

The Hydrogen Bonds in Crystalline Pyridoxonium Chloride

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The positions of the hydrogen atoms in the crystal structure of pyridoxonium chloride were determined by the X-ray structure analysis. The details of their determination by means of the three-dimensional difference Fourier synthesis and their refinement by the least-squares method are discussed. The geometrical and functional analysis of the hydrogen bonds in the above structure is also given.

The hydrogen bonds constitute an important part of the intermolecular forces in the crystal structure of the pyridoxonium chloride (a component of the vitamine B₆). For their more detailed study, the positions of the hydrogen atoms in the unit cell of the above compound were determined by the X-ray structure analysis.

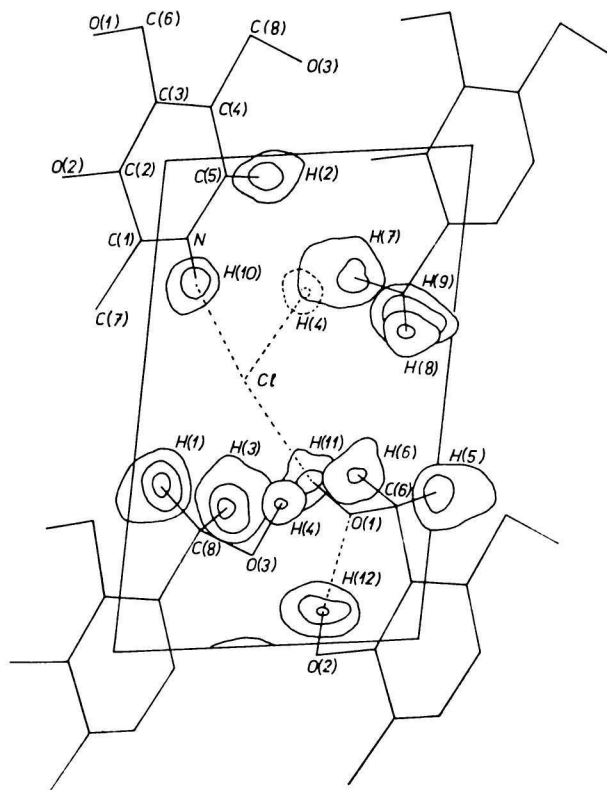


Fig. 1. Sections from a residual ($F_o - F_c$) electron density map (F_c values without hydrogen atoms contributions) projected down the c -axis. The skeletons of the rest of the molecules are also given. The contours are drawn at intervals of 0.5; 0.7 and 0.9 $e/\text{Å}^3$.

The first model of this structure (without hydrogen atoms) was determined recently [1] using a three-dimensional diffractometer-collected intensity data. The structure is triclinic with lattice constants $a = 9.52$ (4); $b = 5.803$ (7); $c = 9.56$ (4) Å; $\alpha = 93.9$; $\beta = 115.4$; $\gamma = 98.6^\circ$; space group $P\bar{1}$, the number of molecules in the unit cell being $Z = 2$. The structure was refined by means of the block-diagonal-least-squares method with the final R -factor 0.093. The total of 2211 reflections were used and the atomic coordinates and their anisotropic temperature factor coefficients were refined. For the standard deviations of the bond lengths and of the bond angles the values of about 0.005 Å and 0.3° respectively were obtained.

The approximate positions of the hydrogen atoms were then determined with the aid of the Fourier ($F_o - F_c$) difference synthesis. Here, the F_o values represent the original observed structure factors and the F_c values include the contributions of all but hydrogen atoms. The difference maps exhibited significant maxima at the expected hydrogen atoms positions, as it is shown in the Fig. 1 which represents the sections from the residual ($F_o - F_c$) electron density map projected down the c -axis as well as the skeletons of the rest of the molecules. The positions of the hydrogen atoms were then refined by means of the least-squares method using the program written by J. J. Daly, F. S. Stephens and P. J. Wheatley [2] for an Elliott 803 computer. This program uses a block-diagonal approximation. Since the atomic factor for a bound hydrogen atom is not known, the data from the *International Tables for X-Ray Crystallography* [3] for an isolated hydrogen atom were used. They were calculated from the quantum-mechanical wave function for a spherically symmetrical atom. Under these circumstances a refinement of the temperature factor coefficients has no physical meaning. Therefore, for the further refinement, the temperature factor coefficients for the chlorine, oxygen, nitrogen and carbon atoms were used from the preceding paper [1]; to the hydrogen atoms were conventionally assigned the temperature factor coefficients of those atoms, to which they were chemically bound. Such temperature factors were fixed during the refinement cycles. The Cruickhank's weighing scheme was used [4]. After two refining cycles the reliability index R dropped to the value of 0.083 and the weighed reliability index $R' = \Sigma w(\Delta F)^2 / \Sigma w F_o^2$ to the value of 0.0075. The final difference synthesis showed no significant maxima. The resulting atomic coordinates are given in Tab. 1.

