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The Crystal Structure of Hydrazonium Diphosphate, $N_2H_6H_4(PO_4)_2$

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Hydrazonium Diphosophate, $N_2H_6H_4(PO_4)_2$의 結晶構造

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要 約

Hydrazonium diphosphate 結晶은 單斜晶系에 屬하며 單位格子는 $a=4.52\pm0.02$, $b=8.06\pm0.03$, $c=10.74\pm0.03$ Å 및 $\beta=100\pm0.5°$이다. 單位格子속에는 2個의 化學單位가 들어있으며 空間群은 $P2_1/C$이다. 이 物質의 結晶構造를 Fourier 合成法과 Patterson 合成法에 依하여 決定하였다.

PO_4^{+++} 이온은 大略 regular한 正四面體를 이루고 있으며 P—O 距離의 平均値는 1.55Å이다. $N_2H_6^{++}$ 이온에서 N—N距離는 1.40Å이며 이값은 $N_2H_6SO_4$ 結晶에서의 값과 一致한다. 한 分子內에는 對稱의 中心이 있으며 各 N原子는 2.62, 2.79 및 2.89Å의 距離를 갖인 N···O型 水素結合을 이루고 있다. 또 다른 PO_4^{+++} 이온 間에는 2.63Å의 距離를 가진 한個의 O···O 水素結合을 이루고 있다. 이 物質의 構造는 上記한 N···O 및 O···O 水素結合으로 三次元的 network를 이루고 있다.

Abstract

Hydrazonium diphosphate crystallizes with the space-group symmetry $P2_1/C$. There are two formular units of $N_2H_6H_4(PO_4)_2$ in the unit cell, for which $a=4.52\pm0.02$, $b=8.06\pm0.03$, $c=10.74\pm0.03$ Å and $\beta=100\pm0.5°$. The determination of the crystal structure was carried out by means of Patterson, Fourier and difference syntheses.

The phosphate group has the configuration of nearly regular tetrahedron with the mean P—O distance of 1.55 Å. The N—N distance found is 1.40Å, which corresponds to previously reported values for the $N_2H_6^{++}$ ion in $N_2H_6SO_4$. A molecule has a transform with a center of symmetry in it. Each nitrogen atom forms three hydrogen bonds with the N···O distances 2.62, 2.79 and 2.89 Å. And a O···O hydrogen bond between different phosphate groups is found with the distance 2.63 Å. The structure is held together by three-dimensional network of the strong hydrogen bonds.

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Introduction

The crystal structures of hydrazonium fluoride,

$N_2H_6F_2$,[1] hydrazonium chloride, $N_2H_6Cl_2$[2] and orthorhombic hydrazonium sulphate, $N_2H_6SO_4$[3] have hitherto been determined by X-ray diffraction methodes. The purpose of this investigation is to obtain some further information about the structure of hydrazine salts.

Experimental

Single crystal specimens used in the structure investigation were grown by slow evaporation of an aqueous solution. Crystals were reduced by slicing and dissolving to cylinder about 0.2mm. in diameter, thus obviating the need for absorption correction. The cylindrizing operations also reduced extinction effect appreciably.

Rotation and equiinclination Weissenberg photographs about the a, b and c axes taken with nickel-filtered Cu—K_α radiation were indexed in the usual manner. The unit cell dimensions and space group were obtained from these photographs, and the more accurate values for the unit cell dimensions were determined by back-reflexion method, using (0 4 12), (0 2 13), (0 10 2), (0 9 5), (3 0 $\bar{10}$), (3 0 12), (0 0 10) and (0 10 0) spectra. They were $a=4.52\pm0.02$, $b=8.06\pm0.03$, $c=10.74\pm0.03$ Å and $\beta=100\pm0.5°$.

The observed systematic extinctions lead uniquely to the space group $P2_1/C$.

The density of the crystal was determined by flotation to be 1.89 g.cm^{-3}, which corresponds to two (calculated 1.965) molecules in the unit cell.

The intensities were estimated visually and relative observed structure factors were obtained in the usual manner.

