

Hydrogen Bond Studies

9. The Crystal Structure of Hydrazinium Dihydrogen Phosphate $N_2H_5H_2PO_4$

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The crystal structure of hydrazinium dihydrogen phosphate, $N_2H_5H_2PO_4$, has been determined from three-dimensional single crystal X-ray data. The crystals are orthorhombic (space group $P2_12_12_1$) with four molecules in a unit cell with the dimensions $a = 5.674$, $b = 7.819$, $c = 10.634$ Å. The $H_2PO_4^-$ ions are linked by hydrogen bonds (bond lengths: 2.555, 2.515 Å) to form an infinite three-dimensional framework through which channels run parallel to the a -axis. The P—O distances are: 1.505, 1.506, 1.550, and 1.573 Å. The $N_2H_5^+$ ions lie in the channels and are linked into infinite zig-zag chains by hydrogen bonds. These are formed between an NH_3^+ group of one ion and an NH_2 group of the next (bond distance: 2.896 Å). The $N_2H_5^+$ are also linked to the $H_2PO_4^-$ framework by hydrogen bonds. The N—N distance in the $N_2H_5^+$ ion is 1.438 Å. A possible assignment of the hydrogen atoms bonded to the hydrazinium ion is given, and is confirmed by the difference Fourier maps.

Two orthophosphates of hydrazine are known, namely $N_2H_4 \cdot H_3PO_4$ and $N_2H_4 \cdot 2H_3PO_4$. Bock¹ has studied these compounds by chemical methods and by infrared spectroscopy in an attempt to determine the form taken by the hydrazinium ion. However, he could not obtain definite information by these methods.

The present investigation involved the structure determination of $N_2H_4 \cdot H_3PO_4$ from single crystal X-ray diffraction data. As will be shown below, this compound consists of $N_2H_5^+$ and $H_2PO_4^-$ ions, and is a hydrazinium (1+) salt. A structure determination of $N_2H_4 \cdot 2H_3PO_4$ based on single crystal X-ray data is in progress by the present author and the results will be published later.

EXPERIMENTAL

Hydrazinium dihydrogen phosphate was prepared from hydrazine hydrate (*purum*) by the addition of phosphoric acid (*pro analysi*) to a pH of about 4 according to Sabanejeff.² The product was recrystallized from dilute alcohol and after filtering the crystals

were dried in air. The amount of N_2H_4 in the sample was determined by analysis at the Central Analytical Laboratory, Institute of Chemistry, University of Uppsala, using the bromate method. The sample contained 24.67 % N_2H_4 ; calculated for $N_2H_4 \cdot H_3PO_4$ this is 24.65 % N_2H_4 .

The crystals were treated with dilute alcohol before mounting in order to dissolve away the edges so that single crystals of a form suitable for the X-ray study could be obtained. After several attempts it was possible to isolate crystals which had an approximately spherical form, and these were mounted on glass fibres.

The crystal used for the single crystal study was a sphere of 0.21 mm diameter. With the crystal rotating about [010], equi-inclination Weissenberg photographs of the zones $0 \leq k \leq 7$, (designated below as data-set 1) were recorded using $CuK\alpha$ radiation and the multiple-film technique (five films). It was then possible to remount the crystal with [100] as the rotation axis and a new set of intensities (denoted data-set 2) were collected. The zones recorded were $0 \leq h \leq 4$. The relative intensities were estimated visually by comparison with a calibrated scale. The intensity range was 1 to 4100.

The data were corrected for the Lorentz and polarization effects and also for absorption on an IBM 7090 computer using the programme ERLPA written by Van den Hende.³ The absorption coefficient μ for $CuK\alpha$ radiation is 45.1 cm^{-1} , and the value of μR is thus 0.46.

The calculation of the interlayer scale factors was carried out on the computer FACIT, using the programme BAS written by P. E. Werner, University of Stockholm. This programme is based on a least squares method presented by Rollett and Sparks.⁴ The number of common reflexions observed on both sets of films was 433 but about 50 of the weakest reflexions were given zero weight, which reduced the number of reflexions used for scaling to about 380. The weighting factor applied in the least squares calculation for these was of the form $1/F_1^2 F_2^2$ where F_1 and F_2 are the observed structure factors obtained from data-sets 1 and 2, respectively.

Hamilton, Rollett and Sparks⁵ reported in a note that the method for calculating interlayer scale factors devised earlier by Rollett and Sparks⁴ can give incorrect results. However, in the present case, the results obtained by the latter method seem to be reliable, since the eight interlayer scale factors of data-set 1 obtained by a least squares refinement with the programme SFLS (see below) showed deviations smaller than $\pm 2\%$ from those given by the programme BAS. The coordinates and isotropic thermal parameters were also varied in this refinement which was based on the data-set 1 before mean values had been taken as described below.

