

Hydrogen Bond Studies

11. The Crystal Structure of Hydrazinium Bis (Dihydrogenphosphate) $N_2H_6(H_2PO_4)_2$

RUNE LIMINGA

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of hydrazinium(2+) bis(dihydrogenphosphate), $N_2H_6(H_2PO_4)_2$, has been determined from three-dimensional single crystal X-ray data. There are two formula units in a monoclinic unit cell with $a = 4.483$, $b = 8.039$, $c = 10.701$ Å, $\beta = 99.68^\circ$; the space group is $P2_1/c$. The $H_2PO_4^-$ ions are linked by hydrogen bonds (lengths: 2.612, 2.642 Å) to form infinite layers. The $N_2H_6^{2+}$ ions lie between these layers and link them to each other by electrostatic forces and by N—H...O bonds; thus forming a three-dimensional network.

The P—O distances within a $H_2PO_4^-$ ion are: 1.504, 1.515, 1.556, and 1.572 Å. The N—N distance in the $N_2H_6^{2+}$ ion is 1.432 Å and the configuration of the ion is *trans*.

An assignment of the hydrogen atoms to the hydrogen bonds is given, and this is confirmed by the difference Fourier maps.

Two orthophosphates of hydrazine, $N_2H_4 \cdot H_3PO_4$ and $N_2H_4 \cdot 2H_3PO_4$, are known. The crystal structure of the first of these has been determined earlier by the author.¹ This salt is correctly formulated as $N_2H_5H_2PO_4$.

The present investigation involves the structure determination of $N_2H_4 \cdot 2H_3PO_4$ from single crystal X-ray diffraction data. As will be shown below, this compound consists of $N_2H_6^{2+}$ and $H_2PO_4^-$ ions, and the correct formula of the salt is then $N_2H_6(H_2PO_4)_2$; designated hereafter as HBDP.

EXPERIMENTAL

HBDP was prepared by mixing suitable amounts of hydrazine hydrate (*purum*) and phosphoric acid (*p.a.*) according to Sabanejeff.² The amount of N_2H_4 in the sample was determined by analysis at the Central Analytical Laboratory at this Institute, using the bromate method. The sample contained 14.41 % N_2H_4 by weight; the calculated value for HBDP is 14.06 % N_2H_4 .

The needle-shaped crystals were treated with dilute alcohol before mounting. After several attempts it was possible to isolate crystals of approximately cylindrical form.

The crystal used for the single crystal study was a cylinder, diameter 0.15 mm and length 0.31 mm, with the crystallographic a axis coincident with the cylinder axis. With the crystal rotating about this axis, equi-inclination Weissenberg photographs of layers $0 \leq h \leq 4$, were recorded using $\text{CuK}\alpha$ radiation and the multiple-film technique (five films). The measurement of the relative intensities was made visually by comparison with a calibrated scale. The intensity range was 1 to 10000. The number of independent reflexions recorded was 766 but 29 of these were too weak to be measured. About 88 % of the reflexions within the Cu-reflexion sphere were thus recorded.

The data were corrected for the Lorentz and polarization effects and for absorption on an IBM 7090 computer using the program ERLPA written by Van den Hende.³ The absorption coefficient μ for $\text{CuK}\alpha$ radiation is 54.8 cm^{-1} .

The density of HBDP was determined, as described in the *International Tables* (Vol. III, p. 18), by weighing the specimen in air and in *m*-xylene. The value of the density obtained was 1.94 g cm^{-3} .

Attempts to cut the needle-shaped crystals to a suitable shape for collecting data with rotation about the b axis were not successful because of bad cleavage.

UNIT CELL AND SPACE GROUP

The dimensions of the monoclinic unit cell were determined from powder photographs recorded in a Guinier-Hägg 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 cell dimensions were calculated by the method of least squares, as was described in an earlier paper,¹ using the programme CELSIUS, (written by J. Tegenfeldt, Uppsala) now adapted for the CD 3600 computer in Uppsala. The cell dimensions (based on 40 observations) with estimated standard deviations are (at 25°C):

$a = 4.4831 \pm 0.0004$, $b = 8.0389 \pm 0.0006$, $c = 10.7014 \pm 0.0008 \text{ \AA}$,
 $\beta = 99.678^\circ \pm 0.008^\circ$. Unit cell volume = 380.18 \AA^3 .

With two molecules of $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$ per unit cell the calculated density is 1.99 g cm^{-3} , whereas the observed density was 1.94 g cm^{-3} .

