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Crystal and Molecular Structure of Pyridoxamine-5'-phosphate Hydrochloride

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Crystals of pyridoxamine-5'-phosphate hydrochloride, $C_8H_{14}ClN_2O_5P$, have been studied by three-dimensional X-ray methods. They are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 10 \cdot 05 \pm 0 \cdot 02$; $b = 7 \cdot 83 \pm 0 \cdot 01$; $c = 15 \cdot 73 \pm 0 \cdot 02$ Å; $\beta = 109 \cdot 0 \pm 0 \cdot 2°$. The structure was solved by a symbolic addition procedure, and refined by least-squares method to a final discrepancy index $R = 0 \cdot 081$ including 1797 independent reflexions. The molecules lie in layers parallel to (101) and are held together through hydrogen bonds between phosphate groups.

Introduction

It is generally accepted that the biological activity of vitamin B_6 is due, in great part, to the participation of a phosphorylated derivative, pyridoxal-5'-phosphate (Umbreit & Gunsalus, 1949; Heyl, Luz, Harris & Folkers, 1951) as the coenzyme in many enzymatic reactions of α-aminoacids, such as transamination, decarboxylation, racemization, *etc*. Despite the importance of the system, it is only recently that the crystal structures of pyridoxine hydrochloride (Hanic, 1966) and, while this paper was in preparation, of pyridoxal

phosphate oxime (Barrett & Palmer, 1969) have been published. The purpose of this paper is a detailed study of the crystal and molecular structure of pyridoxamine-5'-phosphate hydrochloride.

Experimental

Single crystals of pyridoxamine-5'-phosphate hydrochloride, suitable for X-ray analysis, were grown by slow evaporation of an aqueous solution. The unit-cell parameters were determined from Weissenberg and precession photographs. The density of the crystals, measured by flotation, was found to be consistent with four formula units $C_8H_{14}ClN_2O_5P$ per unit cell.

Crystal data

M.W. 284·65, monoclinic; $a = 10·05 \pm 0·02$, $b = 7·83 \pm 0·01$, $c = 15·73 \pm 0·02$ Å, $\beta = 109·0 \pm 0·2°$, $V = 1170$ Å^3, $Z = 4$, $D_c = 1·62$ g.cm^{-3}, $D_m = 1·63$ g.cm^{-3}, $F(000) = 592$.

Space group $P2_1/c$ from systematic absences. The multi-film equi-inclination photographic method with Ni-filtered Cu $K\alpha$ radiation, was used for collecting intensity data.

Eight layers perpendicular to b and five perpendicular to the c axis were recorded, including 1797 independent reflexions with intensities above the background of the 2693 in the limiting sphere of Cu $K\alpha$ radiation. The intensities were estimated by visual comparison with a calibrated film strip and corrected for the Lorentz–polarization factor by a computer program which includes the Phillips (1954) spot-shape correction in upper layer photographs. No absorption correction was applied. The best scale constant was found for every layer by a least-squares method and the intensities of equivalent reflexions were then averaged. Relative $|F|^2$ values were placed on an approximate absolute scale after the method of Wilson (1942) and the overall temperature factor was determined as $B = 2·5$ Å^2. The magnitudes of the normalized structure, $|E_h|$, were computed with the formula:

$$|E_h|^2 = |F_h|^2 / \sum_{j=1}^{N} f_{jh}^2$$

where F_h is the structure factor of the reflexion hkl, N the number of atoms in the unit cell and f_{jh} the scattering factor of the jth atom for the hkl reflexion, corrected with the B value.

Structure determination

The phase determination was carried out using Sayre's sign relationship. A computer program, kindly supplied by Dr G. Avitabile, was used to list all triplet interactions E_h, E_k, E_{h-k} on a selected set of normalized structure factors having absolute value

larger than $\sim 2·0$. The same program computed also the probability of one product $E_h E_k E_{h-k}$ being positive.