The number of independent reflexions recorded with intensities strong enough to be measured was 549 from data-set 1 and 495 from data-set 2. As mentioned earlier, 433 of these intensities were observed on both sets of data. Mean values of the observed F' 's for these reflexions were taken and used in the later calculations. The numbers of independent reflexions observed on only one of the data-sets are thus 116 and 62. Hence the total number of independent reflexions with measurable intensities is 611, and these were used for the subsequent structure determination and refinements. However, a further 28 independent reflexions were observed, but the intensities for these were too weak to be measured, and they were not included in the refinements.

The density of hydrazinium phosphate was determined by weighing the specimen in air and in *m*-xylene, as described in the *International Tables* (Vol. III: 1962, p. 18). The value obtained for the density was 1.81 g cm^{-3} .

UNIT CELL AND SPACE GROUP

The X-ray patterns corresponded to the diffraction symmetry *mmm*. Systematic absences observed were: $h00$ for $h \neq 2n$, $0k0$ for $k \neq 2n$ and $00l$ for $l \neq 2n$. Assuming that these are space group extinctions, the results indicate the space group $P2_12_12_1$ (D_2^4). As shown below, the structure can be described satisfactorily in this space group with the atoms in the general 4-fold positions:⁶ (x, y, z) ; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

The dimensions of the orthorhombic unit cell were determined from powder photographs recorded in a Guinier-Hägg focussing camera using $\text{CrK}\alpha_1$ radiation ($\lambda = 2.28962 \text{ \AA}$) with silicon ($a = 5.43054 \text{ \AA}$ at 25°C) as an internal standard. The reciprocal cell dimensions were calculated from a set of h, k, l and θ data obtained from the powder film, using a programme designated CELSIUS, written by J. Tegenfeldt, Uppsala, for an IBM 1620 computer. This programme is based on a least squares method and minimizes the function

$$R = \sum W_i \left[\frac{\sin^2 \theta_{i,\text{obs}}}{\lambda_i^2} - \frac{\sin^2 \theta_{i,\text{calc}}}{\lambda_i^2} \right]^2$$

Weights were applied according to the scheme $w_i = w_{\theta_i} \times (\lambda_i^4 / \sin^2 2\theta_i)$ in which w_{θ_i} was put equal to 0.5 for the weakest and strongest reflexions and was otherwise equal to 1. The numbers of reflexions in the two groups were 12 and 24, respectively, making a total of 36 observations. The direct cell dimensions with standard deviations are (at 25°C).

$$a = 5.6737 \pm 0.0005, b = 7.8194 \pm 0.0005, c = 10.6338 \pm 0.0007 \text{ \AA}$$

The results indicate that the θ -values were determined with a high precision; however, this ignores possible systematic errors, which can be of a greater magnitude than is indicated by the deviations given above.

The density, calculated on the basis of a unit cell containing four molecules of $\text{N}_2\text{H}_5 \cdot \text{H}_2\text{PO}_4$, is 1.83 g cm^{-3} . As mentioned earlier the observed density was 1.81 g cm^{-3} .

DETERMINATION OF THE ATOMIC COORDINATES

The positions of the atoms belonging to the phosphate group were determined from a three-dimensional Patterson synthesis. Using the known phosphorus and oxygen positions, an F_o -synthesis was then calculated, from which the approximate coordinates of the two independent nitrogen atoms were obtained. All these atoms are in the general 4-fold positions of the space group $P2_12_12_1$.

These preliminary atomic coordinates were first improved in a series of three-dimensional electron density calculations. The Fourier calculations were made on the computer FACIT EDB using the programmes designated STRIX and PROFFS written by Liminga and Olovsson.⁷

The atomic parameters were then further refined by the method of least squares. The first series of these calculations was made on the computer FACIT EDB with the programme designated SFLS, devised by Brändén and Åsbrink. (The main outlines of this programme have been presented earlier⁸). The parameters refined were atomic coordinates, individual isotropic temperature factors and an over-all scale factor. The weights w of the observations were calculated according to an equation suggested by Cruickshank *et al.*⁹ as follows: $w = 1/(a + |F_o| + c|F_o|^2)$ with $a = 5.0$ and $c = 0.075$. After about ten cycles of least squares calculations the "discrepancy index" $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.094. After correction of some errors in the data, further cycles led to an R_1 of 0.090.

At this stage of the refinement a three-dimensional ($F_o - F_c$) synthesis was calculated; only the reflexions with $\sin \Theta/\lambda$ less than 0.5 were included. Possible positions of the hydrogen atoms were now calculated; the location of these was based on the following argument. Peaks could be found in the difference Fourier maps corresponding to the predicted locations of the hydrogen atoms bonded to the $N_2H_5^+$ ion but only low positive regions were observed for those bonded to the $H_2PO_4^-$ ion. Additional peaks of a size comparable to these five, which were assumed to be hydrogen peaks, appeared in the difference maps. These additional peaks, however, could be excluded as possible hydrogen positions.

Some cycles of least squares calculations were now performed with the five hydrogen atoms, bonded to $N_2H_5^+$, included but with fixed parameters. The R_1 -value was reduced to 0.086. The total shifts in the atomic coordinates of phosphorus, oxygen and nitrogen were, at most, about one standard deviation.