The X-ray pattern corresponded to the diffraction symmetry $2/m$. Absent reflexions were: $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$. These observations uniquely indicate the space group $P2_1/c$, assuming that the absences are not accidental. When refined in this space group, the structure gave good agreement with the observed data, thus confirming the choice. The atoms occupy the general fourfold positions:⁴ (x, y, z) ; $(\bar{x}, \bar{y}, \bar{z})$; $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$; $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. The number of independent heavy atoms is: one phosphorus, four oxygen, and one nitrogen. In addition there are five independent hydrogen atoms.

DETERMINATION OF THE ATOMIC COORDINATES

The position of the phosphorus atom could be determined from the Harker vectors in a three-dimensional Patterson synthesis. As there was some difficulty in finding the positions of the oxygen atoms from the Patterson maps, an electron density calculation was made, based only on the known phosphorus position. The four independent oxygen atoms and one nitrogen atom were located without difficulty in these electron density maps. All these atoms are in the general fourfold positions of the space group $P2_1/c$.

These preliminary atomic coordinates were first improved in a series of three-dimensional electron density calculations, and were then further refined by least squares methods. The inter-layer scale factors and isotropic temperature factors were also refined. These calculations were made on the computer FACIT EDB with the same programmes as used earlier.¹ The "discrepancy index" $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ was about 0.10 at this stage.

The refinement of the structure was then continued on the CD 3600 computer in Uppsala using a new set of programmes, which were: 1) A general Fourier programme (called DRF in Uppsala) written by A. Zalkin, Berkeley, Calif., U.S.A. 2) A general full-matrix least squares programme, named LALS, which is Zalkin's version of the least squares programme UCLALS, originally written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Univ. of Calif., Los Angeles, Calif., U.S.A. 3) A programme, called DISTAN, written by A. Zalkin, for the calculation of angles and distances together with the estimated standard deviations. The programmes DRF and LALS have been modified in Uppsala. Options for calculating the weights of the observational equations were included in LALS, together with an analysis of the weighting scheme according to Cruickshank *et al.*⁵

The refinement of the structure on the CD 3600 computer started with two cycles of least squares calculations in which the coordinates, the individual isotropic temperature factors and the five inter-layer scale factors were varied, a total of 29 parameters. The resulting R value, as defined earlier, was 0.10.

Possible positions of the hydrogen atoms were now calculated as will be described below. A three-dimensional ($F_o - F_c$) synthesis was calculated, based only on the reflexions with $\sin \theta/\lambda$ less than 0.5. Peaks could be found in the difference Fourier maps near the predicted hydrogen positions. Some additional peaks, of a size comparable to the five assumed hydrogen peaks, appeared in the difference maps. These additional peaks, however, could be excluded as possible hydrogen positions. The hydrogen atoms are in the general fourfold positions of the space group $P2_1/c$.

Two further cycles were performed with the five hydrogen atoms included with fixed parameters. The isotropic temperature factor B used for all hydrogen atoms was 5 \AA^2 . The parameters varied were the same as previously. The R value was reduced to 0.093. The total shifts in the atomic coordinates of the heavy atoms were, at the most, about one standard deviation.

When the observed and calculated structure factors were compared at this stage, it was found that some low angle reflexions with high intensities systematically had values of F_o smaller than F_c , possibly due to secondary extinction effects. Another explanation of these discrepancies might be that the intensities of these reflexions could be measured only on the last film in the multiple-film set and were too strong to be measured with any certainty. Eight reflexions were excluded from the data. After one cycle, now based on 729 observed reflexions, the R value was reduced to 0.085. The shifts in the scale and isotropic temperature factors were about two standard deviations, whereas the shifts in the atomic coordinates were, at the most, one standard deviation.

The refinement was completed with three cycles of least squares calculations, which now included anisotropic temperature factors for phosphorus,

Table 1. Atomic coordinates with standard deviations. (The hydrogen coordinates listed are those calculated assuming linear O—H...O and N—H...O(4) bonds. See the text.)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
P	0.00236 ± 0.00018	0.16479 ± 0.00010	0.17487 ± 0.00008
O(1)	0.07096 ± 0.00063	0.30991 ± 0.00033	0.09570 ± 0.00026
O(2)	0.10179 ± 0.00066	0.72757 ± 0.00031	0.20020 ± 0.00024
O(3)	0.26939 ± 0.00065	0.56710 ± 0.00038	0.40049 ± 0.00027
O(4)	0.26125 ± 0.00059	0.04427 ± 0.00031	0.21375 ± 0.00023
N	0.49685 ± 0.00071	0.08171 ± 0.00036	0.47319 ± 0.00028
H(1)	0.162	0.848	0.205
H(2)	0.449	0.558	0.357
H(3)	0.410	0.068	0.379
H(4)	0.354	0.156	0.515
H(5)	0.714	0.128	0.484