Determination of the Structure

The approximate structure was solved with the aid of Patterson functions calculated with the $|F_{okl}|^2$ and the $|F_{hol}|^2$ data. The refinement of atomic parameters was accomplished by several two-dimensional Fourier and difference Fourier projections on (1 0 0), (0 1 0) and (0 0 1). Electron density projections are shown in Fig. 1, 2 and 3.

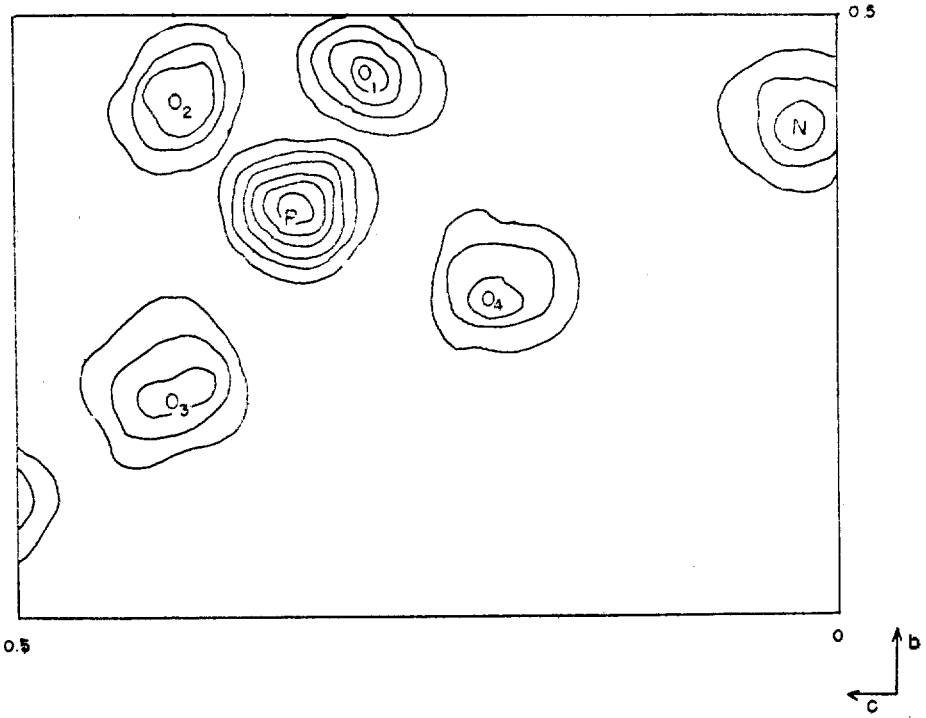

Fig. 1 Fourier projection of the electron density along the [1 0 0]. The contour lines are drawn on an arbitrary scale.

Final atomic parameters thus obtained are given in Table I.

The values of $R=\sum[|F_o|-|F_c|]/\sum|F_o|$ were 0.11, 0.12 and 0.18 for (0 k l), (h 0 l) and (h k 0) zones respectively, non-observed reflexions being omitted. Comparison of F_o and F_c is shown in Fig. 4.

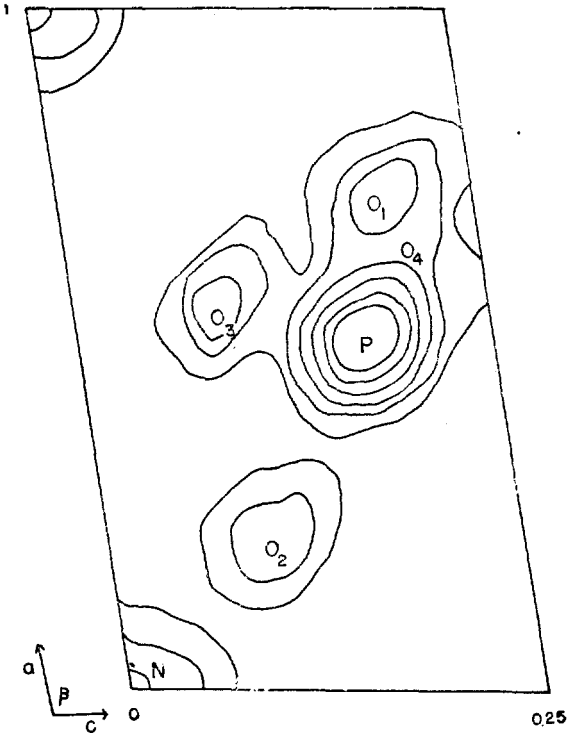

Fig. 2 Fourier projection of the electron density along the [0 1 0]. The contour lines are drawn on an arbitrary scale.