For the class of reflexions $h0l$ useful information was obtained using $\sum_1$ in the form valid for the space group $P2_1/c$ (Karle & Karle, 1965). This formula gave the signs to the three reflexions $20\overline{14}$, 202, $120\overline{12}$ with a probability higher than 0·95. The three reflexions together with their signs are reported in Table 1, where there are also listed three linearly independent reflexions specifying the origin and to which a negative sign was assigned. Three reflexions were then selected from the set, and symbolic signs, a, b, c, were given to them. These nine reflexions were used as the basic set for generating the signs of 170 reflexions and at the end many coincidences showed undoubtedly that $a = b = -$ and $c = +$. As was proved later, all the signs were correctly determined. The phase-determining process was stopped at this point, because it was felt that 170 signs would reveal the approximate structure. It must be noted here that the classes of reflexions $h0l$ and $0k0$ were overestimated by a factor of $\sqrt{2}$, since the appropriate ε factor (Karle & Karle, 1965) was inadvertently neglected in computing the $|E|$ values. Nevertheless this fact did not affect the procedure at all. A three-dimensional electron-density map was computed, and despite the small number of coefficients used, it clearly showed the position of the Cl and P atoms. The result was checked on the three-dimensional Patterson function. Initially the attempt to interpret the vector map, in terms of the coordinates of the heavier atoms P and Cl, had failed because the relative position of the two atoms gave strong superposition of peaks. The map showed the position of all the atoms of the independent unit together with some spurious peaks that made it difficult to interpret it completely. At this stage only positions of the PO_4 group and Cl atoms were used for a successive structure factor calculation and a new map that showed the position of all the independent non-hydrogen atoms.

Table 1. *Basic set*

h	k	l	$|E|$	Sign
2	0	$\overline{14}$	3·92	$-$
2	0	2	3·64	$-$
12	0	$\overline{12}$	2·48	$+$
10	3	$\overline{12}$	3·75	$-$
9	3	$\overline{10}$	3·60	$-$
9	4	$\overline{13}$	3·40	$-$
9	3	$\overline{16}$	3·72	a
8	5	$\overline{2}$	3·52	b
8	0	$\overline{6}$	3·41	c

Refinement

The refinement of structural parameters was carried out by a least-squares program (Albano, Domenicano & Vaciago, 1966) on an IBM 7044 computer. The

function which was minimized was $\sum w(|kF_o| - |F_c|)^2$. The refinement was initially carried out with individual isotropic atomic temperature factors and the program used a 4×4 block-diagonal approximation to the least-squares normal equations. Afterwards the weighting scheme $w = [15 \cdot 0 + 1 \cdot 0|kF_o| + 0 \cdot 007|kF_o|^2]^{-1}$ was used together with anisotropic temperature factors for all the atoms. Ten out of the fourteen hydrogen atoms were also included in the calculation of the structure factors but not refined. Their coordinates were derived, in part stereochemically, and partly from evidence of the difference Fourier map. The refinement was continued until the shifts were small fractions of the standard deviations. The final conventional R index was 0·081 over all the observed reflexions. Final atomic parameters are listed in Table 2 and 3 together with their estimated standard deviations. Table 4 contains a list of observed and calculated structure factors.

Discussion

Bond lengths and angles

The intramolecular bond lengths and angles involving the non-hydrogen atoms are listed in Table 5. The P–O(1) and P–O(3) bond lengths conform to the mean P–O bond length of 1·505 Å. The P–O(2) bond length of 1·563 Å is very close to the normal length of 1·568 Å for the P–OH bond and the unprotonated O(1)–P–O(3) angle is according to usual values (Karle & Britts, 1966). The valence angle of the pyridine N(1) is 123·8°, in good agreement with that found in several compounds (Hanic, 1966).

Molecular conformation

A view of the model of the molecule is shown in Fig. 1. The dihedral angles of pyridoxamine-5'-phosphate hydrochloride are listed in Table 6; for comparison the dihedral angles of pyridoxal phosphate oxime are also reported. The largest variations are observed