Table 2 a. Anisotropic temperature factor parameters with standard deviations, each multiplied by 10⁴. The expression used is: $\exp[-(h^2\beta_{11} + hk\beta_{12} + \dots)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	213 ± 8	63 ± 2	35 ± 1	0 ± 3	58 ± 3	7 ± 1
O(1)	332 ± 17	91 ± 4	54 ± 3	38 ± 11	102 ± 9	39 ± 5
O(2)	413 ± 17	79 ± 4	46 ± 2	26 ± 12	118 ± 9	7 ± 4
O(3)	282 ± 17	156 ± 5	61 ± 3	61 ± 13	61 ± 9	56 ± 5
O(4)	269 ± 15	76 ± 4	53 ± 2	12 ± 10	62 ± 8	17 ± 4
N	317 ± 19	88 ± 5	48 ± 3	9 ± 12	82 ± 10	-8 ± 5
H *	768	193	112	0	90	0

* Isotropic temperature factor in anisotropic form; the *B*-value used for all hydrogen atoms was 5 Å².

Table 2 b. Root mean square components, *R_i*, of thermal vibration along principal axes of the ellipsoids of vibration, calculated from the β_{ij} values in Table 2 a with the programme ORFFE.²³

Atom	<i>R₁</i>	<i>R₂</i>	<i>R₃</i>
P	0.126 Å	0.143 Å	0.154 Å
O(1)	0.144	0.168	0.205
O(2)	0.144	0.159	0.209
O(3)	0.163	0.168	0.240
O(4)	0.151	0.158	0.180
N	0.149	0.171	0.184

oxygen and nitrogen. The atomic coordinates of these atoms were also varied together with an over-all scale factor, making a total of 55 varied parameters. The relative inter-layer scale factors used were obtained from the last calculation with isotropic temperature factors. The five hydrogen atoms were included with fixed parameters as before. In the last cycle, the shifts in the coordinates and thermal parameter values were less than one tenth of the standard deviation for the parameter in question. The R value was 0.070.

A difference Fourier synthesis was calculated based on the final heavy atom parameters but omitting the hydrogen atoms. (The R value in this calculation was 0.080.) The five largest peaks in these maps, about twice as high as all other peaks, were near the calculated positions of the five hydrogen atoms. The differences indicated were, at the most, about 0.2 Å. After one cycle of least squares calculation the shifts in the parameters refined earlier were very small, when the hydrogen atoms were shifted so as to correspond to the observed maxima. The R value did not change.

The least squares calculations were based on F values, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was that devised by Cruickshank *et al.*⁵ as follows: $w = 1/(a + |F_o| + c|F_o|^2)$. The final values used for a and c were 1.50 and 0.038, respectively. These values were suitable, as was shown by the weighting analysis obtained from the program LALS. Reflexions too weak to be measured were given zero weight in all calculations, and are omitted when calculating the R values. The R value was 0.078, when the eight strong reflexions omitted from the final calculations were included.

Tables 1 and 2 list values for the atomic parameters obtained from the final anisotropic least squares refinement. The observed and calculated structure factors are compared in Table 5. Distances and angles are given in Tables 3 and 4. The standard deviations in these were calculated using the programme DISTAN (see above) from the standard deviations of the atomic coordinates obtained from the final calculation with the programme LALS. The errors in the cell dimensions were also included in the calculation with DISTAN. The distances listed in Table 3 are not corrected for thermal motion.

The atomic scattering factors used in the calculations were those for neutral P, O, N, and H, respectively, given in the *International Tables* (Vol. III, p. 202).⁶

DISCUSSION OF THE STRUCTURE

The structure can be described with reference to Fig. 1. As will be shown below the present compound, $N_2H_4 \cdot 2H_3PO_4$, contains $N_2H_6^{2+}$ and $H_2PO_4^-$ ions. The $H_2PO_4^-$ ions are linked to each other by $O-H \cdots O$ bonds to form infinite layers, running parallel to the xy -plane. The z -coordinates of the middle of the layers are equal to 0.25 and 0.75, respectively. Both hydrogen atoms in each $H_2PO_4^-$ ion are engaged in the $O-H \cdots O$ bonding system. Four-membered puckered rings of phosphate groups, joined to each other by hydrogen bonds, can be found in the structure. Only three of the four oxygen atoms in each phosphate group are engaged in hydrogen bonding within a layer; one of these three oxygen atoms is acceptor in two hydrogen bonds of the $O-H \cdots O$ type. The phosphate layers are held together by the $N_2H_6^{2+}$ ions situated be-