A series of least squares calculations was finally performed on an IBM 7090 computer using the programme OR FLS written by Busing *et al.*¹⁰ The same weighting scheme was used as earlier. After one cycle of refinement in which were varied the coordinates, the individual isotropic temperature factors for all atoms except the hydrogens and an over-all scale factor (a total of 29 parameters) the R -values were:

$$R_1 \text{ (as defined earlier)} = 0.085$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.115$$

This calculation started with the values of the parameters obtained with the programme SFSL.

The refinements were completed with three cycles of least squares calculations, which now included anisotropic temperature factors for phosphorus, oxygen, and nitrogen. The other parameters varied were the same as before;

Table 1. Atomic coordinates with their standard deviations in $N_2H_5 \cdot H_2PO_4$.

Atom	x	y	z
P	0.0944 \pm 0.0002	0.1856 \pm 0.0002	0.1527 \pm 0.0001
O(1)	0.8189 \pm 0.0007	0.1894 \pm 0.0006	0.1364 \pm 0.0004
O(2)	0.1838 \pm 0.0008	0.3636 \pm 0.0006	0.1783 \pm 0.0004
O(3)	0.1343 \pm 0.0009	0.0777 \pm 0.0007	0.2732 \pm 0.0004
O(4)	0.2100 \pm 0.0009	0.1039 \pm 0.0006	0.0403 \pm 0.0005
N(1)	0.5916 \pm 0.0010	0.1979 \pm 0.0007	0.4042 \pm 0.0005
N(2)	0.4519 \pm 0.0009	0.3513 \pm 0.0007	0.4063 \pm 0.0005
Hydrogen atoms:			
N(1)–H(1)	0.66	0.18	0.32
–H(2)	0.48	0.09	0.40
N(2)–H(3)	0.355	0.355	0.325
–H(4)	0.561	0.456	0.412
–H(5)	0.339	0.348	0.482

Table 2. Anisotropic temperature factor parameters with their standard deviations in $N_3H_5H_2PO_4$, (each multiplied by 10^4). The expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	86 ± 4	62 ± 2	41 ± 1	- 9 ± 2	1 ± 2	4 ± 1
O(1)	111 ± 12	122 ± 8	52 ± 4	- 3 ± 8	- 1 ± 6	2 ± 5
O(2)	141 ± 12	90 ± 7	67 ± 4	4 ± 8	8 ± 7	- 7 ± 4
O(3)	204 ± 16	147 ± 9	62 ± 4	-46 ± 11	-33 ± 7	35 ± 5
O(4)	159 ± 12	89 ± 7	66 ± 4	25 ± 9	- 1 ± 7	-11 ± 5
N(1)	161 ± 16	120 ± 9	63 ± 5	14 ± 12	-13 ± 8	- 9 ± 6
N(2)	126 ± 14	91 ± 8	62 ± 4	-18 ± 9	1 ± 7	1 ± 5
H(1),H(2) *	427	225	122	0	0	0
H(3),H(4),H(5)*	388	204	111	0	0	0

* Isotropic temperature factors in anisotropic form for the hydrogen atoms; the B -values used were 5.5 and 5 \AA^2 , respectively.

the total number was 64. In the last cycle, the shifts in coordinate or thermal parameter values were less than one tenth of the standard deviation for the parameter in question. The R_1 and R_2 values were now 0.067 and 0.089, respectively.

Tables 1 and 2 list values for the atomic coordinates and thermal parameters with their standard deviations obtained from the final anisotropic least squares refinement. The observed and calculated structure factors are compared in Table 6. Distances and angles with their standard deviations, given in Tables 4 and 5, were calculated using the programme OR FFE written by Busing *et al.*¹¹ The standard errors of the distances and angles were computed from the errors of the atomic coordinates in the form of a variance-covariance matrix, obtained at the final least squares cycle using OR FLS. The deviations of the cell dimensions were also included in the calculations with OR FFE.

The atomic scattering factors used in the above calculations were those for neutral P, O, N, and H, respectively, given in the *International Tables* (Vol. III. p. 202).¹²

DISCUSSION OF THE STRUCTURE

The structure is shown in projection in Fig. 1. The bond distances and angles with their standard deviations are given in Tables 4 and 5, and in Figs. 2-6. These distances and angles are based on the parameters listed in Table 1. No correction for thermal motion was made.