Table 2. *Final fractional atomic coordinates and their standard deviations*

|	x/a	y/b	z/c
Cl	0·0217 (1)	0·1065 (2)	0·6832 (1)
P	0·5031 (1)	0·0668 (2)	0·3243 (1)
O(1)	0·6551 (4)	0·1149 (5)	0·3519 (3)
O(2)	0·4220 (4)	0·1338 (6)	0·2276 (3)
O(3)	0·4647 (4)	−0·1197 (5)	0·3279 (3)
O(4)	0·4405 (4)	0·1706 (5)	0·3910 (2)
O(5)	0·2463 (4)	0·7169 (6)	0·5035 (3)
N(1)	0·1576 (4)	0·2962 (7)	0·5618 (3)
N(2)	0·2384 (5)	0·6470 (7)	0·3149 (3)
C(1)	0·1734 (5)	0·4682 (8)	0·5665 (3)
C(2)	0·2321 (5)	0·5468 (8)	0·5059 (3)
C(3)	0·2738 (5)	0·4455 (8)	0·4447 (3)
C(4)	0·2545 (5)	0·2668 (8)	0·4442 (3)
C(5)	0·1965 (5)	0·1964 (8)	0·5038 (4)
C(6)	0·3402 (5)	0·5372 (9)	0·3837 (4)
C(7)	0·1280 (5)	0·5651 (9)	0·6344 (3)
C(8)	0·2931 (5)	0·1491 (9)	0·3788 (4)
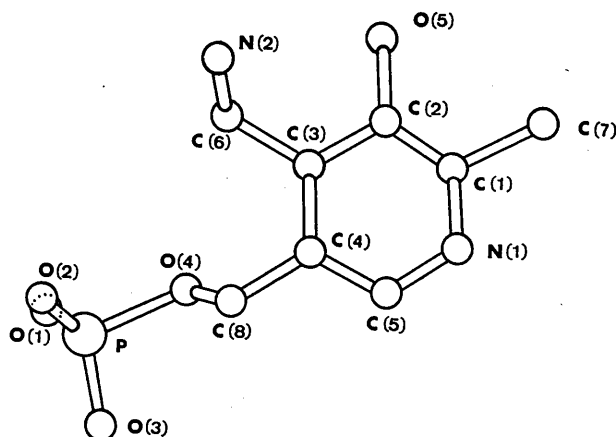
Fig. 1. Molecular conformation viewed in the plane (101).

Table 3. *Final temperature factors*

Temperature factors are of the form exp $[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

The standard deviations given in parentheses are expressed in units of the last digit stated.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cl	0·0060 (1)	0·0003 (3)	0·0061 (1)	0·0141 (3)	0·0046 (2)	0·0040 (1)
P	0·0040 (1)	−0·0013 (3)	0·0041 (1)	0·0055 (2)	−0·0013 (2)	0·0025 (1)
O(1)	0·0047 (3)	−0·0010 (8)	0·0047 (3)	0·0118 (7)	−0·0026 (6)	0·0037 (2)
O(2)	0·0077 (4)	−0·0073 (10)	0·0034 (4)	0·0155 (8)	0·0006 (6)	0·0028 (1)
O(3)	0·0079 (3)	−0·0014 (8)	0·0095 (3)	0·0083 (7)	−0·0004 (6)	0·0052 (2)
O(4)	0·0056 (3)	−0·0013 (8)	0·0053 (3)	0·0116 (7)	−0·0052 (6)	0·0033 (1)
O(5)	0·0099 (4)	−0·0018 (9)	0·0038 (4)	0·0087 (7)	0·0005 (6)	0·0030 (2)
N(1)	0·0057 (4)	−0·0013 (10)	0·0044 (4)	0·0087 (8)	0·0000 (7)	0·0028 (2)
N(2)	0·0055 (4)	0·0009 (11)	0·0051 (4)	0·0119 (9)	0·0041 (8)	0·0035 (2)
C(1)	0·0037 (4)	0·0007 (11)	0·0027 (4)	0·0131 (11)	0·0002 (8)	0·0024 (2)
C(2)	0·0042 (4)	−0·0014 (11)	0·0030 (4)	0·0086 (9)	−0·0001 (8)	0·0027 (2)
C(3)	0·0036 (4)	0·0002 (11)	0·0034 (4)	0·0093 (9)	0·0001 (8)	0·0027 (2)
C(4)	0·0047 (4)	−0·0000 (11)	0·0037 (4)	0·0090 (9)	−0·0002 (8)	0·0028 (2)
C(5)	0·0066 (4)	−0·0021 (12)	0·0047 (5)	0·0089 (10)	0·0005 (8)	0·0032 (2)
C(6)	0·0054 (4)	−0·0007 (12)	0·0050 (4)	0·0139 (11)	0·0033 (9)	0·0032 (2)
C(7)	0·0066 (5)	0·0008 (13)	0·0048 (4)	0·0146 (11)	−0·0026 (8)	0·0025 (2)
C(8)	0·0053 (4)	−0·0028 (12)	0·0056 (5)	0·0120 (11)	−0·0045 (9)	0·0042 (2)

for the rotation angles around O(4)–C(8) and C(8)–C(4) bonds, due to the different hybridization of C(6). In the pyridoxal phosphate oxime, the ring is practically on the same plane of the O(4) and C(8) atoms, whereas, in our case the ring is rotated around the C(8)–C(4) bond of about 60°. The numbering of atoms of pyridoxal phosphate oxime has been changed according to ours.

