twenty C, N, and O atoms of the thymidylate ion, and not for the Ca, P, or six water oxygens. No shift in position as large as 0·005 Å was indicated, and since this was less than one-half the e.s.d. of the position of any of these atoms, no shifts were made. The average value of the ratio of the observed to calculated curvature of the electron density was 0·993, but there was appreciable individual variation (maximum spread of 6% for $\partial^2\varrho/\partial x^2$, 11% for $\partial^2\varrho/\partial y^2$, and 4% for $\partial^2\varrho/\partial z^2$). This variation is not surprising in view of the known absorption errors and indeed it is another indication of the inadequacies of our individual derived 'temperature factors'. An attempt to refine temperature factors by differential Fourier methods might have yielded somewhat better values, but the data did not seem to merit the effort. It is noteworthy also that the observed peak heights were greater than those calculated by 3–4%, suggesting that the scale factor might be somewhat too high (at least for the temperature factors being used). On the other hand, the last five least squares cycles had suggested consistently that the scale factor was about 2% low, although because no cross-terms were calculated the indicated shift could not be considered of great significance and no shift was applied. The sums of F_o and of $|F_c|$ agreed within about 1%.

The final value of the usual discrepancy index, R, was 11·8% for the 1575 observed reflections (11·6% if the hydrogen atoms are included in the calculation). Although $|F_c|$ was larger than the estimated minimum observable F_o for 19 of the 211 unobserved reflections, it was as large as 1·5 $F_{\text{min.}}$ for only three of these, and for none was it as great as 2 $F_{\text{min.}}$. A complete list of h, k, l, F_o, $|F_c|$, $F_o \cos\alpha$, and $F_o \sin\alpha$ is presented in Table 7.

The e.s.d.'s of the atomic positions were estimated from the diagonal elements of the matrix of the least squares normal equations, a procedure which past experience has shown to give values only a few per cent higher than those estimated more rigorously from the inverse matrix. The difference is certainly not significant. The e.s.d.'s for the x and z coordinates (expressed in Å) were about the same for most atoms; those for the y coordinates averaged about 30% larger, occasionally being nearly twice as large. These individual variations were considered in calculation of the e.s.d.'s of bond distances and angles. The e.s.d.'s of atomic positions (in Å) were: 0·003 for Ca, 0·0035 for P, 0·010 to 0·014 for the eight oxygens of the molecule, 0·012 to 0·018 for the water oxygens, 0·013 for the nitrogens, and 0·014 to 0·019 for the carbons.

The structure of the thymidylate ion

In discussing the crystal structure, we shall consider first the different portions of the thymidylate ion separately, then the conformation of the ion as a whole, and finally the packing of the ions and water molecules which constitute the structure. Tables 3 and 4 list the bond distances and angles in the ion, with their e.s.d.'s; certain significant non-bonded intramolecular distances are listed also. The structure of the ion is illustrated in Figs. 7 and 8, which also show the probable hydrogen bonds in which the ion is directly involved.

Table 3. *Distances within the thymidylate ion**

N1–C2	1·377 (0·018)	C7 ··· O6	2·90 (0·02)
C2–N3	1·365 (0·018)	C1′ ··· O2	2·74 (0·02)
N3–C4	1·367 (0·018)	C4 ··· C2′	3·23 (0·02)
C4–C5	1·310 (0·022)	C4 ··· O1′	2·77 (0·02)
C5–C6	1·452 (0·021)	C5′ ··· O$_{\mathrm{I}}$	2·95 (0·02)
C6–N1	1·414 (0·018)	C5′ ··· O$_{\mathrm{II}}$	3·14 (0·02)
C2–O2	1·247 (0·018)		
C5–C7	1·526 (0·023)	Ha on C5′ ··· O$_{\mathrm{I}}$	2·9
C6–O6	1·218 (0·019)	··· O$_{\mathrm{II}}$	3·8
N3–C1′	1·466 (0·018)	Hb on C5′ ··· O$_{\mathrm{I}}$	2·8
C1′–C2′	1·527 (0·028)	··· O$_{\mathrm{II}}$	2·6
C2′–C3′	1·550 (0·019)	Ha on C7 ··· O6	2·8
C3′–C4′	1·491 (0·022)	Hb on C7 ··· O6	2·7
C4′–O1′	1·441 (0·017)	Hc on C7 ··· H on C4	2·5
O1′–C1′	1·438 (0·018)	H on C1′ ··· O2	2·5
C3′–O3′	1·409 (0·018)	H on C4 ··· O1′	2·4
C4′–C5′	1·526 (0·022)		
C5′–O5′	1·472 (0·019)		
O5′–P	1·587 (0·011)		
P–O$_{\mathrm{I}}$	1·486 (0·011)		
P–O$_{\mathrm{II}}$	1·514 (0·011)		
P–O$_{\mathrm{III}}$	1·474 (0·011)		

* The numbers in parentheses are the estimated standard deviations. Units are Å throughout.

Table 4. *Bond angles in the thymidylate ion**

N1–C2–N3	115·8°	C1′–C2′–C3′	103·3
N1–C2–O2	120·8	C2′–C3′–C4′	101·8
N3–C2–O2	123·2	C2′–C3′–O3′	114·3
C2–N3–C4	121·4	C4′–C3′–O3′	113·7
C2–N3–C1′	117·6	C3′–C4′–O1′	106·7
C4–N3–C1′	121·0	C3′–C4′–C5′	117·1
N3–C4–C5	123·3	O1′–C4′–C5′	107·6
C4–C5–C6	120·3	C4′–O1′–C1′	108·9
C4–C5–C7	124·5	C4′–C5′–O5′	109·4
C6–C5–C7	115·1	C5′–O5′–P	118·8
C5–C6–N1	113·4	O5′–P–O$_{\mathrm{I}}$	107·6
C5–C6–O6	128·8	O5′–P–O$_{\mathrm{II}}$	107·6
N1–C6–O6	117·7	O5′–P–O$_{\mathrm{III}}$	102·1
C6–N1–C2	125·7	O$_{\mathrm{I}}$–P–O$_{\mathrm{II}}$	106·0
N3–C1′–C2′	115·0	O$_{\mathrm{I}}$–P–O$_{\mathrm{III}}$	118·4
N3–C1′–O1′	107·4	O$_{\mathrm{II}}$–P–O$_{\mathrm{III}}$	114·4
C2′–C1′–O1′	107·2		

* Estimated standard deviations are about 0·7° for O–P–O angles, 1·0° for C5′–O5′–P, and about 1·4° for the others.

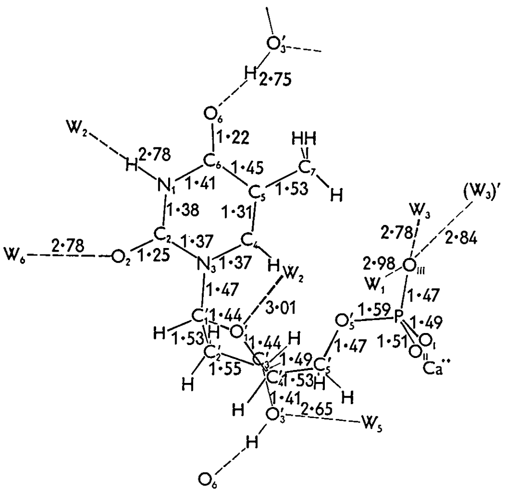


Fig. 7. Bond distances in the thymidylate ion and possible hydrogen bond distances directly involving this ion. The view is along the positive direction of **b**.

The thymine ring

The configuration found for the thymine nucleus is compared in Fig. 9 with those predicted by Spencer (1959*a*) and Pauling & Corey (1956) in their consideration of models of DNA. A precise determination of the structure of thymine itself (as the monohydrate) has recently been made by Gerdil (1961). His results, which are more precise than ours, agree generally well with ours. The only distance which differs by more than 1 e.s.d. is C4–C5, for which he finds 1·35 Å, a more plausible value than our 1·31 Å. The largest deviation in an angle is for C6–C5–C7, for which Gerdil found 119° as contrasted with our 115°; no other angle deviates more than about 2°. We know of no other structural studies of thymine derivatives, although the structure of the related substance, uracil (which has a hydrogen atom in place of the methyl group of thymine) has been determined by Parry (1954). Even if allowance is made for the fact that his e.s.d.'s are probably underestimated by a factor of at least