Table I Final Atomic Parameters.

	x	y	z
N	0.007	0.420	0.026
P	0.493	0.336	0.325
O_1	0.250	0.455	0.282
O_2	0.778	0.434	0.399
O_3	0.420	0.189	0.403
O_4	0.600	0.270	0.199

Discussion of the Structure

Hydrazonium diphosphate has a *trans*-form with a center of symmetry in it. The interatomic distances and bond angles calculated from the final parameters are given in Table II. The N—N distance of 1.40 Å is in a good agreement with the value 1.40 Å found in $N_2H_6SO_4$, but is somewhat shorter than 1.42 Å found in $N_2H_6F_2$ and $N_2H_6Cl_2$. The bond distances and bond angles for phosphate ion are presented in Fig. 5. It can be seen that the PO_4^{***} tetrahedron is regular; a mean P—O bond length of 1.55Å found in this crystal agrees well with the value of 1.54 Å found in tetragonal ammonium dihydrogen phosphate [4] and that of 1.54 Å found in dicalcium phosphate,[5] and a mean O—O length of 2.52 Å and a mean O—P—O angle of

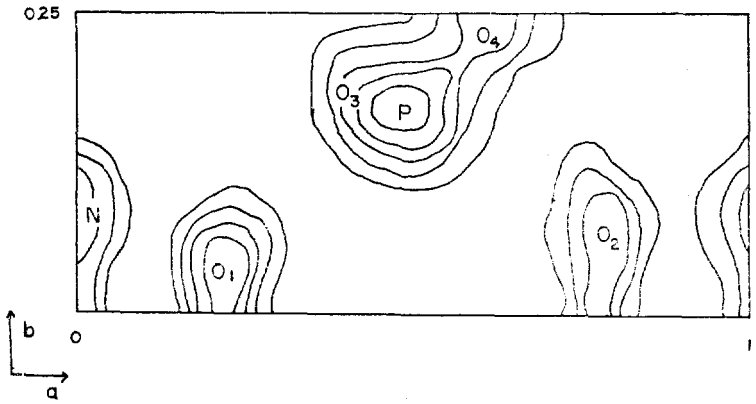

Fig. 3 Fourier projection of the electron density along the [0 0 1]. The contour lines are drawn on an arbitrary scale.