Due to the spherical approximation for the hydrogen atoms a shift of these atoms during the refinement may be expected towards those atoms M, to which they are chemically bound. This will result in the shortening of the M—H distances. The results in the Tab. 2 have to be interpreted accordingly. As it can be seen from the Tab. 2, the average interatomic distance C—H

Table 1

Complete list of the atomic coordinates. Standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	
Cl	0.4530 (1)	0.3290 (2)	0.2048 (1)
O(1)	-0.2568 (4)	-0.2819 (6)	0.3702 (4)
O(2)	0.0177 (4)	-0.3341 (6)	0.4108 (4)
O(3)	-0.1968 (4)	0.4106 (7)	-0.0034 (5)
N(1)	0.1572 (4)	0.0939 (7)	0.2318 (4)
C(1)	0.1527 (5)	-0.0814 (7)	0.3137 (5)
C(2)	0.0141 (5)	-0.1583 (7)	0.3240 (4)
C(3)	-0.1159 (4)	-0.0588 (7)	0.2473 (4)
C(4)	-0.1038 (5)	0.1222 (7)	0.1617 (4)
C(5)	0.0339 (5)	0.1985 (7)	0.1556 (4)
C(6)	-0.2705 (5)	-0.1399 (8)	0.2495 (5)
C(7)	0.2948 (5)	-0.1838 (8)	0.3903 (6)
C(8)	-0.2420 (5)	0.2368 (8)	0.0744 (5)
H(1)	-0.3399 (57)	0.0944 (94)	-0.0258 (60)
H(2)	0.0504 (58)	0.3716 (91)	0.1140 (59)
H(3)	-0.2808 (58)	0.3277 (90)	0.1573 (59)
H(4)	-0.2710 (58)	0.5284 (91)	-0.0208 (59)
H(5)	-0.3173 (59)	0.0232 (92)	0.2706 (61)
H(6)	-0.3507 (59)	-0.2822 (89)	0.1294 (61)
H(7)	0.2439 (60)	-0.3773 (93)	0.3408 (60)
H(8)	0.3695 (61)	-0.1322 (91)	0.3281 (61)
H(9)	0.2899 (60)	-0.2063 (94)	0.4906 (60)
H(10)	0.2714 (59)	0.1209 (91)	0.2122 (58)
H(11)	-0.3486 (59)	-0.4475 (95)	0.3290 (59)
H(12)	-0.0633 (56)	-0.3582 (93)	0.4176 (59)

is 1.135 Å, the average O—H distance in the CH₂OH groups is 1.085 Å. The O—H distance in the hydroxyl group is very short: 0.79 (5) Å. This distance is probably most seriously influenced by the spherical-approximation effect. The N—H distance is 1.17 (6) Å. The pyridoxine molecule contains one intramolecular hydrogen bond O(2)—H(12)...O(1), the corresponding distances and the bond angle at H(12) being 0.79 (5) Å; 1.83 (5) Å and 148 (6)°, respectively. The hydrogen atom H(12)' participates simultaneously in another hydrogen bond with O(2)' from the neighbouring molecule, with the distance O(2)'...H(12): 2.47 (6) Å. The bond angle at H(12) is then 101 (5)° (Fig. 2). The pair of the O(2)...H(12) and O(2)'...H(12) bonds causes the formation of a centrosymmetrical bimolecular complex in the crystal structure. Similar bifurcated hydrogen bonds were observed in the crystal structure of (NH₃)⁺C₆H₄(SO₃)⁻ [5] with O...H lengths 1.92 and 2.26 Å, and in the structure of glycine (2.29 and 2.44 Å) as well [6].

The pyridoxonium chloride has an ionic structure formed by the Cl⁻ anions and complex cations:

