

## Tetrametaphosphimic Acid Dihydrate, a Redetermination\*

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**Abstract.**  $(\text{NHPO}_2\text{H})_4 \cdot 2\text{H}_2\text{O}$ , orthorhombic,  $P2_12_12$ ,  $a = 13.995$  (8),  $b = 8.334$  (4),  $c = 5.064$  (3) Å;  $Z = 2$ ,  $D_m = 1.95$  [Corbridge, *Acta Cryst.* (1953), **6**, 104],  $D_x = 1.979$  g cm<sup>-3</sup>. Contrary to the first structure determination [Migchelsen, Olthof & Vos, *Acta Cryst.* (1965), **19**, 603–610], all six independent H atoms could be located in a difference synthesis. This confirms the oxonium acid salt structure and the presence of P–NH–P groups, and leads to the structural formula  $(\text{H}_3\text{O}^+)_2(\text{NHPO}_2\text{H}_{0.5})_4^{2-}$ . The deviation of the anion atoms from the non-crystallographic  $\bar{4}$  symmetry is now significant.

**Introduction.** The structure of  $(\text{NHPO}_2\text{H})_4 \cdot 2\text{H}_2\text{O}$  was first described by Migchelsen, Olthof & Vos (1965). Because of insufficient material the study was of limited accuracy. H atom positions were not determined, although there was some evidence for them.

In metaphosphimate groups, the positions of the H

atoms are of special interest because of a tautomeric alternative with H bonded to phosphate O only, or to N also. After the structure reports of trimetaphosphimic acid dihydrate and some salts of the tri- and tetrameric acid (Attig & Mootz, 1976a; Berking & Mootz, 1971) we found it worth while to redetermine the present structure to a higher accuracy.

Tetrametaphosphimic acid is very insoluble in water, in striking contrast to the trimeric acid. A transport process in aqueous solution in a temperature gradient (50 to 20°C) yielded well-grown crystals, with dimensions up to 0.4 mm, many of them twinned. The intensities of 1026 independent reflexions were measured on an automatic single-crystal diffractometer (Siemens AED) with the  $\theta$ – $2\theta$  scan up to 30° in  $\theta$  and Nb-filtered Mo  $K\alpha$  radiation. All reflexions were used in the refinements with weights based on counting statistics ( $\sigma_i$ ), according to the expression  $\sigma_i = [\sigma_c^2 + (0.04I)^2]^{1/2}$ . No absorption correction was applied ( $\mu = 6.9$  cm<sup>-1</sup>).

Starting with positional parameters of all non-hydrogen atoms, isotropic full-matrix least-squares refinement yielded  $R = 5.7\%$ ; anisotropic refinement

\* Crystal Structures of Acid Hydrates and Oxonium Salts. XIV. Part XIII: Attig & Williams (1976a). Part XII: Attig & Williams (1976b).

Table 1. Atomic parameters with standard deviations in parentheses (referring to the last decimal digit)

| Positional parameters and $U$ values (Å <sup>2</sup> ) are $\times 10^4$ ; for H $\times 10^3$ . The temperature factors are $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{23}kb^*c^* + \dots)]$ and $\exp[-8\pi^2U \sin^2 \theta/\lambda^2]$ . |          |           |           |          |          |          |           |          |          |
|---|----------|-----------|-----------|----------|----------|----------|-----------|----------|----------|
|   | $x$      | $y$       | $z$       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$  | $U_{13}$ | $U_{23}$ |
| P(1)  | 1251 (1) | 1165 (1)  | 1035 (1)  | 77 (3)   | 156 (3)  | 108 (3)  | –4 (2)    | –4 (2)   | 2 (3)    |
| P(2)  | 690 (1)  | –2107 (1) | –623 (1)  | 94 (3)   | 136 (3)  | 119 (3)  | 8 (2)     | 14 (3)   | 16 (3)   |
| N(1)  | 165 (2)  | 1910 (3)  | 1601 (5)  | 86 (9)   | 211 (11) | 112 (10) | 7 (9)     | –1 (8)   | –42 (10) |
| N(2)  | 1137 (2) | –285 (3)  | –1188 (4) | 141 (10) | 154 (10) | 122 (9)  | –12 (8)   | 22 (9)   | –9 (9)   |
| O(1)  | 1841 (1) | 2469 (2)  | –299 (5)  | 119 (8)  | 187 (8)  | 251 (11) | –40 (7)   | 16 (8)   | 30 (9)   |
| O(2)  | 1623 (2) | 546 (3)   | 3587 (4)  | 167 (9)  | 347 (12) | 103 (9)  | 28 (8)    | –22 (8)  | 21 (9)   |
| O(3)  | 1444 (1) | –3140 (3) | 757 (5)   | 108 (8)  | 210 (9)  | 308 (12) | 28 (7)    | 13 (9)   | 106 (10) |
| O(4)  | 318 (2)  | –2761 (3) | –3165 (4) | 242 (10) | 203 (9)  | 152 (9)  | –21 (8)   | –5 (8)   | –25 (9)  |
| O(5)  | 3483 (2) | –389 (3)  | 4801 (6)  | 376 (14) | 280 (13) | 364 (15) | 20 (11)   | –17 (12) | –16 (12) |
|   | $x$      | $y$       | $z$       | $U$      | $x$      | $y$      | $z$       | $U$      |          |
| H(1)  | 7 (3)    | 206 (5)   | 283 (8)   | 20 (11)  | H(51)    | 360 (6)  | –123 (10) | 250 (20) | 126 (37) |
| H(2)  | 117 (2)  | 1 (4)     | –318 (7)  | 7 (7)    | H(52)    | 280 (3)  | –10 (4)   | 426 (8)  | 19 (9)   |
| H(3) <sup>†</sup>   | 230      | –284      | 53        | 54 (13)  | H(53)    | 418 (4)  | 15 (7)    | 467 (11) | 48 (16)  |