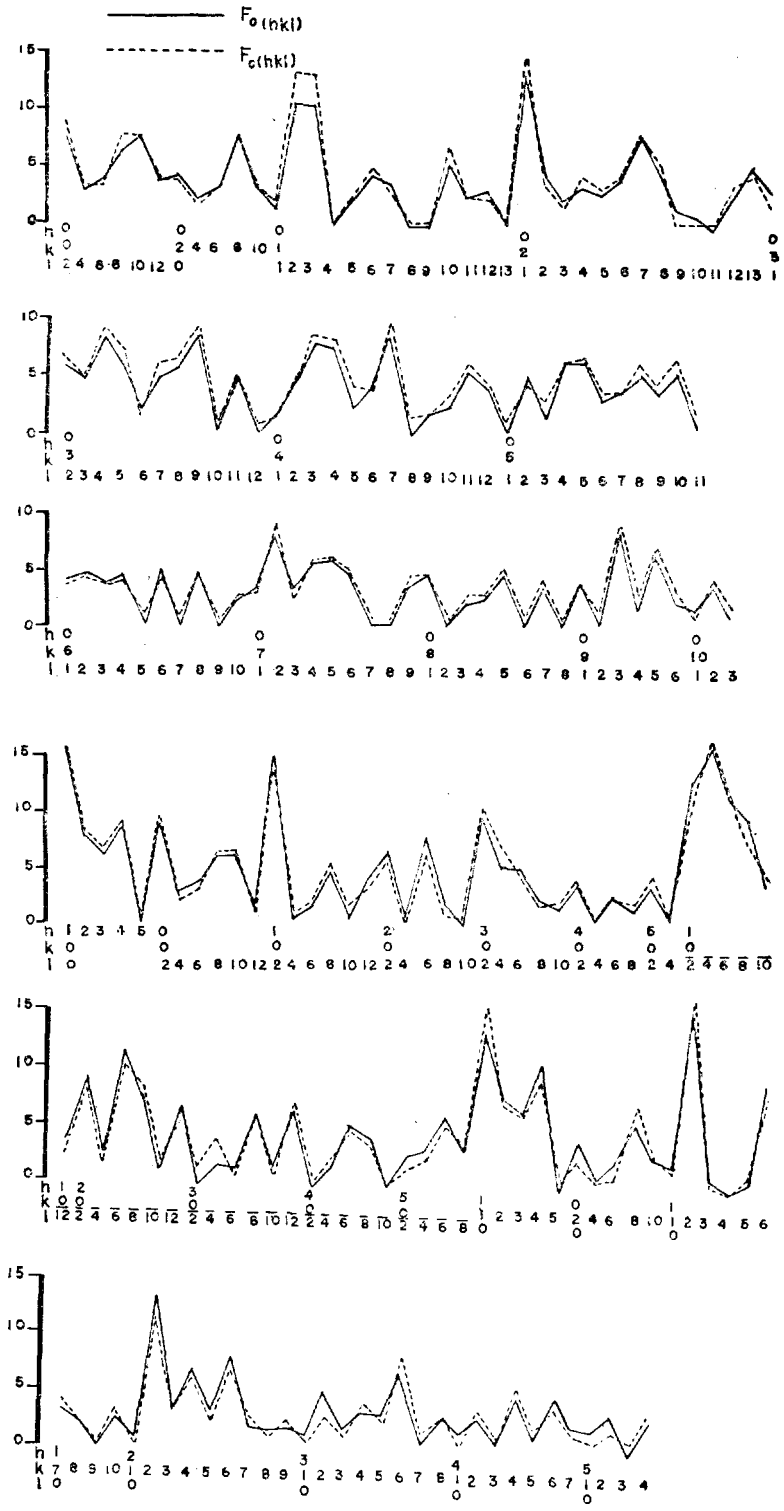

Fig. 4 Comparison of F_o & F_c.

Table Ⅱ Interatomic Distances and Bond Angles.

P—O_1	1.47Å	O_4-P-O_1	105° 11′
P—O_2	1.60	O_1-P-O_3	117 59
P—O_3	1.52	O_4-P-O_3	109 24
P—O_4	1.60	O_1-P-O_2	108 02
		O_2-P-O_3	109 24
O_1—O_2	2.50	O_2-P-O_4	104 31
O_1—O_4	2.45		
O_1—O_3	2.55		
O_2—O_3	2.55		
O_3—O_4	2.55		
O_2—O_4	2.53		
N—N	1.40		
		N-N-O_1	106° 26′
*N···O_1	2.79	N-N-O_3	96 04
*N···O_3	2.62	N-N-O_3	95 20
*N···O_3	2.89	O_3-N-O_1	109 06
*O_1···O_4	2.63	O_3-N-O_3'	110 52
**O_2···O_4	3.11	O_1-N-O_3'	131 56
**O_1···O_3	3.28		
**O_3···O_4	3.16		

* hydrogen bond.
** distance between different PO_4^{+++} ion.

109° agree well with the corresponding values found in these immediately above mentioned compounds.