The structure can be described with reference to Fig. 1, which gives a general view as projected along the a -axis. As will be shown below the com-

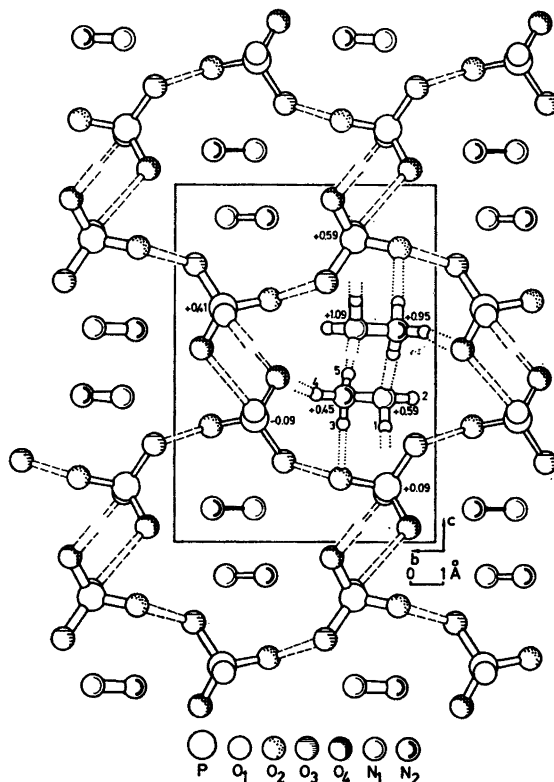


Fig. 1. The structure of $N_2H_5 \cdot H_2PO_4$ projected along the a -axis. Dashed lines indicate $O-H \cdots O$ bonds. The x -coordinate is given for some of the phosphorus and nitrogen atoms. Small circles indicate hydrogen atoms bonded to the $N_2H_5^+$ ion (numbered as in Table 1). The $N-H \cdots O$ and $N-H \cdots N$ bonds are indicated (dotted lines) for two of the $N_2H_5^+$ ions. Broken lines indicate bonds to atoms one unit length above or below the one shown in the diagram.

pond, $N_2H_4 \cdot H_3PO_4$, contains $N_2H_5^+$ and $H_2PO_4^-$ ions. There are two hydrogen atoms in each phosphate group available for hydrogen bonding. Hence, it is possible to link the $H_2PO_4^-$ ions into a three-dimensional framework by $O-H \cdots O$ bonds. In this instance, the linking of these ions is made in a way which results in channels in the framework, running parallel to the a -axis. Six-membered puckered rings of phosphate groups, joined to each other by short hydrogen bonds, can be traced in the structure. The negative charge of the framework is balanced by the charge on the $N_2H_5^+$ ions which lie in the channels where they are linked into infinite zig-zag chains by hydrogen bonds of the type $H_2N^+-H \cdots NH_2$. The $N_2H_5^+$ ions are also linked to the $H_2PO_4^-$ framework by $N-H \cdots O$ bonds. Hydrogen bonding thus seems to play a major role in determining the crystal structure of the compound. Details of the structure and of the hydrogen bonding system are discussed below.

1. THE PHOSPHATE FRAMEWORK

The H_2PO_4^- framework in the present case is similar to that found in KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$, respectively (designated KDP and ADP below). The structures of these two substances have been studied in detail by both X-ray and neutron diffraction techniques in view of their interesting ferroelectric properties and low-temperature transitions. These studies were made at temperatures on either side of the ferro-electric Curie point. The results from some of these investigations are summarized in Table 3 (further references

Table 3. Some bond distances and angles in phosphates.

Compound	Distances in Å			Angle P-(OH)...O	Authors and method for the study
	P-O	P-OH	O-H...O		
KH_2PO_4 (Tetragonal; room-temp.)	1.538 ± 0.005		2.487 ± 0.005	113°	Bacon and Pease ¹³ (Neutrons)
KH_2PO_4 (Orthorhombic, at 77°K)	1.508 ± 0.02	1.583 ± 0.02	2.486 ± 0.004		Bacon and Pease ¹⁴ (Neutrons)
KH_2PO_4 (Orthorhombic, at 116°K)	1.53	1.58	2.51		Frazer and Pepinsky ¹⁷ (X-rays)
$\text{NH}_4\text{H}_2\text{PO}_4$ (Tetragonal, room-temp.)	1.53_0		2.48_0	117	Tenzer, Frazer and Pepinsky ¹⁶ (Neutrons)
H_3PO_4	1.517 ± 0.013	1.577 ± 0.024	2.53 ± 0.02	117	Furberg ¹⁸ (X-rays)
		1.570 ± 0.013	2.53 ± 0.02	123	
		1.568 ± 0.008	$2.84 \pm 0.02^*$		
$\text{N}_2\text{H}_5\text{H}_2\text{PO}_4$	1.505 ± 0.005	1.550 ± 0.005	2.555 ± 0.007	109	Present paper (X-rays)
	1.506 ± 0.005	1.573 ± 0.004	2.515 ± 0.007	115	

* This bond is of a different type, namely O-H...OH (between two different OH groups).

can be found in the papers 13-17). In the tetragonal room-temperature modification of both KDP¹³ and ADP¹⁶ studied by neutrons, the lengths of all P-O bonds were found to be more or less equal, namely 1.538 and 1.536 Å, respectively. The hydrogen atoms in the short hydrogen bonds linking the phosphate groups to a three-dimensional framework, were located, but it was not possible to distinguish between a symmetrical O...H...O bond with a strongly anisotropic oscillation of the hydrogen atom along the bond, and a random distribution of the hydrogens between two off-centre positions. However, in the orthorhombic low-temperature modification of KDP, studied

by neutrons at 77°K,¹⁴ the hydrogen atoms were found to occupy ordered positions. The phosphate group was in this instance asymmetrical with the P—O bonds equal to 1.508 Å and the P—OH bonds equal to 1.583 Å. In an X-ray study of this modification of KDP at 116°K, Frazer and Pepinsky¹⁷ found similar bond distances within the phosphate group. The low-temperature modification of ADP has been studied only by X-rays.¹⁶ It is evident, however, that the phosphate tetrahedron is distorted in this case, also, but the bond distances are uncertain because of an inaccurate positional parameter. In the crystal structure of phosphoric acid, Furberg¹⁸ found the P—O bond to be 1.52 Å while the P—OH bonds were about 1.57 Å.