<sup>†</sup> Position restricted to midpoint of O(3)–O(1<sup>iii</sup>), see Table 2.

led to  $R = 3.8\%$ . At this stage a difference synthesis was calculated with low-angle data. The five highest peaks between  $0.5$  and  $0.4 \text{ e } \text{Å}^{-3}$  could be correlated with H atoms. The missing H atom was found as a peak lower than some peaks situated on bonds within the molecule. This atom resides in a very short  $\text{O} \cdots \text{O}$  contact between two molecules; according to our

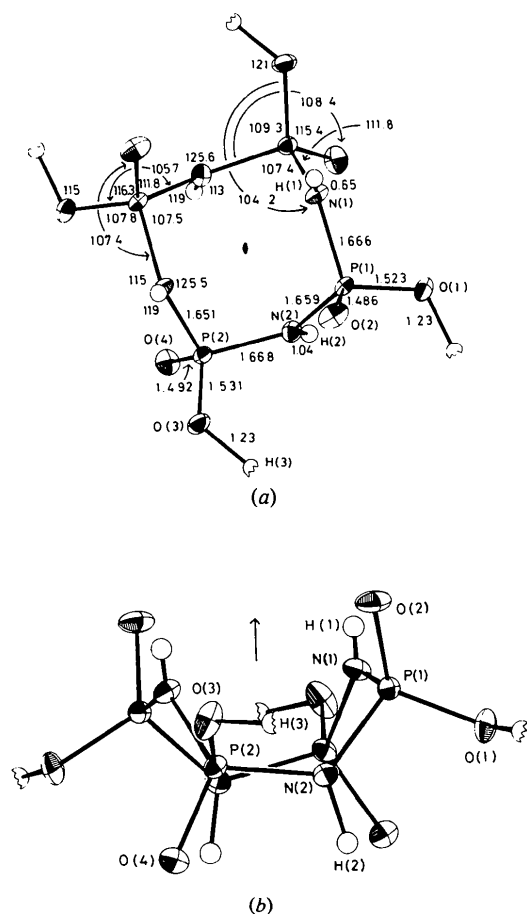


Fig. 1. (a) The anion with its four half-OH protons and bond lengths and angles, e.s.d.'s  $0.003 \text{ Å}$  and  $0.1^\circ$  ( $0.04 \text{ Å}$  and  $3^\circ$  when H is involved); (b) the tub conformation. The twofold axis of the anion (parallel to  $[001]$ ) is only approximately perpendicular to the paper in (a) and parallel in (b).

experience, such a situation invariably leads to unusually low electron density at the H atom position (Attig & Mootz, 1976b; Attig, 1976). All H atoms except the last were included in the refinement with isotropic temperature factors. Attempts to refine the last H atom position gave an unreasonable shift away from the midpoint of the  $\text{O} \cdots \text{O}$  contact, although the resulting position remained equidistant from both O atoms. Therefore, the position was reset to the midpoint between these atoms. Refinements including an isotropic extinction correction led to values of this parameter not significantly different from zero; therefore, no such correction was considered in the final calculation. The final  $R$  was  $0.030$ , the weighted  $R$   $0.047$ . Atomic parameters are listed in Table 1. The atomic form factors of Hanson, Herman, Lea & Skillman (1964) were used for P, O and N, those of Stewart, Davidson & Simpson (1965) for H.\*

**Discussion.** A discussion of the packing and bonding effects in this structure has been given (Migchelsen, Olthof & Vos, 1965). Therefore, only differences which depend on the higher accuracy of this study will be described here.

The detection of three H atoms near each water O atom, one near each N atom, and one on each of the midpoints of four short inter-anionic hydrogen bonds now unambiguously leads to the formulation  $(\text{H}_3\text{O}^+)_2(\text{NHPO}_2\text{H}_0\text{S})_4^{2-}$ . The imino formulation  $\text{P}-\text{NH}-\text{P}$  for metaphosphimic acid groups is now established through direct observation of the H atom positions in this structure as well as in trimetaphosphimic acid dihydrate and the monoammonium salt (Attig & Mootz, 1976a), and the K salt of tetrametaphosphimic acid (Berking & Mootz, 1971).