Table 4. *Observed and calculated structure factors* ($\times 10$)

Table 4 (cont.)

Table 5. Bond lengths and angles and their standard deviations

Bond length		Angle	
P —O(1)	1·494 (4) Å	O(1)–P —O(2)	111·0 (2)°
P —O(2)	1·563 (4)	O(1)–P —O(3)	118·7 (2)
P —O(3)	1·515 (4)	O(1)–P —O(4)	105·3 (2)
P —O(4)	1·608 (3)	O(2)–P —O(3)	107·5 (2)
O(4)–C(8)	1·440 (6)	O(2)–P —O(4)	105·9 (2)
C(8)–C(4)	1·522 (7)	O(3)–P —O(4)	107·7 (2)
C(4)–C(5)	1·371 (6)	P —O(4)–C(8)	117·3 (3)
C(5)–N(1)	1·352 (7)	O(4)–C(8)–C(4)	108·5 (4)
N(1)–C(1)	1·355 (8)	C(8)–C(4)–C(5)	118·6 (5)
C(1)–C(7)	1·497 (6)	C(8)–C(4)–C(3)	122·6 (4)
C(1)–C(2)	1·415 (6)	C(4)–C(5)–N(1)	120·7 (6)
C(2)–O(5)	1·341 (8)	C(5)–N(1)–C(1)	123·8 (4)
C(2)–C(3)	1·412 (6)	N(1)–C(1)–C(7)	119·0 (4)
C(3)–C(4)	1·412 (9)	N(1)–C(1)–C(2)	117·6 (4)
C(3)–C(6)	1·516 (7)	C(7)–C(1)–C(2)	123·5 (5)
C(6)–N(2)	1·495 (7)	C(1)–C(2)–C(3)	119·8 (5)
		C(1)–C(2)–O(5)	121·5 (4)
		O(5)–C(2)–C(3)	118·7 (4)
		C(2)–C(3)–C(4)	119·3 (4)
		C(2)–C(3)–C(6)	117·1 (5)
		C(3)–C(4)–C(5)	118·9 (6)
		C(4)–C(3)–C(6)	123·6 (4)
		C(3)–C(6)–N(2)	113·1 (4)

Table 6. Comparison of dihedral angles of pyridoxamine-5'-phosphate hydrochloride and pyridoxal phosphate oxime

The dihedral angles have been measured following Natta, Corradini & Bassi (1961).

	Pyridoxamine phosphate hydrochloride	Pyridoxal phosphate oxime
O(1)–P —O(4)–C(8)	180°	189°
O(2)–P —O(4)–C(8)	62	71
O(3)–P —O(4)–C(8)	−53	−46
P—O(4)–C(8)–C(4)	184	144
O(4)–C(8)–C(4)–C(3)	58	176
O(4)–C(8)–C(4)–C(5)	−123	−3
N(2)–C(6)–C(3)–C(4)	112	—
N(2)–C(6)–C(3)–C(2)	−69	—

Least-squares plane

The least-squares plane through the pyridine ring, referred to the crystallographic monoclinic axis, is:

$$7\cdot365\ x - 0\cdot800\ y + 6\cdot243\ z = 4\cdot434$$

The pyridine ring atoms lie in the plane within the

standard deviations, while the atoms directly attached to the ring show larger deviations (Table 7).

Table 7. Equation of the best plane through the pyridine ring expressed in direct space coordinates

$$7\cdot365x - 0\cdot800y + 6\cdot243z = 4\cdot434$$

Individual deviations from the best plane

N(1)	−0·003 Å
C(1)	0·005
C(2)	−0·004
C(3)	0·002
C(4)	0·000
C(5)	0·001
C(6)	0·037
C(7)	0·017
C(8)	−0·030
O(5)	−0·051
Cl	−0·094

The Cl⁻ ion lies close to the mean plane (0·094 Å) approaching the pyridine nitrogen along its sp_2 direction at a distance of 3·07 Å.