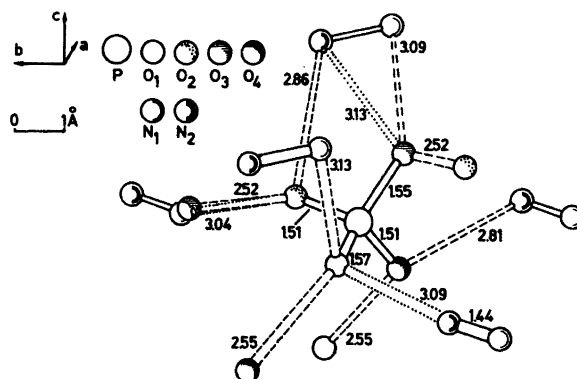


Fig. 2. Bond distances within the phosphate framework and to the nitrogen neighbours of the oxygen atoms. Dashed lines indicate hydrogen bonds, dotted lines other types of contacts.

In the present compound the phosphate tetrahedron again deviates significantly from tetrahedral symmetry (see Tables 3 and 4, Figs. 2 and 3). When the distances within the phosphate group are compared with those of similar compounds, it seems reasonable to suppose that the hydrogen atoms are ordered in this case and that the distances of 1.505 and 1.506 Å correspond to the P—O bonds, while the remaining two, 1.550 and 1.573 Å, correspond to the P—OH bonds. These distances are in good agreement with those found earlier for these types of bonds. The O—H...O bonds, 2.555 and 2.515 Å, respectively, are also consistent with those reported earlier. The positions of the hydrogen atoms in the O—H...O bonds were calculated, assuming linear hydrogen bonds with an O—H distance of 1.07 Å.^{14,16} However, only low positive regions but no peaks could be found in the difference Fourier maps at the predicted hydrogen positions. In fact, no peaks at all could be found on or near the line joining these hydrogen-bonded oxygen atoms. These hydrogen atoms were not included in the final refinements as was mentioned earlier.

The angle within the phosphate group involving two P—OH bonds is 104°, while the angle between the two P—O bonds is 113°. The angles of the

O—P—OH type have values between 108° and 111° . The OH—P—OH angles in H_3PO_4 ¹⁸ were all near 106° .

The P—(OH)···O angles in the present case are 109° and 115° , respectively. Tetrahedral values for this type of angle might be favourable, but large variations have been reported. Some earlier published values are given in Table 3 and in a paper by Calleri and Speakman.¹⁹

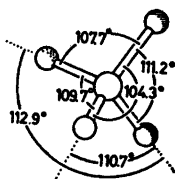


Fig. 3. Bond angles within the phosphate group. The orientation and notation of the atoms are the same as in Fig. 2.

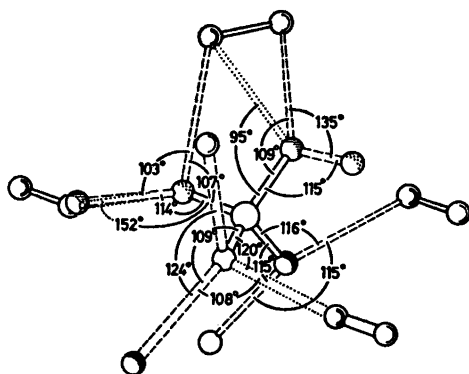


Fig. 4. Bond angles around the oxygen atoms. The orientation and notation of the atoms and the bonds are the same as in Fig. 2.

The environment of the four independent oxygen atoms is shown in Fig. 2. In each instance the number of hydrogen-bonded neighbours is two, namely one oxygen and one nitrogen (possibly only one for O(3); see below). It is noteworthy that the nitrogen neighbours of O(1) and O(3) are at much greater distances than those of O(2) and O(4). (For further details see the discussion of the N_2H_5^+ ion.) As was described earlier, O(1) and O(3) are members of the OH groups of the H_2PO_4^- ions. Besides these neighbours, O(1), O(2), and O(3) each have a further neighbour at a distance of 3.14 \AA or less. Some of the more significant angles subtended at the oxygen atoms are listed in Table 4 and shown in Fig. 4.

When a correction was made for thermal motion assuming that the oxygen atoms ride on the phosphorus atom, the P—O distances were 1.515 and 1.514 \AA , and the P—OH distances 1.568 and 1.581 \AA , respectively, with a standard deviation of 0.005 \AA . (This correction was performed using the programme OR FFE¹¹).