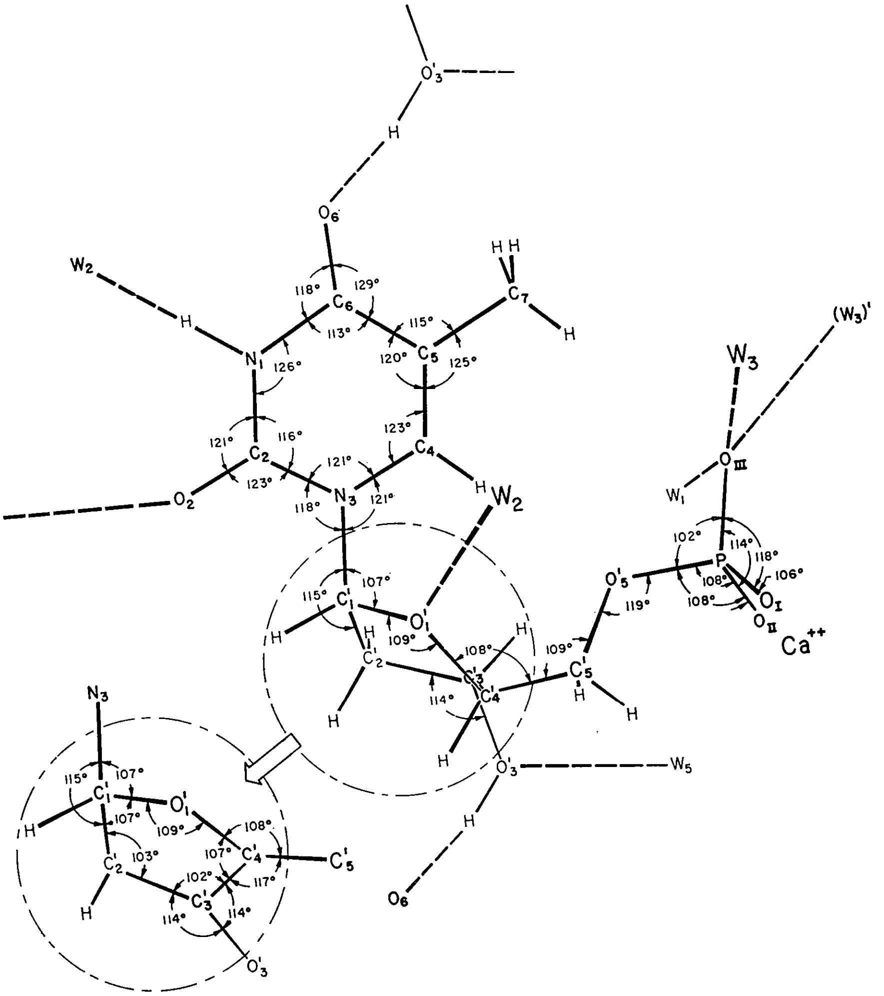
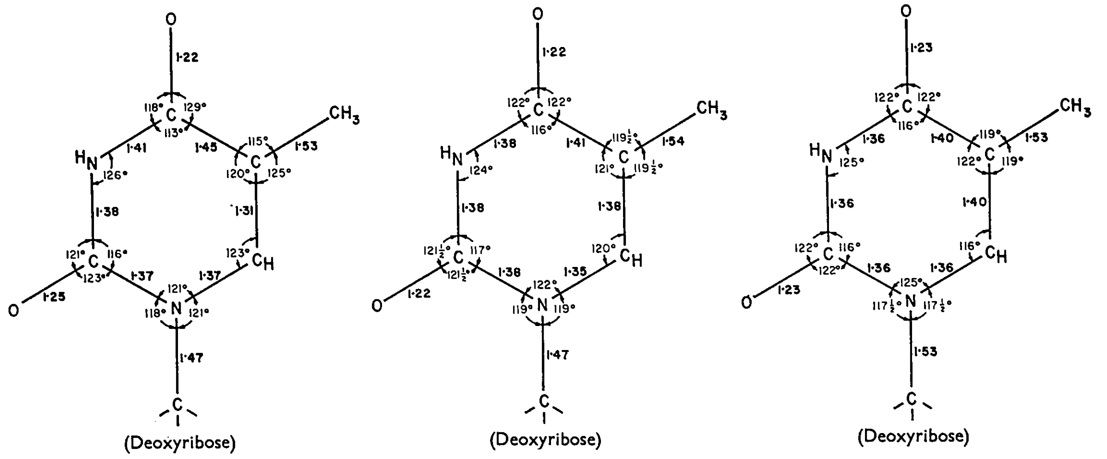


Fig. 8. Bond angles in the thymidylate ion. The view is along the positive direction of **b** except for the insert which shows the deoxyribose ring viewed from a more convenient direction.



Calcium Thymidylate

Predicted by Spencer

Predicted by Pauling and Corey

Fig. 9. Structures of the thymine residue (*a*) found in calcium thymidylate, (*b*) predicted by Spencer (1959*a*), (*c*) predicted by Pauling & Corey (1956).

two because so large a proportion of the reflections were weak (Sparks, 1958), one major discrepancy with our results, and with Gerdil's, remains. Parry finds the C4–C5 distance to be 1·41 Å; it is of course possible that there is a real difference between thymine and uracil here, although it seems unlikely that it would be so large. The two studies of thymine and that of uracil agree on one important point: the C2–O2 and C6–O6 distances are so nearly the same as those characteristic of ketones and aldehydes (average 1·23 Å, Sutton, 1958) that there can be no question concerning the tautomeric form of the molecules in the crystals. They are in the keto, not the enol, form.

Table 5. *Some least-squares planes**

Plane	Atoms comprising the plane	Displacements	Displacements of other atoms			Angles of plane normal†
I	N1	−0·003 Å	O2		0·101	88·7°
	C2	—0·004	C1′		−0·050	6·0
	N3	−0·012	C7		0·061	
	C4	0·009	O6		−0·064	84·1
	C5	0·008				
	C6	0·007	C2′	1·27		
			O1′	−1·01		
II	C1′	0·021	C3′		−0·53	49·7°
	C2′	−0·013	C5′		−0·73	110·5
	C4′	0·014	O3′		−0·13	
	O1′	−0·022	N3		−1·10	47·4
III‡	Ca	−0·07	W4		2·25	35·3°
	W1	0·08	W5		−2·41	92·3
	O_{IA}	−0·05				54·8
	O_{IIA}	−0·03				
	O_{IB}	0·01				
	O_{IIB}	0·07				
IV	P	—	Ca	3·56		91·1°
	O5′	—	O_{I}	−1·04		17·4
	C5′	—	O_{II}	1·33		72·6
			O_{III}	−0·19		
			C4′	0·60		

* All planes were calculated in a manner similar to that described by Schomaker, Waser, Marsh & Bergman (1959).

† For each plane the three values listed are, respectively, the angles with the positive directions of **a***, **b**, and **c**.

‡ These atoms are those involved in the angles shown in Fig. 10; see also the footnote to Table 6.

The only significant differences between the geometry of the thymine residue as observed by us (and by Gerdil) and that predicted recently by Spencer (1959*a*) are in the region of C5 and C6. The C4–C5 bond seems to be more nearly a pure double bond than predicted, with the angles at C5 in accord with this view. The C5–C6 bond is somewhat longer than predicted, and is indeed about twice the expected radius (0·73 Å) for trigonally hybridized carbon (Dewar & Schmeising, 1959). The bond angles at C6 are significantly distorted, presumably chiefly as a result of the short nonbonded intramolecular contact between the methyl group (C7) and O6 (see Table 3). The distortion of the angles increases this distance by about 0·1 Å.

All six atoms of the pyrimidine nucleus lie in the same plane (plane I of Table 5), the maximum deviation being less than the e.s.d. of an atomic position. The displacements of C7 and O6 from this plane are significant and are equal in magnitude and opposite in direction; presumably this results also from the close C7 · · · O6 contact. The displacements of O2 and C1′ from the plane of the ring are also significant and opposed, although the former atom is about twice as far from the plane as the latter.

The sugar

The deoxyribose ring may be described in various alternative ways. Least-squares planes were calculated for all five atoms of the ring and for all possible combinations of four atoms in the ring. One of the latter combinations (plane II in Table 5) was far more satisfactory than the others. Atoms C1′, C2′, C4′, and O1′ are essentially coplanar, with C3′ 0·53 Å from this plane; O3′ is only 0·13 Å from the plane. Spencer (1959*a*) correctly anticipated this puckering, stating that either C2′ or C3′ should lie out of the plane of the other ring atoms by about 0·5 Å.

The only bond distance in the sugar that differs appreciably from the expected value is that between C3′ and C4′, observed to be $1{\cdot}49_1$ Å. The 'normal' value is about $1{\cdot}53_3$ Å (Bartell, 1959) and thus the discrepancy is less than twice the e.s.d. and so cannot be considered significant. With certain exceptions the bond angles are close to the average values predicted by Spencer from a survey of similar molecules—internal angles of 105° and 108° at C and O atoms respectively, and external angles of about 112° at carbon. Two of the angles deviate from the latter value by as much as 5°; if the effect is real, it is not especially surprising for angle deformation requires comparatively little energy. For an average force constant, a 5° bend would require only about 0·7 kg.cal./mole. The exigencies of packing in so complex a molecule could readily provide energies of this magnitude.

The phosphate group

The phosphorus–oxygen distances in the phosphate group are in general accord with expectation, although there are no precise distances in similar molecules for comparison. The ester bond is much the longest of the four and that to the oxygen with no formal charge is the shortest, although its difference from one of the two bonds to the formally negative oxygens is only about 1 e.s.d. Whether the difference between the P–O_I and P–O_{II} distances is real is questionable; it is, however, at about the 99% significance level if one accepts the e.s.d.'s calculated in the usual way on the assumption that the errors are random. It is noteworthy that the shorter distance (P–O_I) involves the oxygen which is further from both of the calcium ions to which each of these oxygens is coordinated (Fig. 10); this would tend to produce an effect in the observed direction but it may be mere coincidence.