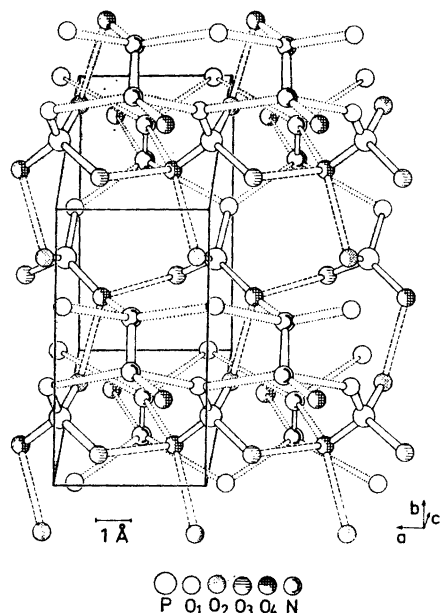


Fig. 1. The structure of $N_2H_6(H_2PO_4)_2$. Solid lines indicate P—O bonds, dashed lines O—H...O bonds and dotted lines N—H...O bonds. Only one of the layers of $H_2PO_4^-$ ions is shown. The z -coordinate of the middle of this layer is 0.25. (The corresponding z -coordinate of the other layer is 0.75.) The centres of the $N_2H_6^{2+}$ ions are at $z = 0$ and $z = \frac{1}{2}$, respectively.

tween them. Each hydrazinium(2+) ion forms six N—H...O bonds. The centre of the $N_2H_6^{2+}$ ion lies in a centre of symmetry, which is the twofold special position d of the space group $P2_1/c$: $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$. This implies that the configuration of the ion is *trans*. Details of the structure and of the hydrogen bonding system will be discussed below.

1. The phosphate layers

a) *The phosphate tetrahedron.* In the present compound, the phosphate tetrahedron deviates significantly from tetrahedral symmetry (see Table 3, Figs. 2 and 4). It is assumed that the distances of 1.504 and 1.515 Å correspond to the P—O bonds, while the other two 1.556 and 1.572 Å, correspond to the P—OH bonds. This assumption is based on the same facts as referred to in the paper on the crystal structure of $N_2H_5H_2PO_4^1$ (designated HYDP hereafter). The P—O and P—OH bonds in HBDP are in very good agreement with those in HYDP: P—O: 1.505, 1.506 Å and P—OH: 1.550, 1.573 Å, respectively.¹ (For further references consult this paper, in which a summary is also given of some data about other dihydrogen phosphates studied earlier.) The above mentioned P—O and P—OH bond lengths are also in agreement with those in $(NH_4)_2H_2P_2O_6$,⁷ viz. P—O: 1.501, 1.503 Å, P—OH: 1.572 Å.

Table 3. Distances and angles with standard deviations within the phosphate layers.

a) Within the phosphate group (cf. Figs. 2 and 4)

P—O(1)	$1.504 \pm 0.003 \text{ \AA}$	O(1)—P—O(2)	$110.4 \pm 0.1^\circ$
—O(2)	$1.572 \pm 0.003 \text{ \AA}$	—O(3)	108.4 ± 0.2
—O(3)	$1.556 \pm 0.003 \text{ \AA}$	—O(4)	115.5 ± 0.2
—O(4)	$1.515 \pm 0.003 \text{ \AA}$	O(2)—P—O(3)	106.5 ± 0.2
		—O(4)	107.2 ± 0.1
		O(3)—P—O(4)	108.5 ± 0.2

b) Hydrogen bonds (cf. Figs. 2 and 4)

O(2)—H(1)...O(4)	$2.642 \pm 0.004 \text{ \AA}$
O(3)—H(2)...O(4)	$2.612 \pm 0.004 \text{ \AA}$

c) Selected angles subtended at the oxygen atoms. (Hydrogen bonds are indicated with an "H" on the donor atom. Angles of the O—O—N type etc. are also listed here; cf. Fig. 3.)

P—O(1)—HN	$104.1 \pm 0.2^\circ$	P—O(2)H—O(4)	$112.3 \pm 0.1^\circ$
P—O(1)—HN	140.3 ± 0.2	P—O(2)—N	133.5 ± 0.1
NH—O(1)—HN	110.3 ± 0.2	N—O(2)H—O(4)	102.9 ± 0.1
P—O(3)—O(3) *	164.4 ± 0.2	P—O(4)—HO(2)	114.4 ± 0.2
P—O(3)H—O(4)	114.5 ± 0.2	P—O(4)—HO(3)	117.8 ± 0.2
O(3)—O(3)H—O(4)	77.7 ± 0.2	P—O(4)—HN	110.2 ± 0.1
		O(2)H—O(4)—HO(3)	105.9 ± 0.1
		O(2)H—O(4)—HN	102.1 ± 0.1
		O(3)H—O(4)—HN	104.8 ± 0.1