2. THE HYDRAZINIUM ION

The N—N distance of 1.438 \AA in the N_2H_5^+ ion, is in agreement with earlier reported values for this type of ion. Thus values of 1.440 and 1.427 \AA , respectively, have been found in $(\text{N}_2\text{H}_5)_2\text{SO}_4$ by Liminga and Lundgren²⁰ (consult this paper for further references).

Table 4. Distances and angles with standard deviations within the phosphate framework in $N_2H_5H_2PO_4$.

Within the phosphate group (cf. Figs. 2 and 3).			
P—O(1)	$1.573 \pm 0.004 \text{ \AA}$	O(1)—P—O(2)	$109.7 \pm 0.3^\circ$
—O(2)	1.506 ± 0.005	—O(3)	104.3 ± 0.3
—O(3)	1.550 ± 0.005	—O(4)	110.7 ± 0.3
—O(4)	1.505 ± 0.005	O(2)—P—O(3)	107.7 ± 0.3
		—O(4)	112.9 ± 0.3
		O(3)—P—O(4)	111.2 ± 0.3
Hydrogen bonds (cf. Fig. 2)			
O(1)—H...O(4)	$2.555 \pm 0.007 \text{ \AA}$		
O(3)—H...O(2)	$2.515 \pm 0.007 \text{ \AA}$		
Angles around the oxygen atoms (Hydrogen bonds are indicated with an "H" on the donor atom. Cf. Fig. 4).			
P—O(1)H—O(4)	$109.5 \pm 0.3^\circ$	P—O(2)—HO(3)	$114.3 \pm 0.3^\circ$
P—O(1)—HN(1)	108.1 ± 0.2	P—O(2)—N(1)	152.2 ± 0.3
P—O(1)—N(2)	119.6 ± 0.3	P—O(2)—HN(2)	107.5 ± 0.3
N(1)H—O(1)H—O(4)	$123.8 \pm 0.3^\circ$	O(3)H—O(2)—N(1)	$77.7 \pm 0.2^\circ$
N(1)H—O(1)—N(2)	87.0 ± 0.2	O(3)H—O(2)—HN(2)	103.3 ± 0.2
N(2)—O(1)H—O(4)	108.2 ± 0.3	N(1)—O(2)—HN(2)	92.9 ± 0.2
P—O(3)H—O(2)	$115.3 \pm 0.3^\circ$	P—O(4)—HO(1)	$114.9 \pm 0.3^\circ$
P—O(3)—HN(1)	109.2 ± 0.3	P—O(4)—HN(2)	115.8 ± 0.3
P—O(3)—N(2)	94.9 ± 0.2		
N(1)H—O(3)H—O(2)	$135.4 \pm 0.2^\circ$	O(1)H—O(4)—HN(2)	$115.3 \pm 0.2^\circ$
N(2)—O(3)H—O(2)	140.7 ± 0.2		
N(2)—O(3)—HN(1)	26.7 ± 0.2		

Table 5. Hydrazinium ion. Bond distances and angles with standard deviations (cf. Figs. 5 and 6).

N(1)—N(2)	$1.438 \pm 0.008 \text{ \AA}$		
N(1)...H(5)—N(2)'	$2.896 \pm 0.008 \text{ \AA}$	N(2)—H(5)...N(1)'	$2.896 \pm 0.008 \text{ \AA}$
N(1)—H(1)...O(1)	3.127 ± 0.007	N(2)—H(3)...O(2)	2.864 ± 0.007
N(1)—H(2)...O(3)	3.091 ± 0.007	N(2)—H(4)...O(4)	2.811 ± 0.007
N(1)—O(2)	3.037 ± 0.007	N(2)—O(1)	3.091 ± 0.007
N(1) to other atoms	$> 3.25 \text{ \AA}$	N(2)—O(3)	3.135 ± 0.007
		N(2) to other atoms	$> 3.50 \text{ \AA}$
N(2)—N(1)—N(2)'	$119.3 \pm 0.3^\circ$	N(1)—N(2)—N(1)'	$106.8 \pm 0.3^\circ$
—O(1)	105.0 ± 0.4	—O(2)	107.9 ± 0.4
—O(3)	78.3 ± 0.3	—O(4)	102.3 ± 0.2
—O(2)	162.5 ± 0.4	—O(1)	170.1 ± 0.4
N(2)′—N(1)—O(1)	109.8 ± 0.2	—O(3)	75.0 ± 0.3
—O(3)	150.0 ± 0.3	N(1)′—N(2)—O(2)	102.6 ± 0.3
—O(2)	77.9 ± 0.2	—O(4)	115.8 ± 0.2
O(1)—N(1)—O(3)	85.9 ± 0.2	—O(1)	82.2 ± 0.2
—O(2)	63.0 ± 0.2	O(2)—N(2)—O(4)	120.6 ± 0.2
O(3)—N(1)—O(2)	87.7 ± 0.2	—O(1)	65.3 ± 0.2
		O(4)—N(2)—O(1)	76.6 ± 0.2