The only precise published determination of the structure of an organic phosphate is that of dibenzyl phosphoric acid (Dunitz & Rollett, 1956). In this molecule, however, there are two ester P–O bonds and one P–OH bond, the lengths being 1·57, 1·55, and 1·55 Å respectively; the fourth bond length is 1·47 Å. The bond angles at the ester oxygen atoms (O_5′ in the present structure) are 119° and 122°, in good agreement with the present value of 119°. Chemically equivalent O–P–O angles differ by 5° and 6°, these deviations being attributed to short non-bonded C···O contacts, which in the least favorable case differ by only 0·1 Å across the chemically equivalent angles. In the present molecule, the relatively short contacts of C5′ with O_I and O_{II} (Table 3) may serve to enlarge the corresponding angles (O5′–P–O_I and O5′–P–O_{II}) somewhat at the expense of the angle on the opposite side (O5′–P–O_{III}), although if the above-cited explanation for dibenzyl phosphoric acid is correct one might have expected some difference in the O5′–P–O_I and –O_{II} angles to result from the 0·19 Å difference in the non-bonded contacts. The relatively large values of the O_{III}–P–O_I and O_{III}–P–O_{II} angles are to be expected from consideration of the electrostatic repulsion of lone pairs and bonding pairs of electrons near these atoms (Gillespie & Nyholm, 1957). Although

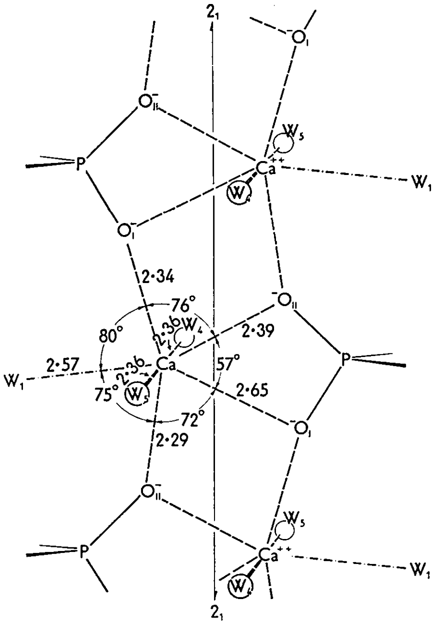


Fig. 10. Coordination of calcium ions with phosphate groups and water molecules.

Table 6. *Angles in suggested hydrogen-bonding scheme and calcium coordination not shown in Fig.* 10 *or* 12*

At atom	Subtended by	Angle	At atom	Subtended by	Angle
W1	O_{III}, W2	95°	Ca^{++}	W4, O_{IA}	80°
	O_{III}, W3	58		O_{IIA}	96
				O_{IB}	97
W3	O_{III}, W1	97°		O_{IIB}	88
	O_{III}, W6	102		W1	82
	W6, O_{IIIB}	119		W5	173
W6	O2, W4	134°		W5, O_{IA}	95°
	W3, W5	112		O_{IIA}	91
				O_{IB}	83
				O_{IIB}	87
				W1	102

* O_{IIIB} is related to O_{III} by the 2_1 at 0, *y*, ½. O_{IA} and O_{IIA} are respectively above and below the calcium ion (Fig. 10). O_{IB} and O_{IIB} are opposite the calcium ion, across the 2_1 (Fig. 10). Since O_{IA}, O_{IIA}, O_{IB}, O_{IIB}, W1, and Ca^{++} are essentially coplanar, the angle subtended at the calcium ion by any non-adjacent pair of the first five atoms may be calculated merely by summation of the angles given in Fig. 10.

in an isolated ion, or one in a more isotropic environment, one might expect the O_I–P–O_{II} angle to be the largest of all for similar reasons, the presence of the calcium ion in the median plane of the phosphate group across the two-fold screw axis (Fig. 10) may act to decrease this angle significantly. (The calcium ions above and below will have much less effect on the bond angle because the corresponding Ca–O lines are much more nearly parallel to than perpendicular to the P–O bonds.)

Calcium ion environment

Fig. 10 depicts the packing of the phosphate groups and calcium ions, together with the water molecules directly coordinated with the latter. Each calcium ion has seven-fold coordination, with four phosphate oxygens (from three different molecules) and one water molecule lying approximately in a plane (Table 5), and two other waters on a line through the calcium nearly perpendicular to this plane (Table 6). This calcium environment is remarkably similar to that for one of the two non-equivalent calcium ions in $CaHPO_4$ (MacLennan & Beevers, 1955), where the seven Ca–O distances range from 2·29 to 2·69 Å with an average value of 2·44. In the present structure, the range is almost the same (Fig. 10), with the average being 2·42 Å. The coordination number of calcium varies in different structures, with, as expected, smaller average distances for lower coordination number. For example, in $Ca(OH)_2$ (Busing & Levy, 1957), with six oxygens around each calcium, the Ca–O distance is 2·37 Å; for 8-fold coordinated calcium the average distance is about 2·5 Å (2·49 in $CaHPO_4$; 2·52 in $Ca(H_2PO_4)_2.H_2O$, MacLennan & Beevers, 1956).

Conformation of the thymidylate ion

One of the most interesting structural parameters is the conformation about the glycosidic C–N bond. Fig. 11 presents schematic views along this bond for the thymidylate ion in the present structure, as well as for the original Crick–Watson (1954) model of DNA and the revision of that model by Langridge *et al.* (1957). In discussing this conformation, it is convenient (Donohue & Trueblood, 1960) to define a torsion angle, φ_{CN}, as the angle formed by the trace of the plane of the base with the projection of the C1′–N bond. This angle, illustrated in Fig. 11, is taken as zero when O1′ is *anti-planar* to C2 of the pyrimidine or purine ring, and positive angles are taken as those measured in a clockwise direction when viewing from C1′ to N.

Fig. 11 shows that the torsion angle in the thymidylate ion lies about midway between the value proposed originally for DNA by Crick & Watson (1954) and the revised value of Langridge *et al.* (1957). Inspection of molecular models suggests that the difference between these three values is not significant in terms of non-bonded contacts. As has been discussed elsewhere (Donohue & Trueblood, 1960), consideration of molecular models suggests that there are two ranges of φ_{CN} within which relatively stable conformations might be assumed. Each of these ranges covers more than 90°, one being centered about *ca.* −30° (the *anti* range) and the other about *ca.* 150° (the *syn* range). Spencer (1959*b*) has noted that only the *anti* conformation, as here defined, has yet been observed in the three natural and synthetic pyrimidine nucleosides previously studied. The present structure provides another example of a natural *anti* conformation, but it is noteworthy that none of the structures so far reported involves a purine nucleotide. It may be significant that the only purine nucleoside whose structure has been reported, a cyclic adenosine nucleoside (Zussman, 1953) has the *syn* conformation; this is not a naturally occurring material, but the ease with which it is formed indicates that, at least with adenosine, the *syn* conformation is not difficult to achieve.

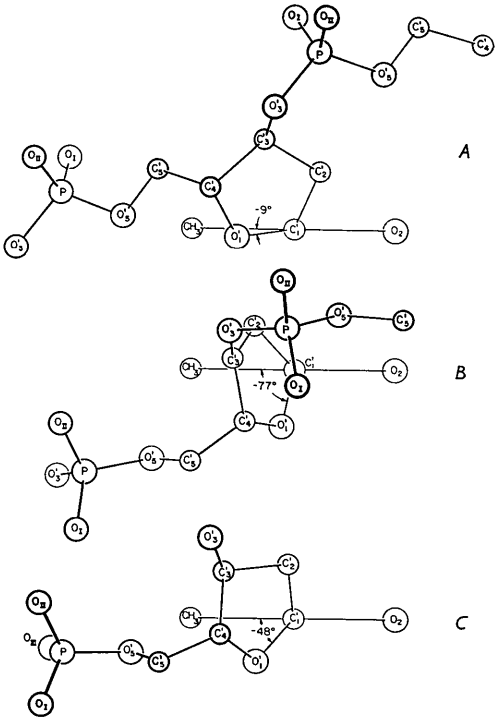


Fig. 11. Views showing the conformation about the glycosidic C1′–N3 bond viewed from C to N along the bond. *A*, the structure of DNA according to Crick & Watson, 1954; *B*, the structure of DNA according to Langridge *et al.*, 1957; *C*, the thymidylate ion. The angles shown are the values of φ_{CN}, defined in the text.

The plane of the three atoms C5′–O5′–P in the thymidylate ion (IV in Table 5) has been rotated some 80° from the position assumed by Crick & Watson, essentially normal to the plane of the base, to a position in which it makes an angle of only about 12° with the plane of the base (Fig. 11). The situation of this chain of atoms in the present structure is rather similar to that assumed in the model of Langridge *et al.* The difference from the Crick–Watson model involves rotation about the bonds C4′–C5′ and O5′–P; in mononucleotides at least, this difference would not seem important energetically. The plane of the deoxyribose ring (II in Table 5) makes an angle of 75° with the plane of the pyrimidine nucleus. The general orientation is thus almost identical to that in cytidine, for which a value of 76° can be calculated from Furberg's (1950) parameters, and thus is very similar to that assumed by Crick & Watson in constructing their model.