The shortest O···O distance 2.63 Å between different

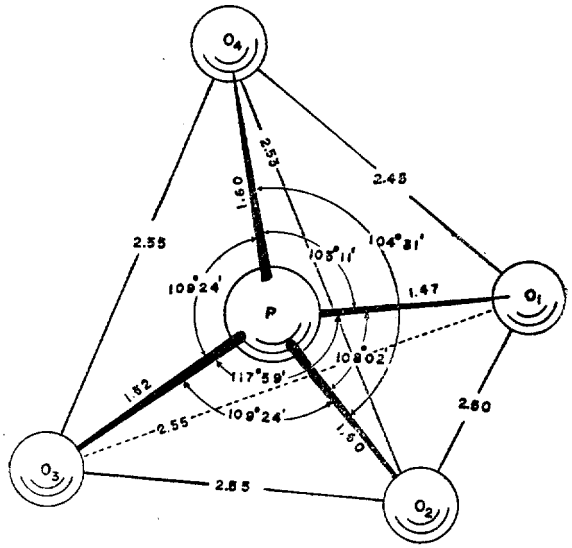

Fig. 5 Bond distances and bond angles for the phosphate ion.

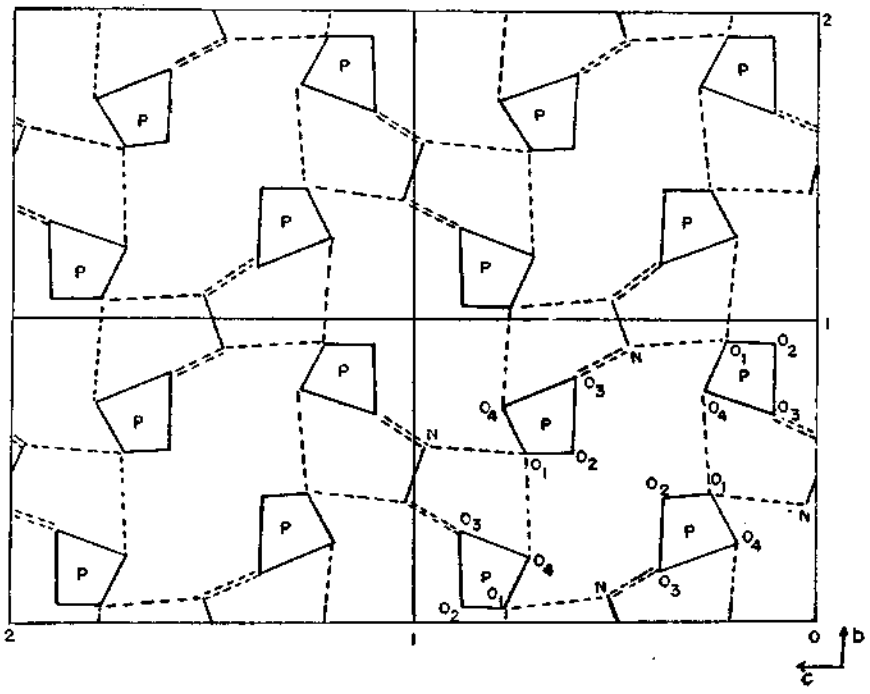

Fig. 6 The Structure of $N_2H_6H_4(PO_4)_2$ projected along the [1 0 0].

phosphate groups can be interpreted as a hydrogen bond. The structure of the crystal projected along the (1 0 0) is shown in Fig. 6. The nitrogen atom has three nearest oxygen neighbours. O_3, O_1 and O_3', the N···O distances being 2.62, 2.79 and 2.89 Å. The N atom thus takes part in three hydrogen bonds, twice as the donor and once as the acceptor of a hydrogen atom. The hydrogen bond N···O of length 2.62 Å is somewhat shorter than those previously found in hydrazonium sulfate, lithium hydrazinium sulphate [6,7] and others of hydrazine salt, although the N···O hydrogen bonding contacts of 2.55 Å in crystal of cysteylglycine-sodium iodide [8] and 2.62 Å in crystal of guanine hydrochloride monohydrate [9] are reported.

As already suggested in the discussion of the structure of hydrazonium sulfate, the existence of such a very strong N···O hydrogen bond in the crystal seems probablely due to the increased ionic character of N—H bonds.

Thus, each $N_2H_6^{++}$ group forms six N···O hydrogen bonds. These six hydrogen bonds and a O···O hydrogen bond between tetrahedron groups form three dimensional network in the crystals.

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