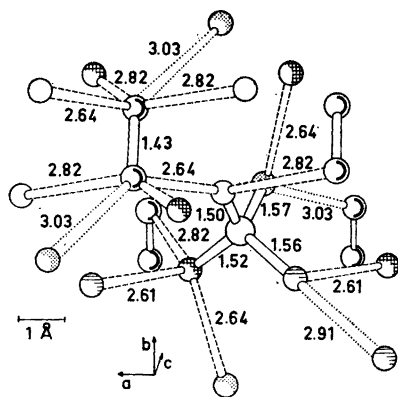
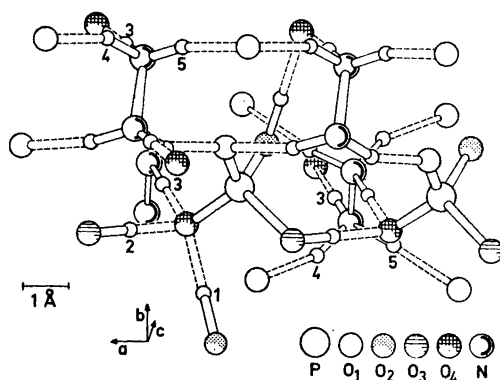
* Short O(3)—O(3) distance ($2.914 \pm 0.006 \text{ \AA}$) between two different layers.

Fig. 2a. Bond distances. Hydrogen bonds (O—H...O or N—H...O) are indicated with dashed lines; other types of contacts with dotted lines.

Fig. 2b. The location of the hydrogen atoms in $N_2H_6(H_2PO_4)_2$. Small circles indicate hydrogen atoms, numbered as in Table 1. Note that the midpoint of the N—N bond lies in a centre of symmetry.

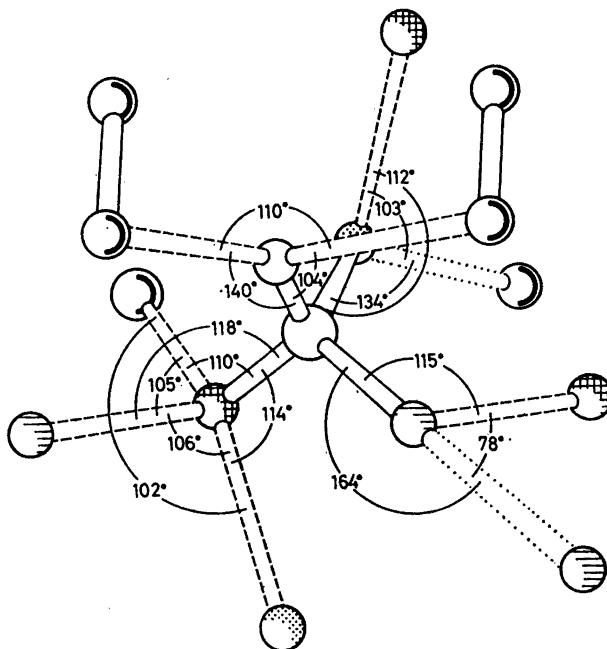


Fig. 3. Bond angles subtended at the oxygen atoms. The orientation and notation of the atoms and the bonds are the same as in Fig. 2.

The angle within the phosphate group involving two P—OH bonds is 106.5° , while the angle between the two P—O bonds is 115.5° . The angles of the O—P—OH type are in the range of 107.2° to 110.4° . These angles are in accordance with what is to be expected. All these angles are comparable with those found in HYDP.¹

The P—(OH)···O angles, where O···O represents a hydrogen bond are 112° and 115° , respectively (Fig. 3). For that type of angle a tetrahedral value has been assumed to be favourable,⁸ but large variations have been observed,^{1,9} as the O—H···O bonds often are bent.

When a correction was made for thermal motion, the P—O distances were 1.513 and 1.521 Å, and the P—OH distances 1.571 and 1.580 Å, respectively. It was assumed in this calculation, performed with the programme DISTAN, that the oxygen atoms ride on the phosphorus atom.

b) *Hydrogen bonding within the phosphate layers.* As was mentioned earlier, the H_2PO_4^- ions in HBDP are bonded to each other by O—H···O bonds, forming infinite layers. This linking of the H_2PO_4^- ions differs from that found in HYDP,¹ where these ions were bonded to a three-dimensional framework. A similar type of framework also exists in KH_2PO_4 ¹⁰⁻¹² and $\text{NH}_4\text{H}_2\text{PO}_4$.¹³

The hydrogen atoms of the H_2PO_4^- ions in HBDP are bonded to the oxygens O(2) and O(3), which both donate hydrogen to a bond to the oxygen