Suggested hydrogen-bonding scheme and molecular packing

Fig. 12 shows the close contacts which might represent hydrogen bonds, and also the calcium ion–water bonds. The tentative hydrogen positions deduced from the difference map in accord with geometrical considerations are indicated also for the hydrogen atoms on the water molecules, as well as for those on N1 and O3′. If these suggested positions are correct, only one of these fourteen hydrogen atoms (one of the two on W4) is not involved in a hydrogen bond. W4 has only one possible acceptor (W6) within a distance of 3·0 Å; the next nearest ones are $O_{\rm I}$ of the neighboring phosphate group across the z-axis (3·03 Å) and $O_{\rm II}$ of the phosphate group across the x-axis (3·28 Å). Each of these contacts is unusually long (Fuller, 1959) for a hydrogen bond from a water molecule to an oxygen atom in an anion; furthermore, no possible position for the second hydrogen on W4 is consistent with the shorter of these contacts if the W4–W6 contact is a hydrogen bond involving a hydrogen atom from W4, as seems likely. Thus it seems reasonably sure that W4 is involved in only one hydrogen bond.

There is only one apparent hydrogen bond in the structure which does not involve a water molecule, that from O3′ to O6. The only other potential hydrogen-donor atom in the thymidylate ion, N1, forms a hydrogen bond with W2. The distances and angles in both of these contacts are normal (Fuller, 1959). The five water–water contacts range in distance from 2·74

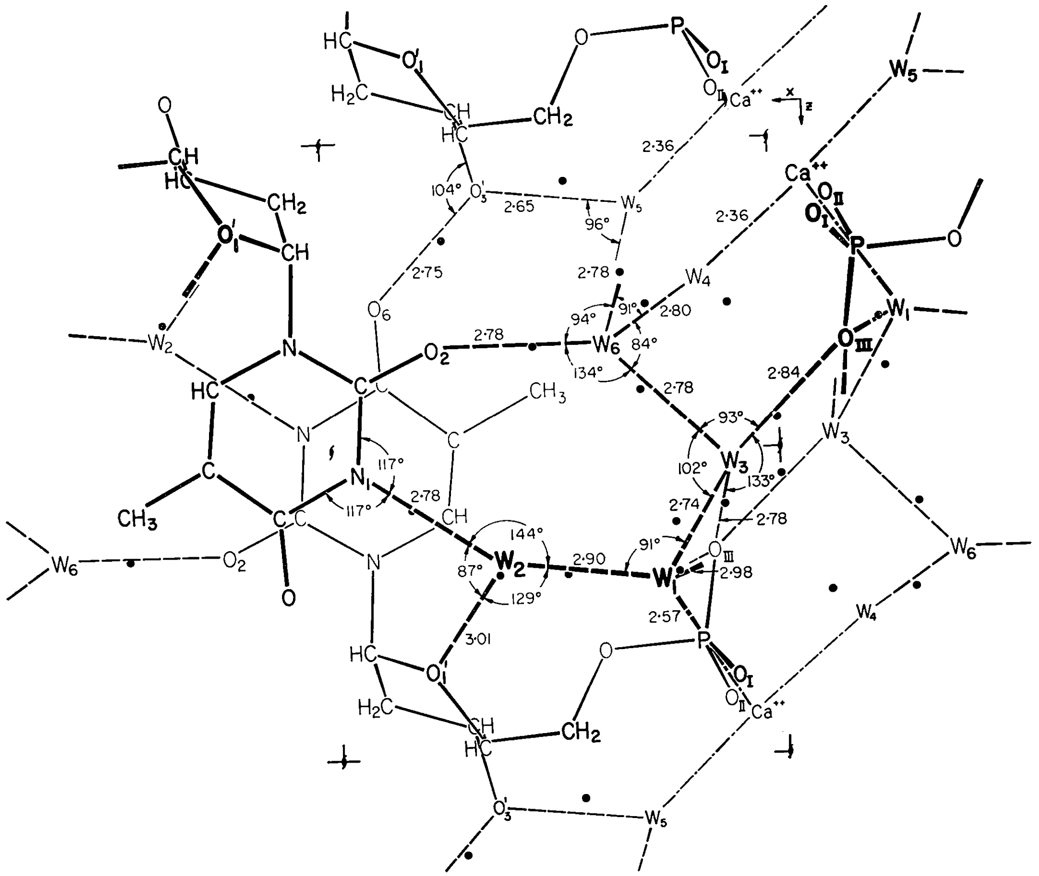


Fig. 12. Suggested scheme of hydrogen-bonding and calcium ion-water molecule coordination. The suggested positions (Table 2) for the hydrogen atoms on the water molecules and on N1 and O3′ are indicated by black dots. Possible hydrogen bonds are shown by dashed lines and calcium ion-water molecule bonds by alternate dots and dashes. Pertinent angles not shown here are given in Table 6.

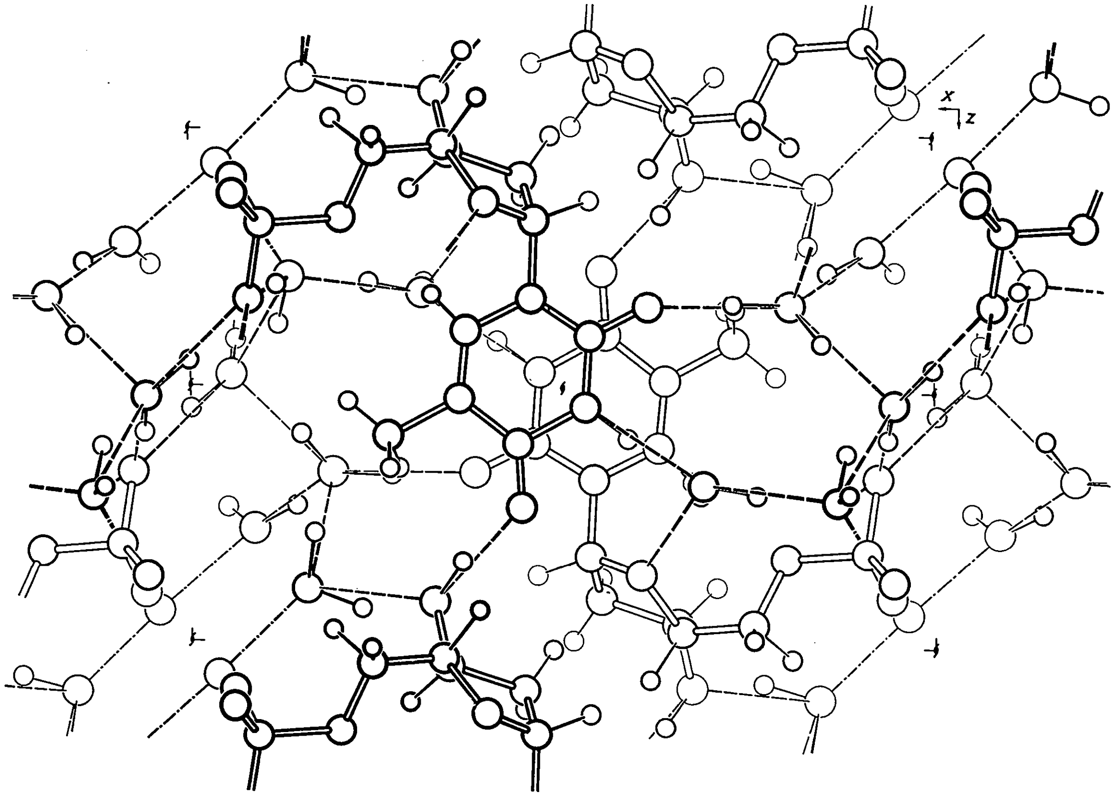


Fig. 13. A portion of the structure (slightly more than one unit cell) viewed along **b**. Atoms may be identified by comparison with Fig. 12. Hydrogen atoms are shown in the suggested positions of Table 2; these positions are at best tentative. Possible hydrogen bonds are shown by dashed lines and calcium ion-water molecule bonds by alternate dots and dashes.

to 2·90, with the average 2·80; presumably all or at least most of these involve hydrogen bonds. Bonds of this sort have been observed to vary in length from 2·64 to 2·91 Å, with the average of twenty values 2·75 Å (Fuller, 1959). Of the other possible hydrogen bonds, those from W3 to two different O_{III} atoms, from W6 to O2, and from W5 to O3′ seem very plausible. On the other hand, identification of the contact from W2 to O1 as a hydrogen bond is questionable, both because of the rather long distance (3·01 Å), and the unfavorable suggested position for the corresponding hydrogen atom on W2. Similarly the contact between W1 and O_{III} is rather long (2·98 Å), although the suggested position of the hydrogen atom on W1 is consistent with the hypothesis that this contact involves a hydrogen bond.

Three of the six water molecules are bonded to the calcium ion; it is noteworthy (Table 1) that the apparent thermal motions of these three are lower than those for the other three water molecules, which are held in the structure only by hydrogen bonds. It seems significant also that the oxygen atom of W2 has the highest apparent thermal vibration amplitude of any atom in the structure; it is involved only in one strong hydrogen bond (with N1), the contacts with W1 and O1′ being at best weak hydrogen bonds.