The assumptions concerning the location of the hydrogen atoms were the same as in the case of $(\text{N}_2\text{H}_5)_2\text{SO}_4$ ²⁰ as follows: (a) The angles N—N—H and H—N—H are about 109° ; (b) the N—H distances are about 1.03 Å; (c) the NH_3^+ end of the N_2H_5^+ ion may participate in three hydrogen bonds as a hydrogen donor while the NH_2 end only can donate two hydrogen atoms but can accept one (or possibly more) to its lone pair of electrons; (d) the hydrogen bonds from the NH_3^+ end can be expected to be shorter than those from the NH_2 end. When these facts were applied, it was concluded that the nitrogen N(2) must be part of the NH_3^+ end of the hydrazinium ion. (See Table 5 and Figs. 5 and 6). The nitrogen atoms involved in a hydrogen bond function as the hydrogen donors.

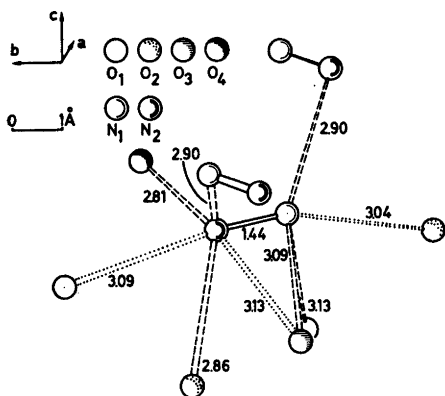


Fig. 5. Bond distances within and to the neighbours of the hydrazinium ion. Dashed lines indicate hydrogen bonds, dotted lines other types of contacts.

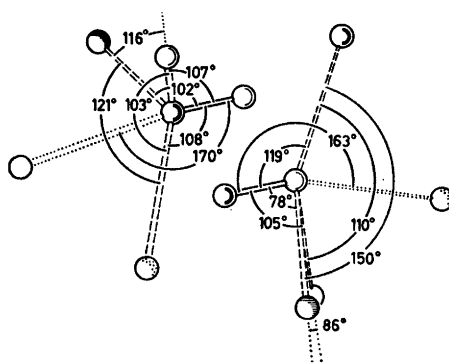


Fig. 6. Bond angles to the neighbours of the hydrazinium ion. The orientation and notation of the atoms and the bonds are the same as in Fig. 5.

(a) *Hydrogen bonds from the NH_3^+ end of the N_2H_5^+ ion.* The nitrogen atom N(2) has three neighbours at 2.90, 2.81, and 2.86 Å (one nitrogen and two oxygen atoms), which are assumed to be bonded to N(2). The N(2)—O(2) bond was thought to be linear; the hydrogen atom H(3) was placed on this line and the positions of H(4) and H(5) were calculated according to the assumptions made above (Fig. 7). (The positions of the hydrogen atoms were calculated with a programme named KOORDINAT, written by Lindgren and Lundgren, Uppsala, for an IBM 1620 computer). Well resolved peaks could be found in the difference Fourier maps close to these predicted hydrogen positions.

Chains of N_2H_5^+ ions are formed by hydrogen-bond links of the $\text{H}_2\text{N}^+ - \text{H} \cdots \text{NH}_2$ type with a bond distance of 2.90 Å. Similar chains were found in the crystals of $\text{N}_2\text{H}_5\text{Cl}$ and $\text{N}_2\text{H}_5\text{Br}$ by Sakurai and Tomiie²¹; the $\text{N}^+ - \text{H} \cdots \text{N}$ bonds are in these cases 2.95 and 2.93 Å, respectively. Chains of N_2H_5^+ ions have also been reported in $\text{LiN}_2\text{H}_5\text{SO}_4$,^{22,23} but in this compound the ions are connected by two NH_2 groups; the $\text{HN} - \text{H} \cdots \text{NH}_2$ distance is 3.01 Å. Hydrogen bonds of the $\text{H}_2\text{N}^+ - \text{H} \cdots \text{NH}_2$ type were also found in $(\text{N}_2\text{H}_5)_2\text{SO}_4$,²⁰ (distances

Table 6. Observed and calculated structure factors. Reflexions which were too weak to be measured are indicated with an asterisk. The $|F_o|$ values for these are given as $1/2 F_{min}$.