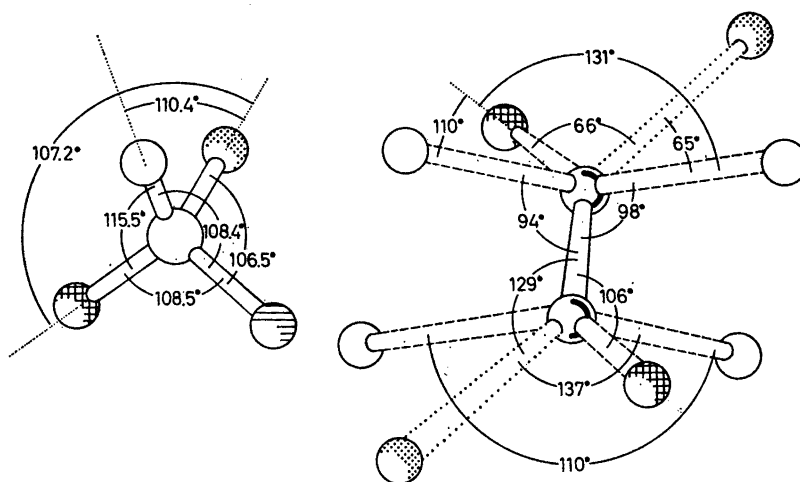


Fig. 4. Bond angles within the phosphate group and around the nitrogen atoms. Bonds and atoms are drawn as in Fig. 2. The midpoint of the N—N bond lies in a centre of symmetry.

atom O(4); bond lengths 2.61 and 2.64 Å, respectively (see Table 3 and Figs. 2 and 3). The oxygen atom O(1) is thus not engaged in hydrogen bonding within the phosphate layers. These bond lengths are about 0.10 Å longer than the same type of bonds (*i.e.* between the same functional groups) found in HYDP,¹ (2.52 and 2.56 Å, respectively). Still shorter O—H...O bonds of this type were observed in KH_2PO_4 ¹⁰⁻¹² (2.48 to 2.49 Å) and $\text{NH}_4\text{H}_2\text{PO}_4$ ¹³ (2.48 Å). In these last three compounds all oxygen atoms in the phosphate group participate in the O—H...O bonding system, while in HBDP only three of the four oxygen atoms are engaged; O(4) then serves as the acceptor of hydrogen in two O—H...O bonds. The oxygen atom O(4) accepts one additional hydrogen atom, donated by nitrogen; the N—O distance being 2.82 Å (see further below).

In HBDP oxygen O(4) is thus used as the acceptor atom in three hydrogen bonds. There are comparable oxygen atoms in HYDP,¹ each of which serves as the acceptor of only two hydrogen atoms, one from an O—H...O bond and another from an N—H...O bond. (The N—H...O bonds in HYDP were 2.81 and 2.86 Å, respectively.) As was mentioned above the O—H...O bonds in the latter case were significantly shorter (2.52, 2.56 Å) than those in HBDP (2.61, 2.64 Å). The longer O—H...O bonds in HBDP may be due to the larger coordination number of O(4) in this compound when compared with the coordination number of the similar oxygen atoms in HYDP.¹ Lindgren and Olovsson¹⁴ found a lengthening of the N—H...X bonds with increased coordination number of X in a series of ammonium and alkylammonium halides.

The increased coordination number of O(4) in HBDP could also be expected to lengthen the N—H...O bond (2.82 Å), when compared with the same kind of bonds in HYDP,¹ which were 2.81 and 2.86 Å. (Both these bonds originate from the NH_3^+ end of the N_2H_5^+ ion.) However, there is another

effect, which may shorten the N—H...O bond in HBDP when compared with those in HYDP,¹ namely the attaching of the hydrogen atom to the lone pair of $N_2H_5^+$, to give the $N_2H_6^{2+}$ ion (Olovsson,¹⁵ p. 447). The net effect is not easy to predict, but these two counteracting effects seem in this case to balance each other.

The assignment of hydrogen atoms to the O—H...O bonds was made with the assumption that these bonds are linear with an O—H distance of 1.00 Å (p. 6486)¹⁶ (see Fig. 2 b). The hydrogen positions obtained (listed in Table 1) were included in the refinements with fixed parameters as described earlier. Well resolved peaks could be found near these predicted hydrogen positions in a difference Fourier synthesis, which indicated moderately bent O—H...O bonds (O—H...O angles 168°) and O—H distances shorter than assumed above. (The coordinates deduced from these maps were: H(1): 0.13, 0.83, 0.20, H(2): 0.44, 0.54, 0.36; O—H distances: 0.85 and 0.95 Å, respectively.) However, the errors in the hydrogen positions obtained from the difference Fourier maps are naturally rather large.