Fig. 13 is a drawing of a portion of the entire structure, including the hydrogen atoms in their suggested positions. Different thymidylate ions are in contact in two regions of the unit cell: the bases are stacked along the two-fold screw axis at $(\frac{1}{2}, y, \frac{1}{2})$, and the sugar rings approach each other around the screw axis at $(\frac{1}{2}, y, 0)$. If the planes of the bases were just normal to **b**, they would be parallel and separated by $b_0/2 =$ 3·44 Å which is very nearly the value assumed by Crick & Watson (1954). However, in fact they are tipped slightly (Table 5), successive planes being at 12° to one another. Because of this tip, the closest approach is 3·20 Å, between C2 and C6 of successive residues. These atoms overlap slightly in the view along **b** in Fig. 13.

There are no unusually close contacts between the atoms of successive sugar rings related by the screw axis. The closest approach of any pair of 'heavy' atoms is 3·37 Å, from C2′ of one ring to O1′ of the next. Several of the suggested hydrogen positions imply rather short contacts: H on C1′ to H(*a*) on C2′, 2·0 Å, and to H on O3′, 2·2 Å; H(*a*) on C2′ to O1′, 2·4 Å, and to H on C4′, 2·4 Å. However, since even those hydrogen positions which are reasonably well established by virtue of the tetrahedral nature of the carbon atom could easily be in error by 0·1 Å, and that for the

Table 7. *Observed and calculated structure factors*

The running index, listed at the left, is h; k and l are constant for each group of reflections and are listed on a separate line above each group. The other columns are, from left to right: $10F_o$, $10|F_c|$, $10F_o \cos \alpha$ and $10F_o \sin \alpha$. For those reflections too weak to be observed, the value of F_o listed is $7{\cdot}07F_{\text{min.}}$, where $F_{\text{min.}}$ represents an approximate minimum observable F_o in the corresponding region of reciprocal space. These values are marked with a minus sign in the F_o column, and the last two columns are blank.

The parameters used in the calculations of the observed structure factors were those of Set 17 (see text), without the contributions of the hydrogen atoms. The unobserved structure factors were calculated with the parameters of Set 15.