Packing and hydrogen bonds

In Fig. 2 is shown a projection of the structure along the b axis. The molecules are packed together in layers parallel to (101). The phosphate groups are linked along the screw axis in infinite chains by hydrogen bonds, as found in other phosphate derivatives (Giordano & Ripamonti, 1967). The layer are packed together with unusually short intermolecular contacts and hydrogen bonds.

Most of the shortest intermolecular contacts (Table 8) can be explained on the basis of hydrogen bond formation. In the phosphate group O(2) makes hydrogen bond (2·54 Å) with O(3) of a screw related molecule. The protonated amino nitrogen N(2) makes four short contacts, three of which are roughly directed tetrahedrally to two Cl⁻ (3·17 and 3·26 Å respectively) and O(1) (3·15 Å), the fourth one being a short contact (2·87 Å) with a O(3) of the molecule translated by b, the angle $C(6)-N(2)-O(3^V)$ is about 60°.

Table 8 (cont.)

Contact	Length
$N(2) \cdots O(3^V)$	2·87 Å
$N(2) \cdots Cl^{IV}$	3·26
$C(1) \cdots C(1^{IV})$	3·46
$P \cdots O(5^{VI})$	3·47
$O(1^I) \cdots O(5^{II})$	2·53
$O(1^I) \cdots C(5^{III})$	3·33
$O(2^I) \cdots N(1^{VI})$	3·10
$O(2^I) \cdots C(1^{VI})$	3·02
$O(2^I) \cdots C(7^{VI})$	3·23

Code for symmetry-related atoms

Superscript	Atom at		
	x	y	z
None	x	y	z
I	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
II	x	$\frac{3}{2}-y$	$-\frac{1}{2}+z$
III	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
IV	$-x$	$1-y$	$1-z$
V	x	$1+y$	z
VI	$1-x$	$1-y$	$1-z$

Table 8. Intermolecular contacts less than 3·5 Å

Contact	Length
$N(1) \cdots Cl$	3·07 Å
$C(6) \cdots O(2^I)$	3·47
$N(2) \cdots O(1^I)$	3·15
$O(2) \cdots O(3^I)$	2·54
$O(1) \cdots O(3^I)$	3·39
$O(1) \cdots C(7^{VI})$	3·28
$O(1) \cdots C(2^{VI})$	3·41
$O(4) \cdots O(5^{VI})$	3·16
$N(2) \cdots Cl^{III}$	3·17

It seems that the situation around the NH_3^+ is governed more by pure electrostatic interaction than by the directional properties of hydrogen bonds, in fact O(1) and O(3) are negatively charged and act as acceptor in strong hydrogen bonds with O(5) (2·53 Å) and O(2) respectively. The Cl⁻ ion makes three short contacts almost in trigonal directions to two amino nitrogen and to a pyridine nitrogen N(1) (3·07 Å). The efficient disposition of all the hydrogen bonds
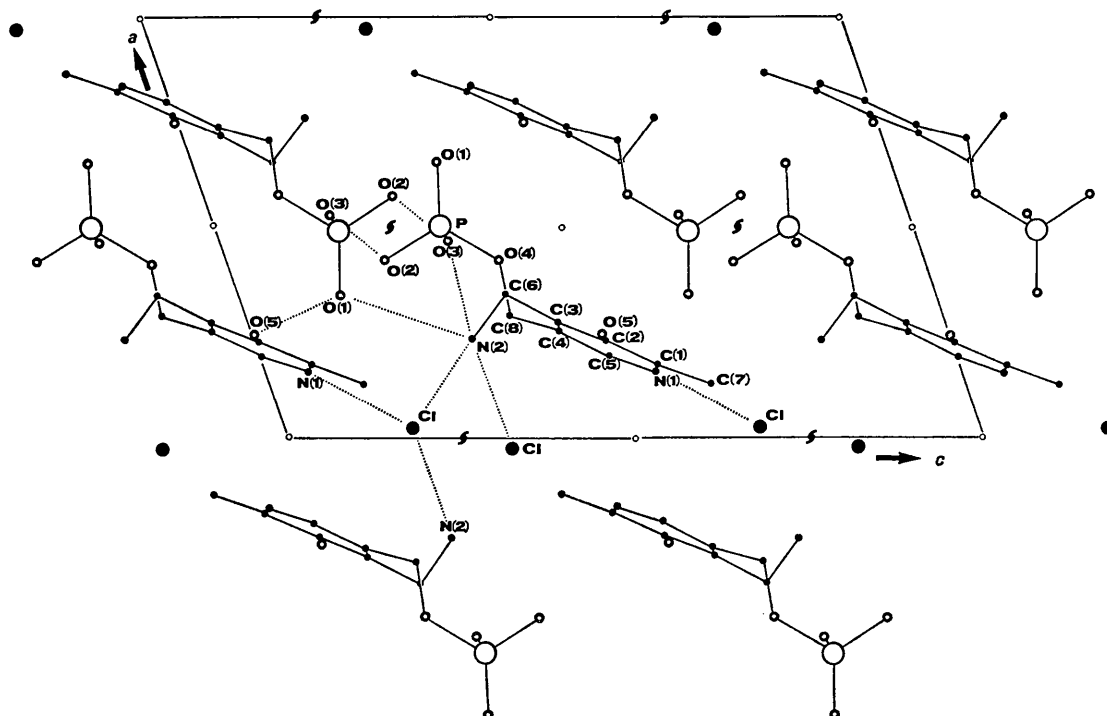