The anion is shown in Fig. 1. Deviations from the non-crystallographic symmetry  $\bar{4}$  (exact symmetry only 2) are now significant. In particular, the phosphate O atoms disturb the higher symmetry, with distances of  $0.028(4)$  and  $0.017(4) \text{ Å}$  away from the averaged

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32234 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Geometry of the hydrogen bonds

Symmetry code: (i)  $-x, -y, 1+z$ ; (ii)  $x, y, -1+z$ ; (iii)  $\frac{1}{2}-x, -\frac{1}{2}+y, -z$ ; (iv)  $\frac{1}{2}-x, \frac{1}{2}+y, -z$ .

| $D-H \cdots A$   | $D \cdots A$         | $D-H$               | $H \cdots A$        | $\angle \text{DHA}$ |
|--|----------------------|---------------------|---------------------|---------------------|
| $\text{N}(1)-\text{H}(1) \cdots \text{O}(4^{\text{i}})$          | $2.826(3) \text{ Å}$ | $0.65(4) \text{ Å}$ | $2.18(4) \text{ Å}$ | $175(6)^\circ$      |
| $\text{N}(2)-\text{H}(2) \cdots \text{O}(2^{\text{ii}})$         | $2.818(3)$           | $1.04(4)$           | $1.81(4)$           | $162(3)$            |
| $\text{N}(3) \cdots \text{H}(3) \cdots \text{O}(1^{\text{iii}})$ | $2.464(3)$           | $1.23$              | $1.23$              | $180$               |
| $\text{O}(5)-\text{H}(51) \cdots \text{O}(1^{\text{iii}})$       | $2.931(4)$           | $1.37(9)$           | $1.67(9)$           | $149(6)$            |
| $\text{O}(5)-\text{H}(52) \cdots \text{O}(2)$                    | $2.786(14)$          | $1.03(4)$           | $1.76(4)$           | $174(4)$            |
| $\text{O}(5)-\text{H}(53) \cdots \text{O}(4^{\text{iv}})$        | $2.881(4)$           | $1.08(6)$           | $2.02(5)$           | $134(4)$            |

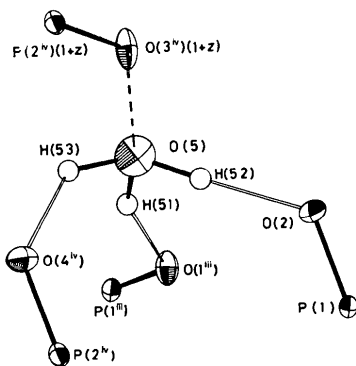


Fig. 2. The oxonium ion with four O atoms nearer than 3.0 Å to O(5); three of these are hydrogen bonded. The symmetry code is explained in Table 2.

positions. The larger difference for the transformation  $O(1) \rightarrow O(3)$  can be explained by the strong hydrogen bond between these two atoms belonging to different molecules; the hydrogen-bonding pattern does not conform to  $\bar{4}$  symmetry. All hydrogen bonds are listed in Table 2.

The one independent oxonium ion is shown in Fig. 2, with its four O atom neighbours having distances less than 3.0 Å from the central O atom. Only three of these O atoms are hydrogen bonded to the oxonium ion, at rather long distances; O(3) with a distance of 2.930

Å to O(5) has no H atom of the oxonium ion nearer than 2.85 Å, and its own H(3) does not bond to O(5). But O(3) as well as one more O(4) with a contact of 3.107 Å to O(5) would certainly belong to the coordination sphere of the cations in the acid alkali salts of this acid,  $M_2H_2(NHPO_2)_4$ , which are isomorphous with the dihydrate (Corbridge, 1953). There are no more contacts up to 3.34 Å.

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## *p*-Cyanophenol

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**Abstract.**  $C_7H_5NO$ , orthorhombic, *Pbcn*,  $a = 9.190(4)$ ,  $b = 10.750(3)$ ,  $c = 25.460(4)$  Å,  $Z = 16$ ,  $D_x = 1.259$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 7.16$  cm<sup>-1</sup>. The final  $R$  was 0.081 for 1825 reflexions measured photographically. The two independent molecules have similar dimensions, indicating a probable contribution from the quinonoid resonance structure, and are joined alternately head-to-tail by O–H...N hydrogen bonds to form infinite helical chains around  $2_1$  axes parallel to  $c$ .

**Introduction.** Colourless, plate-like crystals were grown from benzene solution. The systematic absences:  $hk0$ ,  $h + k = 2n + 1$ ;  $0kl$ ,  $k = 2n + 1$ ;  $h0l$ ,  $l = 2n + 1$ , indi-

cate the space group *Pbcn*. As  $Z = 16$ , there are two independent molecules in the asymmetric unit.

Intensity data were visually estimated from equi-inclination Weissenberg photographs taken around  $a$  and  $b$  axes with Ni-filtered Cu  $K\alpha$  radiation, and reduced to a unique set of 1825  $F$  values by application of the usual corrections. No absorption correction was applied.

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The  $R$  value was reduced to 0.16 by block-diagonal least squares with isotropic thermal parameters. Anisotropic refinement, including isotropic H atoms located from a difference synthesis, converged to  $R = 0.11$ .