0 0				
1	147	59	147	
2	672	872	672	
3	255	191	255	
4	282	287	282-	
5	273	187	273-	
6	321	237	321-	
7	531	480	531-	
8	471	466	471-	
9	120	80	120-	
10	321	330	321-	
11	174	174	174	
12	243	231	243-	
13	99	83	99	
14	219	212	219-	
15	51	24	51	
16	159	154	159-	
0 1				
16-	132	130	132-	
15-	120	107	120-	
14-	126	86	126-	
13-	225	206	225-	
12-	171	163	171	
11-	378	378	378-	
10-	186	169	186-	
9-	90	27	90-	
8-	117	109	117-	
7-	261	191	261-	
6-	60	54	60-	
5-	288	234	288-	
4-	561	519	561-	
3-	165	119	165-	
2-	315	366	315-	
1-	270	311	270	
	411	440	411	
1	753	1018	753	
2	342	367	342	
3	756	885	756	
4	462	442	462	
5	375	370	375	
6	228	193	228	
7	117	65	117-	
8	309	284	309-	
9	126	18	126-	
10	180	155	180-	
11	216	202	216-	
12	51	41	51	
13	189	155	189-	
14	168	136	168-	
15	51	71	51-	
16	177	165	177-	
0 2				
16-	51	46	51-	
15-	51	24	51	
14-	51	3	51	
13-	225	202	225-	
12-	237	196	237-	
11-	300	329	300-	
10-	342	321	342-	
9-	204	183	204-	
8-	42	19	42	
7-	213	153	213-	
6-	165	208	165-	
5-	507	472	507-	
4-	456	413	456	
3-	189	158	189	
2-	60	52	60	
1-	513	518	513-	
	60	24	60	
1	324	347	324	
2	51	12	51	
3	795	1067	795	
4	321	240	321	
5	792	836	792	
6	693	821	693	
7	42	8	42-	
8	159	131	159	
9	159	157	159-	
10	393	419	393-	
11	120	98	120-	
12	111	69	111	
13	252	233	252-	
14	135	134	135-	
15	165	158	165-	
16	51	22	51-	
0 3				
16-	198	225	198	
15-	144	107	144	
14-	42	21	42	
13-	42	26	42	
12-	144	114	144-	
11-	144	96	144-	
10-	255	237	255-	
9-	108	96	108-	
8-	138	110	138-	
7-	30	20	30-	
6-	351	338	351-	
5-	546	542	546-	
4-	267	286	267-	
3-	285	307	285-	
2-	315	292	315-	
1-	252	302	252-	
	144	94	144	
1	324	330	324-	
2	261	203	261-	
3	690	706	690	
4	399	374	399	
5	678	747	678	
6	627	741	627	
7	336	349	336	
8	168	160	168	
9	171	176	171	
10	153	154	153-	
11	51-	22		
12	132	119	132-	
13	180	122	180-	
14	60	84	60-	
15	78	73	78-	
16	42-	24		
0 4				
15-	51-	53		
14-	150	168	150	
13-	60	64	60	
12-	120	86	120	
11-	165	129	165	
10-	246	229	246-	
9-	123	107	123-	
8-	132	115	132-	
7-	291	216	291-	
6-	99	68	99	
5-	423	502	423-	
4-	399	429	399-	
3-	147	143	147-	
2-	99	84	99-	
1-	30-	15		
	420	397	420-	
1	84	28	84	
2	51	24	51-	
3	108	117	108	
4	432	439	432	
5	144	133	144	
6	126	95	126	
7	171	173	171	
8	303	326	303	
9	450	513	450	
10	186	164	186	
11	177	140	177-	
12	168	162	168	
13	225	222	225-	
14	51-	15		
15	117	118	117-	
0 5				
15-	42-	31		
14-	138	134	138	
13-	51-	17		
12-	135	135	135	
11-	282	258	282	
10-	51-	58		
9-	186	174	186-	
8-	60	69	60-	
7-	246	266	246-	
6-	366	387	366-	
5-	78	48	78-	
4-	66	64	66-	
3-	30-	52		
2-	213	235	213-	
1-	135	96	135-	
	360	397	360-	
1	189	176	189-	
2	192	182	192-	
3	282	253	282-	
4	60	46	60	
5	123	118	123-	
6	42-	40		
7	105	124	105	
8	354	400	354	
9	438	493	438	
10	411	396	411	
11	330	327	330	
12	198	155	198	
13	51-	14		
14	51	71	51-	
15	84	79	84-	
0 6				
14-	72	28	72-	
13-	99	87	99	
12-	117	87	117-	
11-	258	241	258	
10-	267	255	267	
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8-	120	117	120	
7-	225	209	225-	
6-	273	277	273-	
5-	51	51	51	
4-	267	283	267-	
3-	99	68	99-	
2-	135	136	135-	
1-	51	116	51-	
	60	44	60	
1	42-	12		
2	147	128	147-	
3	252	249	252-	
4	42-	96		
5	132	138	132-	
6	42-	34		
7	279	258	279-	
8	51-	35		
9	117	117	117	
10	339	347	339	
11	153	138	153	
12	213	205	213	
13	171	193	171	
14	99	107	99	
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13-	90	83	90-	
12-	51-	22		
11-	51-	33		
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9-	96	82	96	
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7-	51-	13		
6-	276	244	276	
5-	213	214	213-	
4-	60	83	60-	
3-	330	382	330-	
2-	267	269	267-	
1-	447	510	447-	
	255	262	255-	
1	42-	45		
2	42-	44		
3	42-	15		
4	51-	20		
5	279	276	279	
6	252	240	252-	
7	351	323	351	
8	186	173	186-	
9	60-	65		
10	60-	16		
11	105	65	105-	
12	72	103	72	
13	141	171	141	
0 8				
12-	42-	17		
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10-	96	66	96-	
9-	96	64	96-	
8-	123	130	123	
7-	288	254	288	
6-	177	135	177-	
5-	468	489	468	
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2-	51-	37		
1-	414	400	414-	
	303	275	303-	
1	51-	69		
2	150	134	150-	
3	162	141	162-	
4	60-	52		
5	306	280	306-	
6	195	176	195	
7	60-	61		
8	60-	17		
9	78	76	78-	
10	51-	5		
11	51-	12		
0 9				
10-	105	82	105	
9-	117	115	117-	
8-	51-	44		
7-	51-	27		
6-	60-	12		
5-	96	83	96	
4-	60-	14		
3-	150	137	150	
2-	105	98	105	
1-	60-	2		
	228	230	228-	
1	60-	15		
2	234	224	234-	
3	213	199	213-	
4	78	89	78-	
5	135	130	135-	
6	51-	17		
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8	51-	10		
9	51-	32		
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6-	51-	16		
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4-	51-	4		
3-	51-	9		
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1-	51-	8		
	51-	46		
1	51-	70		
2	225	183	225-	
3	192	187	192-	
4	126	106	126-	
5	207	209	207-	
6	108	130	108-	
7	42-	47		
8	42-	95		
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5-	42-	85		
4-	42-	29		
3-	42-	53		
2-	135	109	135	
1-	51-	41		
	51-	26		
1	51-	60		
2	51-			
3	138	148	138-	
4	42-	9		
1 0				
1	321	400	167-	274
2	414	447	413	9-
3	366	423	243-	273
4	60	31	51	30
5	318	341	14-	317
6	279	280	278	22
7	462	501	62-	457-
8	588	617	172	562-
9	450	477	128-	431-
10	336	346	65-	329-
11	216	215	180	119-
12	225	206	198-	105
13	138	127	112	80
14	150	125	70-	132
15	132	112	12-	131
16	141	130	53-	130
1 1				
16-	30-	1		
15-	120	101	41	112-
14-	138	120	114-	76
13-	285	270	116	260-
12-	177	154	176-	13-
11-	240	249	112	212-
10-	78	64	66	41-
9-	237	233	47-	232
8-	342	345	20-	341
7-	567	614	143	548
6-	246	274	59	238
5-	219	249	200	89-
4-	309	328	15-	308
3-	207	205	75-	192
2-	96	80	59	75
1-	141	167	139	21-
	390	548	70	383-
1	288	307	178-	226
2	195	145	126	148-
3	414	405	401-	101
4	207	211	206-	19
5	213	200	165	105-
6	123	69	75	97
7	408	443	408-	5-
8	297	321	206	213-
9	165	138	44-	158-
10	285	295	3	285-
11	183	175	56	174-
12	207	165	56-	199-
13	132	94	6-	131-
14	30-	14		
15	42	32	30	29-
16	147	132	28-	144
1 2				
16-	99	87	85-	49
15-	51	51	15-	48-
14-	30-	27		
13-	111	116	105-	35
12-	162	152	89	134-
11-	78	50	3-	77
10-	222	239	49-	216-
9-	225	214	20	224-
8-	117	98	13-	116-
7-	231	211	119	198
6-	204	224	188	79
5-	633	814	429-	465
4-	489	578	387	298
3-	567	774	150-	546
2-	525	762	127-	509
1-	165	200	127	105
	300	431	41-	297-
1	264	290	261-	34-
2	315	365	314	16-
3	318	360	197	249-
4	66	65	32	57
5	393	436	198	339-
6	309	299	293-	97-
7	339	343	227	251-
8	150	164	88-	121
9	105	121	96	41
10	171	138	166-	38-
11	153	122	60	140-
12	300	256	48-	296-
13	201	170	78-	185-
14	180	174	94	153-
15	159	128	55-	148-
16	30	26	28-	7
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15-	138	120	22-	136-
14-	90	79	47-	76-
13-	123	106	2	123-
12-	159	118	91-	130-
11-	231	197	48-	225
10-	66	42	62-	21-
9-	216	230	123	176-
8-	135	121	116-	68-
7-	171	158	60	160-
6-	159	161	93-	128
5-	261	311	255	54
4-	378	439	24	377
3-	384	463	195	330
2-	411	490	182	368
1-	354	504	136-	326
	213	252	8	212-
1	126	121	28-	122-
2	150	165	85	123
3	294	331	277-	97-
4	324	354	176-	271
5	186	193	141-	120
6	198	218	62	187-
7	186	152	141-	120
8	60	38	5-	59-
9	108	106	25-	105
10	78	60	76-	16
11	276	277	160	224-
12	234	203	42-	230-
13	258	253	64	249-
14	150	138	57	138-
15	171	152	79-	151-
16	117	107	3	116-
1 4				
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14-	171	172	16	170-
13-	177	177	62-	165-
12-	246	223	58-	239-
11-	96	72	94	19
10-	108	115	85-	65
9-	108	97	104-	25-