Fig. 2. The packing of pyridoxamine-5′-phosphate hydrochloride molecules in the unit cell. Projection along the b axis. Dotted lines indicates the shortest intermolecular distances.

explains the tight packing of the structure that presents rather unusual short intermolecular contacts.

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Electron Density Distribution in Cyanuric Acid. I. An X-ray Diffraction Study at Low Temperature

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Cyanuric acid crystallizes in the monoclinic space group $C2/n$. The crystal structure was refined at both room and low temperature. The following data refer to the low-temperature work. The cell dimensions are $a = 7\cdot749$ (1), $b = 6\cdot736$ (3), $c = 11\cdot912$ (4) Å, $\beta = 130\cdot69$ (2)° (e.s.d. in parentheses). The 965 independent reflexions with $\sin \theta/\lambda < 0\cdot8$ Å^{-1} were measured carefully at 100°K with a non-automated diffractometer. Mo radiation with balanced Zr and Y filters and the ω-scan technique were used. Details of the apparatus are given. The structure was refined by anisotropic least-squares techniques, converging to $R = 0\cdot038$. Average values for bond lengths and angles are: C–N = $1\cdot372$ (1), C–O = $1\cdot220$ (2) Å, N–C–N = $115\cdot3$ (1), C–N–C = $124\cdot7$ (1)°. Two types of N–H···O hydrogen bonds with lengths of $2\cdot778$ (3) and $2\cdot798$ (3) Å link the molecules together in layers nearly parallel to the plane $x = 0\cdot25$. The residual density map shows maxima at the middles of the bonds and negative regions on either side of a bond. Lone pairs at angles of 120° to the C–O bonds are found at the oxygen atoms. There is no hole in the middle of the six-membered ring. Average values (in e.Å^{-3}) for the maxima on the bonds are 0·40 for C–N, 0·24 for C–O and 0·25 for N–H. The maxima are extended in the π direction. It appears that the maxima and minima due to bonding effects become less pronounced if only reflexions within the copper sphere ($\sin \theta/\lambda < 0\cdot6$ Å^{-1}) are considered. Thermal analysis according to Cruickshank showed that cyanuric acid cannot be regarded as a rigid body. A least-squares refinement with aspherical scattering factors for atoms in the valence state gave a poorer agreement between F_o and F_c ($R = 0\cdot055$) than the refinement with spherical scattering factors for atoms in the ground state.

Introduction

During the formation of chemical bonds there is a change in the electron distribution of the participating atoms. Attempts have been made by Smith & Richardson (1965, 1967) to give a picture of these changes by quantum-mechanical calculations for some diatomic molecules consisting of first-row atoms. Even for these simple cases, the work showed that the calculated changes depend very much on the assumptions made for the wave functions of the molecules. This clearly shows the need for direct experimental information. In principle this information can be obtained by X-ray diffraction as by this method the one-electron density function in a molecule can be determined. The study of cyanuric acid described in this paper was undertaken seven years ago to determine with what accuracy the electron density distribution in a molecule could be obtained. The work was carried out at low temperature in order to observe high order as well as low order reflexions and so to improve the resolution of the electron density maps. Moreover in this way errors due to thermal diffuse scattering, for which no corrections could be applied, were considerably reduced. A preliminary re-

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