There is one short O(3)—O(3) distance (2.91 Å) between atoms from adjacent layers. This distance is approximately twice the formal van der Waals radius of oxygen. Such short non-hydrogen bonded O—O contacts are not unusual (see for example Ref. 9).

Table 4. Hydrazinium ion. Bond distances and angles with standard deviations (*cf.* Figs. 2 and 4).

1. Distances			
a) Within $N_2H_6^{2+}$		b) Hydrogen bond distances and other N—O contacts less than 3.20 Å	
N—N	1.432 ± 0.006 Å	N—H(3)...O(4)	2.816 ± 0.004 Å
		N—H(4)...O(1)	2.639 ± 0.004 Å
		N—H(5)...O(1)	2.823 ± 0.004 Å
		N—O(2) *	3.029 ± 0.004 Å
		N—O(1)	3.091 ± 0.004 Å
2. Angles			
a) Where N and O are hydrogen bonded.		b) Where N and O are not hydrogen bonded.	
N—N—O(1)	94.1 ± 0.3°	N—N—O(1)	58.4 ± 0.2°
—O(1)	98.2 ± 0.3	—O(2) *	128.8 ± 0.3
—O(4)	106.0 ± 0.3	O(1)—N—O(2) *	70.5 ± 0.1
O(1)—N—O(1)	110.3 ± 0.1		
—O(4)	110.0 ± 0.1		
—O(4)	130.7 ± 0.1		
c) Where the N—O contacts are one of each type.			
O(1)—N—O(1)	152.5 ± 0.1°	O(1)—N—O(2) *	136.9 ± 0.1°
—O(1)	76.7 ± 0.1	—O(2) *	64.9 ± 0.1
—O(4)	80.5 ± 0.1	O(2)—N—O(4)	66.5 ± 0.1

* Possibly part of a bifurcated hydrogen bond (see the text).

2. The hydrazinium (2+) ion

a) *The $N_2H_6^{2+}$ ion and evidence for its existence.* The composition of HBDP is $N_2H_4 \cdot 2H_3PO_4$, and the two possible formulations of the compound are $N_2H_6(H_2PO_4)_2$ and $N_2H_5 \cdot H_2PO_4 \cdot H_3PO_4$.¹⁷ If the latter is correct, two types of phosphate groups would exist in the structure, but as has been demonstrated above, only one type is observed.

Further evidence for the existence of a $N_2H_6^{2+}$ ion is that the midpoint of the N—N bond lies in a centre of symmetry. This also implies that the configuration of the ion is *trans*. The same geometry of the $N_2H_6^{2+}$ ion has been reported in $N_2H_6SO_4$,¹⁸ $N_2H_6F_2$,¹⁹ and $N_2H_6Cl_2$.²⁰ The correct formulation of HBDP is thus $N_2H_6(H_2PO_4)_2$.

The N—N distance in the $N_2H_6^{2+}$ ion is 1.432 Å (Table 4). Some earlier reported values for the N—N distance in this type of ion are: 1.40 Å in $N_2H_6SO_4$,¹⁸ 1.42 Å in $N_2H_6F_2$,¹⁹ and $N_2H_6Cl_2$,²⁰ respectively. There seems to be insufficient support for the assumption,^{18,19} that the N—N distance in $N_2H_6^{2+}$ should be significantly shorter than that in $N_2H_5^+$, as distances for the latter have been observed as short as 1.427 Å in $(N_2H_5)_2SO_4$ ²¹ and 1.432 Å in 5-aminotetrazole.²² On the other hand the usually observed N—N distance in $N_2H_5^+$ is 1.44 to 1.45 Å,^{1,21} (Further references can be found in Ref. 21.)

b) *Hydrogen bonding from the $N_2H_6^{2+}$ ion.* The assumptions concerning the identification of the hydrogen bonds and the location of the hydrogen atoms were: a) the $N_2H_6^{2+}$ ion may participate in six hydrogen bonds, three from each end; b) the N—N—H and H—N—H angles are about 109°; c) the N—H distances are about 1.03 Å.²¹