Table 2

Interatomic distances and bond angles. Standard deviations in parentheses

Bond lengths (in Angströms)	Bond angles (in degrees)
O(1)—H(11) : 1.12 (5)	C(6)—O(1)—H(11) : 113.6 (2.7)
O(2)—H(12) : 0.79 (6)	C(2)—O(2)—H(12) : 108.4 (4.0)
O(3)—H(4) : 1.03 (6)	C(8)—O(3)—H(4) : 106.9 (3.5)
N—H(10) : 1.17 (6)	C(1)—N—H(10) : 111.7 (2.7)
C(5)—H(2) : 1.12 (6)	C(5)—N—H(10) : 122.9 (2.6)
C(6)—H(5) : 1.15 (6)	N—C(5)—H(2) : 121.6 (2.7)
—H(6) : 1.23 (5)	C(4)—C(5)—H(2) : 118.1 (3.0)
C(7)—H(7) : 1.14 (5)	C(3)—C(6)—H(5) : 108.0 (2.8)
—H(8) : 1.13 (4)	—H(6) : 105.9 (3.1)
—H(9) : 1.00 (6)	O(1)—C(6)—H(5) : 108.9 (3.2)
C(8)—H(1) : 1.17 (4)	—H(6) : 102.4 (2.7)
—H(3) : 1.14 (6)	H(5)—C(6)—H(6) : 119.3 (3.3)
O(1)...H(12) : 1.83 (6)	C(1)—C(7)—H(7) : 100.7 (2.6)
O(2)...H(12) : 2.47 (6)	—H(8) : 105.1 (2.7)
Cl...H(4) : 2.19 (5)	—H(9) : 99.6 (3.3)
Cl...H(10) : 1.99 (6)	H(7)—C(7)—H(8) : 102.4 (2.7)
Cl...H(11) : 1.95 (4)	—H(9) : 92.2 (4.3)
	H(8)—C(7)—H(9) : 118.2 (3.6)
	O(3)—C(8)—H(1) : 104.8 (3.0)
	—H(3) : 107.6 (2.8)
	C(4)—C(8)—H(1) : 107.5 (2.8)
	—H(3) : 111.4 (2.4)
	H(1)—C(8)—H(3) : 115.9 (3.9)
	O(2)—H(12)...O(1) : 148.3 (5.7)
	O(2)—H(12)...O(2) : 101.1 (4.2)
	H(4)...Cl...H(10) : 85.1 (2.1)
	...H(11) : 114.8 (2.1)
	H(10)...Cl...H(11) : 144.7 (2.4)

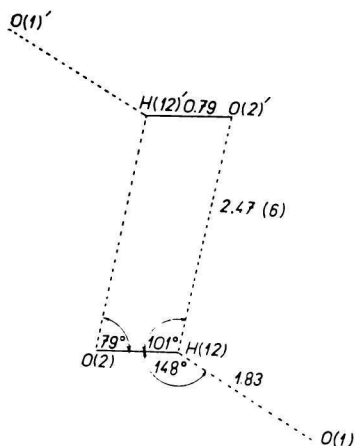
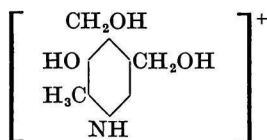


Fig. 2. A bimolecular complex in the crystalline pyridoxonium chloride.



The positive charge of the complex cation is localized on several atoms. Under assumption of a preferred hydrogen-bond interaction between the Cl^- ions and those hydrogen atoms on which a partial positive charge is localized, the carriers of such a positive charge are the hydroxyl hydrogen atoms from the CH_2OH groups and the hydrogen atom from the NH group. With these hydrogen atoms the Cl^- ion forms closest contacts in such a way that three hydrogen atoms from the three different pyridoxine molecules surround a Cl^- ion at the distances of 1.99 (6) Å (the hydrogen atom from the NH group), 1.95 (4) Å (the hydrogen atom from one CH_2OH group) and 2.19 (5) Å (the hydrogen atom from another CH_2OH group). The angles $\text{H}\dots\text{Cl}\dots\text{H}$ (at Cl) are 85 (2), 115 (2) and 145 (2)°, respectively. The hydrogen atoms from the OH groups do not participate in the hydrogen bonds with the Cl^- ions.

The three-dimensional difference Fourier synthesis was calculated at the Monsanto Research S. A., Zürich, with the program available at the Crystallographic Laboratory. The author would like to express his gratitude for this help to Dr. J. J. Daly.

VODÍKOVÉ VÁZBY V KRYŠTALICKOM CHLORIDE PYRIDOXÓNIA

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Metódami röntgenovej štruktúrnej analýzy sa stanovili polohy vodíkových atómov v kryštálovej štruktúre chloridu pyridoxónia. V práci sa uvádza spôsob ich stanovenia pomocou trojrozmernej Fourierovej diferenčnej syntézy, spresnenie metódou najmenších štvorcov, ako aj geometrická a funkčná analýza vodíkových väzieb v tejto štruktúre.

ВОДОРОДНЫЕ СВЯЗЫ В КРИСТАЛЛИЧЕСКОМ ПИРИДОКСИН ГИДРОХЛОРИДЕ

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Методом рентгеноструктурного анализа определены позиции атомов водорода в кристаллической структуре пиридоксин гидрохлорида. Обсужден способ их определения с помощью трехмерного разностного синтеза Фурье и их уточнения методом наименьших квадратов. Проведен геометрический и функциональный анализ водородных связей в этой структуре.

Перевел С. Дюрович

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