Table with 16 columns: h, k, l, |Fo|, |Fc|, h, k, l, |Fo|, |Fc|, h, k, l, |Fo|, |Fc|, h, k, l, |Fo|, |Fc|. It contains numerical data for various reflections, with asterisks indicating weak or unmeasured values.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
4	7	5	5.3	4.9	0	8	8	6.1	7.5	2	8	3	9.2	8.4	4	8	1	6.2	7.2
4	7	7	7.6	8.7	1	8	8	5.5	2.4	2	8	4	4.1	3.4	4	8	2	3.0	3.1
* 5	7	0	0.7	0.9	1	8	0	12.8	12.7	2	8	5	2.6	2.3	4	8	3	9.7	12.4
5	7	1	4.0	3.3	1	8	2	4.4	4.2	2	8	6	6.2	6.0	0	9	1	8.8	8.8
5	5	0	13.0	13.1	1	8	3	3.8	3.3	2	8	7	8.6	11.3	0	9	2	9.3	8.3
0	8	0	18.8	19.0	1	8	4	6.0	5.7	3	8	0	7.1	7.0	0	9	3	7.3	8.5
0	8	1	8.6	8.4	1	8	5	12.8	11.8	3	8	1	6.1	5.5	0	9	4	6.1	5.7
0	8	2	8.2	8.0	1	8	6	6.5	6.2	3	8	2	20.4	18.9	0	9	5	3.7	3.8
0	8	3	4.5	5.0	1	8	7	2.2	2.6	* 3	8	3	1.1	0.0	0	9	6	6.9	7.3
0	8	4	14.5	14.7	1	8	8	1.9	2.9	3	8	4	6.3	6.0	* 1	9	0	1.2	0.9
0	8	5	5.4	5.1	2	8	0	9.1	8.0	3	8	5	2.8	2.8	* 1	9	1	1.2	1.8
* 0	8	6	6.9	7.4	* 2	8	1	1.4	1.7	3	8	6	6.4	6.3	* 1	9	2	10.6	10.2
* 0	8	7	1.0	0.7	* 2	8	2	1.3	0.8	4	8	0	11.6	13.8	1	9	3	6.1	5.8

3.03 and 3.14 Å), but in this case the bonds were assumed to be components of bifurcated hydrogen bonds.

The chains of hydrazinium ions are linked to the phosphate framework by hydrogen bonds, which are strongest at the NH₃⁺ end of the ions (the situations around the NH₂ group is discussed below). The N⁺—H...O bonds are: N(2)—O(2) at 2.86 Å and N(2)—O(4) at 2.81 Å. These bond distances may be compared with the H₃N⁺—H...O bonds, of 2.92 Å, found in NH₄H₂PO₄.¹⁶ A longer bond is to be expected in the latter compound, according to the ideas presented by Olovsson.²⁴

In addition to the neighbours of N(2) discussed above there is a further oxygen neighbour which is of significance, namely O(1) at 3.09 Å. This oxygen atom lies close to the extension of the N—N axis, the N—N—O angle being 170°. Similar contacts have been found in several other compounds, for example in (N₂H₅)₂SO₄²⁰ and LiN₂H₅SO₄.^{22,23} (The N(2)—O(3) distance of 3.13 Å is of no particular interest).

(b) *Hydrogen bonds from the NH₂ end.* The nitrogen atom N(1), which forms part of the NH₂ end of N₂H₅⁺, has one close nitrogen neighbour at 2.90 Å. This distance corresponds to the length of the hydrogen bond which links the N₂H₅⁺ ions into chains, N(2) being the hydrogen donor. It is thus reasonable to suppose that the lone pair of N(1) is available close to this bond and that the angle formed between the lone pair and N—H is about 109°. Hence, it was possible to predict the approximate positions of the two hydrogens bonded to N(1) according to the assumptions made earlier; H(1) was thus found to lie near the line joining N(1) to O(1) (distance 3.13 Å) and is assumed to form a weak N—H...O bond while H(2) might be engaged in a considerably bent, weak hydrogen bond N(1)—H(2)...O(3), the N(1)—O(3) distance being 3.09 Å (Fig. 7). Peaks were found in the difference maps close to these cal-

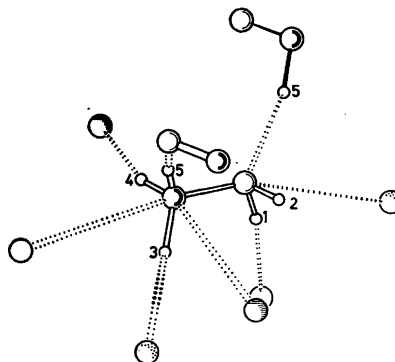


Fig. 7. The location of the hydrogen atoms bonded to the N₂H₅⁺ ion is shown in this figure. Small circles indicate hydrogen atoms (numbered as in Table 1). The orientation and notation of the oxygen and nitrogen atoms are the same as in Fig. 5. The possible bent, weak hydrogen bond N(1)—H(2)—O(3) is not shown in the figure.

culated hydrogen positions. In addition to the neighbours of N(1) mentioned above, there is a further oxygen O(2) at 3.04 Å; the N—N—O angle is 162°. This oxygen lies close to the extension of the N—N axis. As described earlier similar contact was also found at N(2). The hydrogen bonds from the NH₂ group to the phosphate framework are thus very weak.

(c) *Dihedral angle within the N₂H₅⁺ ion.* The dihedral angle defined by the planes N—N—H(1) and N—N—H(3) is about 45°. This means that the hydrazinium ion has an approximately staggered configuration. In (N₂H₅)₂SO₄²⁰ the configuration of one hydrazinium ion was found to be approximately staggered, while that of the other was about eclipsed. The location of the hydrogen atoms, however, was uncertain.

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