Each end of the $N_2H_6^{2+}$ is surrounded by four oxygen neighbours which may participate in N—H...O bonding (see Table 4, Figs. 2 and 4). Only one of these possible bonds, N—O(4), (length: 2.82 Å, N—N—O(4) angle: 106°) can be approximately linear according to the assumptions made above, while the rest must be more or less bent (bond lengths and N—N—O angles: N—O(1): 2.64 Å, 94°; N—O(1): 2.82 Å, 98°; N—O(2): 3.03 Å, 129°). Possible positions of the hydrogen atoms could be deduced by placing one hydrogen atom on the line N—O(4) and calculating the positions for the other two (see Fig. 2 b). These coordinates, listed in Table 1, were used in the refinements with fixed values as mentioned earlier. The hydrogen peaks, observed in the difference Fourier maps, were near to those predicted; the shifts indicated were about 0.2 Å or less. (The coordinates obtained from the Fourier maps were H(3): 0.45, 0.06, 0.39; H(4): 0.35, 0.14, 0.51; H(5): 0.70, 0.13, 0.48.) These positions corresponded to N—H distances of about 0.95 Å, N—N—H and H—N—H angles in the range of 103° to 112° and 98° to 120°, respectively. However, the errors in these hydrogen positions can be rather large as was pointed out above.

Two of the oxygen neighbours, namely O(1) at 2.64 Å and O(4) at 2.82 Å, can now be interpreted as being hydrogen bonded to nitrogen by linear or bent bonds. The third short N—O contact (O(1) at 2.82 Å) can either be interpreted as a bent N—H...O bond or part of a bifurcated bond of which N—O(2) (3.03 Å) is the other part. The hydrogen atom H(5) is so oriented that it can be assumed to exert an attraction for O(1), but there may also be a weak interaction with O(2). However, in the figures this bond is drawn as an N—H...O(1)

Table 5. Observed and calculated structure factors. Reflexions which were too weak to be measured are indicated with one asterisk. The |F_o| values for these are given as 1/2 F_min. Two asterisks indicate reflexions which were excluded from the final calculations.

Table with 20 columns: 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|. Contains observed and calculated structure factor data for various h, k, l reflections.

Acknowledgement. The author wishes to thank Prof. G. Hägg for all the facilities put at his disposal and Dr. I. Olovsson for his great interest in this work.

The author wishes also to thank the people mentioned in the text for the use of their crystallographic programmes, and Dr. L. Gustafsson for the analysis of $N_2H_4(H_2PO_4)_2$.

This work has been supported by grants from the *Swedish Natural Science Research Council* and the *Malmfonden — Swedish Foundation for Scientific Research and Industrial Development* — which are here gratefully acknowledged.

R E F E R E N C E S

1. Liminga, R. *Acta Chem. Scand.* **19** (1965) 1629.
2. Sabanejeff, A. *Z. anorg. allgem. Chem.* **17** (1898) 480.
3. Van den Hende, J. H. *Esso Research and Engineering Company CBRL — 27 M — 62*, July 1962.
4. *International Tables for X-ray Crystallography*, Vol. I, Kynoch Press, Birmingham 1952.
5. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, Pergamon, Oxford 1961, p. 45.
6. *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962.
7. Wilson, A. and McGeachin, H. McD. *Acta Cryst.* **17** (1964) 1352.
8. Donohue, J. J. *J. Phys. Chem.* **56** (1952) 502.
9. Calleri, M. and Speakman, J. C. *Acta Cryst.* **17** (1964) 1097.
10. Bacon, G. E. and Pease, R. S. *Proc. Roy. Soc. (London)* **A 220** (1953) 397.
11. Bacon, G. E. and Pease, R. S. *Proc. Roy. Soc. (London)* **A 230** (1955) 359.
12. Peterson, S. W., Levy, H. A. and Simonsen, S. H. *J. Chem. Phys.* **21** (1953) 2084.
13. Tenzer, L., Frazer, B. C. and Pepinsky, R. *Acta Cryst.* **11** (1958) 505.
14. Lindgren, J. and Olovsson, I. *Acta Cryst.* *In press*.
15. Olovsson, I. *Arkiv Kemi* **16** (1960) 437.
16. Nakamoto, K., Margoshes, M. and Rundle, R. E. *J. Am. Chem. Soc.* **77** (1955) 6480.
17. Bock, H. *Z. Naturforsch.* **17b** (1962) 426.
18. Nitta, I., Sakurai, K. and Tomiie, Y. *Acta Cryst.* **4** (1951) 289.
19. Kronberg, M. L. and Harker, D. J. *J. Chem. Phys.* **10** (1942) 309.
20. Donohue, J. and Lipscomb, W. N. *J. Chem. Phys.* **15** (1947) 115.
21. Liminga, R. and Lundgren, J.-O. *Acta Chem. Scand.* **19** (1965) 1612.
22. Bryden, J. H. *Acta Cryst.* **11** (1958) 31.
23. Busing, W. R., Martin, K. O. and Levy, H. A. *ORNL-TM-306*, Oak Ridge National Laboratory, Oak Ridge, Tennessee 1964.

Received June 8, 1966.