8-	30-	10		
7-	147	148	139-	45-
6-	30	33	7	29
5-	126	139	1-	126
4-	120	108	106-	55
3-	111	121	26-	107
2-	240	265	113	211
1-	237	331	68	226
	345	419	290	186
1	300	322	33	298
2	249	261	188	163
3	123	132	74-	97-
4	60	73	38	45
5	201	227	195	47-
6	180	171	148-	101-
7	78	89	57-	52
8	84	86	1	84-
9	96	85	74-	60
10	135	127	71-	114
11	150	151	67	133-
12	159	137	89-	131-
13	108	92	26-	104-
14	42	51	27	31-
15	108	101	19	106-
1 5				
15-	90	79	23	87-
14-	168	154	47	161-
13-	123	104	56-	109-
12-	249	256	62	241-
11-	99	72	85-	50-
10-	108	76	89-	60-
9-	135	129	74-	112-
8-	51	52	39	32-
7-	153	154	46-	145-
6-	147	149	90	115-
5-	141	157	70-	122
4-	180	197	18	179-
3-	147	151	54	136-
2-	168	187	58-	157
1-	189	243	171	80-
	510	726	176-	476
1	432	616	60	427
2	516	661	80-	509
3	207	232	154	137
4	117	119	92-	71
5	30	38	29-	6-
6	162	200	78-	141-
7	156	173	105	114-
8	159	162	57-	148-
9	153	142	17	152-
10	96	72	85	43
11	147	132	138-	48
12	111	101	60	92-
13	144	145	88-	114
14	105	112	103	18-
1 6				
14-	60	53		60-
13-	165	159	61	153-
12-	147	130	41-	141-
11-	186	193	49	179-
10-	126	103	92-	85-
9-	207	198	42	202-
8-	105	87	104-	10-
7-	189	189	167-	87-
6-	90	95	26	85-
5-	84	81	73-	40
4-	117	94	116-	14-
3-	111	124	31	106-
2-	159	179	149	54-
1-	243	296	227-	85-
	201	240	194	50-
1	303	380	92	288
2	282	338	41	278
3	291	366	134	258
4	165	186	7-	164
5	225	257	61	216
6	135	137	118	64
7	222	239	76-	208
8	168	170	55	158-
9	195	155	101-	166-
10	78	62	75-	21-
11	99	94		99-
12	60	44	43-	41-
13	30	30	24-	17
14	30-	19		
1 7				
13-	72	61	32-	64-
12-	120	137	55	106-
11-	246	251	75	234-
10-	198	178	31-	195-
9-	252	253	66	243-
8-	156	131	21-	154-
7-	96	79	39-	67-
6-	105	81	101-	27-
5-	30	27	21	21-
4-	150	153	148-	23
3-	90	101	70-	55
2-	117	123	7-	116
1-	108	110	62-	88-
	189	216	75	173-
1	51	40	50-	4
2	99	128	51-	84-
3	138	151	24	135
4	120	104	86	83
5	234	235	12-	233
6	378	410	34	376
7	282	312	64	274
8	270	249	101-	250
9	72	64	62	35-
10	30	14	30	1
11	96	96	15	94-
12	105	109	13	104-
13	60	65	42-	42-
1 8				
12-	66	57	51	40
11-	78	75	14	76-
10-	189	159	30	186-
9-	213	186	15	212-
8-	315	303	122	290-
7-	177	154	160-	74-
6-	258	243	165	197-
5-	177	139	150-	92-
4-	213	185	125-	172-
3-	78	52	22	74-
2-	150	152	88-	121
1-	96	70	7-	95
	72	57	25-	67-
1	30-	19		
2	126	145	22	124-
3	117	126	117	
4	51	30	12	49
5	30-	3		
6	243	239	109	217
7	243	236	37-	240
8	222	217	12	221
9	120	113	30	116
10	105	121	8-	104
11	60	55	58-	13
1 9				
10-	78	76	78	1-
9-	30-	18		
8-	162	161	42	156-
7-	192	185	19	191-
6-	117	114	31	112-
5-	234	225	37	231-
4-	231	204	21-	230-
3-	237	203	36	234-
2-	117	85	85-	79-
1-	141	114	120-	72
	117	102	113-	28
1	84	79	74	38-
2	255	263	230-	109
3	126	115	125	15-
4	147	120	84-	120
5	51	49	40-	30-
6	117	101	109	40
7	72	64	22	68
8	78	64	61	48
9	138	134	58	125
10	132	141	26	129
1 10				
8-	30-	33		
7-	90	72	46-	76-
6-	120	115	45	111-
5-	171	154	70	155-
4-	168	156	49-	160-
3-	186	192	52	178-
2-	156	146	18-	154-
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3-	99	120	17-	97
2-	144	151	144	3-
1-	78	90	68-	37-
	165	167	144-	79-
1	96	80	91	28-
2	150	148	120-	89
3	189	193	168	84
4	300	343	291	70-
5	261	234	257	40-
6	285	314	280	52-
7	267	259	254	80-
8	66	45	64	15-
9	72	87	63	34-
10	42	60	41-	9-
11	111	115	85-	71-
12	108	111	22-	105
13	108	127	89-	60-
4 4				
13-	60	48	50	21-
12-	30-	2		
11-	30-	16		
10-	225	224	209-	82
9-	225	238	224-	14
8-	189	202	174-	72
7-	216	232	214-	28
6-	177	158	172-	38
5-	186	170	158-	97
4-	162	164	161-	10
3-	30-	33		
2-	150	171	150	
1-	42	35	27	31-
	60	60	40	44-
1	144	145	69-	126-
2	159	170	87-	132-
3	150	158	109	102
4	174	170	148	90-
5	30-	42		
6	171	155	160	59
7	168	151	163	39
8	219	197	218	8-
9	273	316	265	62-
10	72	85	68	22
11	30-	40		
12	30-	51		
13	30-	27		
4 5				
12-	111	127	85	70-
11-	117	108	110	37-
10-	30-	36		
9-	99	121	98-	12-
8-	135	143	134-	15
7-	330	374	329-	15-
6-	183	190	168-	70
5-	225	257	202-	98
4-	195	193	194-	7
3-	72	63	31	64
2-	252	278	39-	249
1-	90	111	8	89
	105	116	61	85
1	72	66	71	4
2	231	215	116-	199-
3	96	75	51	80-
4	159	158	14-	158-
5	186	182	111-	148-
6	30	19	16-	25-
7	171	150	134	106-
8	123	99	107	59
9	288	322	287	5-
10	228	289	219	62
11	72	86	70	16-
12	156	195	150	40
4 6				
11-	99	107	98	12-
10-	138	147	124	59-
9-	51	50	49	12-
8-	30-	31		
7-	246	265	240-	53-
6-	144	131	144-	2
5-	225	196	224-	8-
4-	276	266	264-	77
3-	204	168	191-	71-
2-	258	246	229-	118
1-	126	111	105-	69
	84	64	18	81
1	195	169	156	116
2	99	56	80-	58
3	51	64	50	9
4	30-	11		
5	96	95	25	92-
6	153	152	60-	140-
7	30-	37		
8	96	94	74-	60-
9	141	141	141	3
10	171	201	170	18-
11	72	98	56	44
4 7				
10-	78	85	75	20
9-	108	105	108	2-
8-	105	115	102	24
7-	141	146	135	40-
6-	171	184	142-	94-
5-	168	169	68	153
4-	285	299	278-	59-
3-	189	162	187-	26
2-	330	303	329-	20-
1-	342	327	339-	41
	177	121	176-	18-
1	105	114	65-	82
2	30-	29		
3	99	101	46	87
4	189	189	109	154
5	132	138	30-	128-
6	213	233	175	121
7	159	167	83-	135-
8	60	85	36	47-
9	99	113	28-	94-
10	72	79	33	63-
4 8				
8-	78	102	68	37
7-	138	144	95	99-
6-	111	112	93	60
5-	78	77	8	77-
4-	66	44	61	23
3-	72	71	71-	5-
2-	174	160	173-	16-
1-	282	275	277-	48
	240	213	230-	67-
1	198	193	173-	95
2	105	85	89-	54-
3	105	97	80-	67
4	135	107	71-	114
5	126	81	17-	124
6	78	59	56	54-
7	123	150	82	91
8	30-	34		
4 9				
6-	105	103	15	103-
5-	66	100	48	45
4-	96	83	63	72-
3-	30-	12		
2-	66	72	59	29
1-	111	132	109-	20-
	123	150	96-	76
1	120	148	120-	1-
2	150	190	144-	41
3	126	151	126-	1
4	105	131	92-	50
5	96	131	72-	62-
6	30-	29		
4 10				
	30	69	27-	12-
5 0				
1	108	116	27-	104
2	177	181	176-	6
3	132	137	104-	81
4	156	164	151-	36
5	66	66	16	63-
6	120	106	61	103-
7	339	309	51-	335-
8	315	290	98	299-
9	288	287	4-	288-
10	144	147	23	142-
11	99	90	4-	98-
12	42	34	3	41
13	42	34	26-	33
5 1				
13-	126	149	107-	65-
12-	165	181	151	66-
11-	42-	54		
10-	72	82	10	71-
9-	234	234	89	216
8-	237	220	126-	200
7-	336	318	24	335
6-	189	178	112	152
5-	225	222	177-	138
4-	168	167	12	167
3-	90	73	10-	89
2-	108	82	74-	78
1-	213	227	111	181-
	108	114	92	56-
1	201	209	124	157-
2	183	160	45-	177
3	30-	33		
4	174	166	31-	171
5	30-	37		
6	42-	50		
7	42-	46		
8	201	171	47-	195-
9	207	187	29	204-
10	285	276	13-	284-
11	99	84	13	98-
12	231	219	89-	213-
13	42-	8		
5 2				
12-	42-	50		
11-	117	114	73	91-
10-	105	78	21-	102-
9-	123	120	112	50-
8-	42-	34		
7-	171	130	92	143
6-	276	253	87	261
5-	336	285		336
4-	342	310	116-	321
3-	324	325	25	323
2-	264	267	116-	237
1-	189	159	149-	116
	153	136	15-	152-
1	123	113	30	119-
2	204	189	144	144-
3	186	145	102	155-
4	123	108	120	24-
5	117	87	53-	104-
6	141	117	126	63
7	237	175	236-	14-
8	42-	18		
9	42-	27		
10	159	145	74-	140-
11	153	157	22	151-
12	180	183	82-	160-
5 3				
12-	42-	28		
11-	42-	24		
10-	84	90	1	84-
9-	135	132	76	111-
8-	96	79	20-	93-
7-	111	102	75-	81-
6-	186	182	135	127
5-	186	177	170-	75
4-	279	264	110	256
3-	342	306	145	309
2-	321	321	115-	299
1-	282	246	30	280
	186	167	12	185
1	117	75	104-	53-
2	144	137	131	58-
3	30-	17		
4	72	68	67-	25-
5	108	82	101	37-
6	126	124	22	123-
7	72	53	9-	71
8	120	102	116-	28
9	111	120	30	106
10	51	67	44-	24-
11	84	76	29	78-
12	171	170	43	165-
5 4				
11-	42-	46		
10-	42-	24		
9-	42-	50		
8-	78	59	39-	67-
7-	105	113	17	103-
6-	99	100	93	32-
5-	111	97	96-	55
4-	108	99	80-	72
3-	204	191	124	162
2-	264	234	127-	231
1-	276	250	72	266
	300	273	85	287
1	276	223	59-	269
2	165	119	36	160
3	51	49	23	45
4	159	112	123-	99-
5	72	95	32	64-
6	171	167	84	148-
7	30	44	2-	29-
8	99	97	40-	90-
9	60	61	35	48

H on O3′ even more, these short apparent contacts are not inconsistent with the usual van der Waals radius for hydrogen, 1·1–1·2 Å. The only other apparent H–H contact of less than 2·4 Å is that between H(*a*) on C5′ and H(*a*) on W5, 2·2 Å.

It has been emphasized above that the limitations of the data preclude any extensive discussion of anisotropic thermal motion in this structure. However, comparison of Figs. 10 and 13 with the gross indications of anisotropy included with the temperature

Table 7 (*cont.*)

10	60	56	35-	48
11	51	43	44-	25-
5 5				
11-	90	84	28-	85-
10-	84	94	67-	50-
9-	42-	26		
8-	42-	54		
7-	105	115	65	81-
6-	141	155	134	41-
5-	96	82	59	75-
4-	84	61	57-	61-
3-	90	86	82	36-
2-	42-	11		
1-	213	181	178-	116
	420	336	101	407
1	489	411	253-	418
2	408	312	72	401
3	297	217	40	294
4	165	133	136-	92
5	171	142	87	146
6	141	117	112	84-
7	120	92	8-	119-
8	186	176	138	124-
9	126	116	67	106-
10	51	64	34-	37-
5 6				
9-	117	119	53-	104-
8-	96	98	62-	72-
7-	42-	23		
6-	96	105	44	85-
5-	72	51	37	61
4-	90	99	70	55-
3-	120	104	118	16-
2-	132	98	40	125-
1-	90	58	71	55-
	90	69	36-	82
1	189	155	106-	156
2	261	205	28-	259
3	267	219	21	266
4	255	249	155-	201
5	138	108	52	127
6	195	181	3-	195
7	42-	33		
8	42-	15		
9	117	128	71	92-
5 7				
8-	126	123	31-	122-
7-	156	169	74-	137-
6-	42-	33		
5-	99	128	64-	74-
4-	51	48	46-	21
3-	42-	33		
2-	78	66	71	31
1-	132	110	100	86-
	159	136	146	62-
1	42-	40		
2	72	58		72
3	192	166	95	166
4	150	158	104-	107
5	231	213	4-	231
6	228	230	45	223
7	225	234	158-	159
8	147	144	11	146
5 8				
6-	108	130	11-	107-
5-	126	157	6	125-
4-	84	74	79-	26-
3-	132	112	49-	122-
2-	42-	74		
1-	42-	30		
	42-	23		
1	96	92	90	33-
2	99	78	16-	97-
3	90	93	88	14
4	42-	42		
5	135	125	31-	131
5 9				
	42-	21		
6 0				
	708	583	707	21-
1	354	310	333	119
2	378	305	370	75-
3	150	139	146	33
4	42-	33		
5	90	103	39-	80-
6	120	134	119-	4
7	141	161	113-	83-
8	126	174	110-	60-
9	72	103	64-	31
10	84	97	63-	55
11	66	80	17-	63
6 1				
11-	147	212	144-	27
10-	51	53	9-	50
9-	90	133	26-	86
8-	96	120	91-	30
7-	51	61	46-	21
6-	177	201	169-	50
5-	90	101	87-	20-
4-	195	193	134-	141-
3-	30-	62		
2-	153	135	53-	143-
1-	303	254	302	20
	243	213	228	81-
1	531	474	513	135-
2	384	344	383	13
3	303	259	298	55-
4	279	231	278	13
5	171	153	145	90-
6	171	160	88	146
7	108	85	71-	81-
8	144	140	144-	3-
9	150	185	149-	13
10	30-	45		
6 2				
10-	144	163	141-	29-
9-	84	105	80-	22
8-	66	92	48-	45
7-	42-	43		
6-	141	162	55-	129
5-	168	155	152-	70
4-	42-	67		
3-	195	189	158-	114
2-	123	123	86-	87-
1-	84	76	59-	59-
	78	50	77	12-
1	213	160	178	116-
2	381	291	380	13
3	426	344	421	59-
4	405	329	391	103-
5	408	343	400	80-
6	291	269	287	42
7	78	75	69	35
8	42-	38		
9	123	127	122-	11
10	99	109	97-	14-
6 3				
10-	144	145	143-	6-
9-	132	152	130-	20-
8-	144	164	143-	5
7-	42-	17		
6-	135	149	114-	71
5-	144	150	118-	82
4-	42-	29		
3-	99	105	96-	22
2-	96	83	87-	40-
1-	150	116	141-	51-
	180	158	180-	3-
1	195	161	149-	124-
2	162	105	155	44
3	225	183	224	14
4	324	281	320	45-
5	324	296	323	13-
6	321	304	319	31-
7	270	292	269	8
8	183	197	171	62-
9	30-	73		
10	30-	32		
6 4				
9-	84	122	83-	5
8-	135	165	133-	18-
7-	117	189	115-	16
6-	105	129	121-	25-
5-	171	182	158-	64
4-	96	74	77-	56-
3-	51-	87		
2-	105	128	10-	104
1-	51-	16		
	186	145	164-	66
1	186	174	122-	139-
2	51-	55		
3	51-	47		
4	117	79	94	68-
5	177	148	176	16-
6	180	169	179	7-
7	237	254	226	71-
8	231	279	231	2-
6 5				
8-	105	109	104-	14-
7-	111	140	110-	8
6-	156	175	153-	27-
5-	177	190	176-	12
4-	150	124	148-	19
3-	183	163	182-	9
2-	132	142	95-	90
1-	90	73	57	69
	132	78	66-	113
1	132	79	127-	34-
2	168	84	68-	153-
3	123	98	121-	22-
4	135	112	57-	122-
5	111	79	45	101-
6	60	56	55-	23-
7	84	130	82	17
8	162	182	161	5
6 6				
7-	51-	50		
6-	126	122	122-	28
5-	60	70	57-	17
4-	198	191	198-	4-
3-	165	152	156-	52-
2-	216	216	208-	58
1-	126	115	95-	82
	99	93	85-	49
1	165	118	34-	161
2	51-	31		
3	51-	61		
4	51-	55		
5	90	97	65-	61-
6	51-	56		
7	99	109	71-	68-
6 7				
4-	51-	5		
3-	186	163	173-	68-
2-	219	205	219-	2-
1-	237	202	228-	63-
	180	157	176-	34-
1	105	85	100-	31
2	51-	37		
3	51-	84		
4	147	133	45-	139
7 0				
1	96	74	86-	41
2	99	116	77-	61
3	84	93	75-	37
4	99	108	80-	58-
5	90	80		90-
6	96	101	7-	95-
7	150	201	16-	149-
8	150	209	29	147-
7 1				
8-	111	153	7	110
7-	141	173	26	138
6-	186	231	11	185
5-	144	142	30-	140
4-	198	198	31	195
3-	123	103	19	121
2-	51	42	49	12
1-	108	96	101	38
	132	109	29-	128-
1	162	138	158	32-
2	99	82	95-	24-
3	60	51	3	59
4	111	102	111-	1-
5	90	72	73-	52
6	84	67	1	84-
7	105	137	81-	66-
8	201	145	19	200-
7 2				
7-	72	111	36	62
6-	111	119	61	92
5-	195	189	35-	191
4-	207	216	53	200
3-	219	194	13-	218
2-	255	215	84-	240
1-	105	91	10	104
	42-	21		
1	123	99	62	106-
2	117	89	111	36-
3	42-	13		
4	42-	35		
5	42-	4		
6	42-	36		
7	42-	40		
7 3				
7-	78	67	35	69-
6-	42-	44		
5-	78	106	36	69
4-	198	193	13	197
3-	219	209	99	195
2-	276	215	5-	276
1-	279	258	57	273
	117	105	19-	115
1	99	76	35	92
2	42-	66		
3	90	65	54-	71-
4	84	73	39	74-
5	66	60	46-	47-
6	78	72	3	77-
7	66	82	65-	5
7 4				
6-	51-	89		
5-	51-	31		
4-	51-	18		
3-	105	112	79	68
2-	78	100	28	72
1-	288	246	33	286
	252	229	93	234
1	279	237	20-	278
2	186	166	125	137
3	105	84	4-	104
4	51-	62		
5	51-	50		
7 5				
4-	72	76	1	72-
3-	42	74	38	17-
2-	51-	19		
1-	51-	36		
	189	167	35	185
1	225	191	22-	223
2	246	212	44	241
3	171	153	15	170
8 0				
	150	159	139	54
1	135	167	135	1-
2	90	103	87	19
8 1				
1-	84	75	81	20
	168	158	164	36-
1	171	180	162	52

factors in Table 1 does provide a reasonable overall picture. Most of the atoms of the thymine ring and the first three carbon atoms of the sugar show greatest apparent vibration amplitude in the **b** direction. Since the three hydrogen bonds holding the thymine ring lie essentially in the plane of the ring, which is in turn about normal to **b**, it is reasonable that the greatest motion of these atoms is parallel to **b**. It is noteworthy that in the thymine residue, the 'side-chain' atoms, O2, O6, and C7 have somewhat greater vibration amplitudes than the atoms of the pyrimidine ring itself. It also seems significant in terms of the packing shown in Fig. 10 that the calcium ions and phosphate groups show the greatest apparent freedom of motion in the *x*–*z* plane, since these atoms are bound in sheets approximately parallel to (201).

We are indebted to Mary Burke for help in the calculation of the three-dimensional Patterson function and to Maryellin Reinecke, who prepared all of the illustrations. We are also grateful to la Compagnie BULL for their assistance in early structure factor calculations, to the United States Office of Naval Research for their partial support of the computer SWAC, and to the staff of Numerical Analysis Research on the U.C.L.A. campus for their cooperation in our use of SWAC.

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The Structure Analysis of the T_3(AlMnZn) Compound

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(*Received* 27 *May* 1959 *and in revised form* 9 *December* 1960)

Of the three aluminium-rich intermetallic compounds, T_1, T_2 and T_3, which separate as primary constituents in the Al–Mn–Zn system, T_3 is shown to be structurally similar to $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$, although it is T_1 which corresponds in composition and in electron concentration (e/a) with the latter two. In the final stage of the structure analysis of the T_3 compound, interatomic distances and the atomic environments had to be used as the criteria for determining the distribution of different atoms amongst some of the available sites. A possible explanation is given for the fixed composition of $Ni_4Mn_{11}Al_{60}$ and the varying composition of T_3.

1. Introduction

In an examination of the Al–Mn–Zn system in the range from 0 to 95 wt.% of zinc and from 0 to 3 wt.% of manganese, Raynor & Wakeman (1947) found three aluminium-rich ternary phases, T_1, T_2 and T_3, which may crystallize as primary constituents from slowly cooled alloys. The structures of these phases were not known. The ideal formula of the T_1 phase is $ZnMn_5Al_{24}$. Its composition can be related to those of $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$; it was suggested that the formation of all three phases is controlled to a considerable extent by two factors:

(i) a ratio of four aluminium atoms to one atom of heavy element, and
(ii) the attainment of a definite electron-to-atom ratio.

Robinson (1952*a*, 1954) has solved the structure of the $Ni_4Mn_{11}Al_{60}$ compound and has shown that the basic structure of $Cu_2Mn_3Al_{20}$ is essentially the same as that of $Ni_4Mn_{11}Al_{60}$, but that the structure of T_1 is appreciably different, its unit-cell dimensions being related to, but different from, those of $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$. In this paper it is shown that the structure of the ternary T_3 compound is essentially similar to that of $Ni_4Mn_{11}Al_{60}$, though its composition does not satisfy the above requirements for the formation of the compounds $Ni_4Mn_{11}Al_{60}$ and $Cu_2Mn_3Al_{20}$.

2. Preparation of crystals

For the preparation of alloys the following materials were used.

(i) pure zinc presented by the Imperial Smelting Corporation, Ltd., of Avonmouth. The major impurities are lead and cadmium, but both in quantity less than 0·0007%,
(ii) super-purity aluminium kindly presented by the British Aluminium Co. Ltd., and
(iii) aluminium–manganese master alloy containing 13·65 wt.% of manganese. The alloy was prepared from the super-pure elements by the British Aluminium Co. Ltd.

Ingots of about 50 g. were prepared by melting together in a sintered alumina crucible weighed-out quantities of aluminium and aluminium–manganese

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