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Preliminary structural data on tetraphosphonitrilic acid and some salts.

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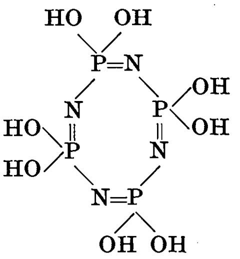
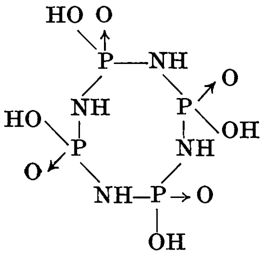
An earlier X-ray study of the crystal structure of tetraphosphonitrilic chloride $P_4N_4Cl_8$ (Ketelaar & de Vries, 1939) has shown the molecule to exist in the form of a puckered 8-membered ring consisting of alternate phosphorus and nitrogen atoms. Hydrolysis of the chloride yields tetraphosphonitrilic acid which has the probable formula



(I)

or



(II)

Some of the acid was prepared by hydrolysis of an ethereal solution of the chloride, using the method of Stokes (1895). Single crystals of the acid dihydrate were obtained as very small colourless prisms by slow evaporation of an aqueous solution. Rotation, oscillation, and Weissenberg photographs taken with Cu $K\alpha$ radiation showed the crystals to be orthorhombic with

$$a = 13{\cdot}92 \pm 0{\cdot}04,\ b = 8{\cdot}34 \pm 0{\cdot}04,\ c = 5{\cdot}05 \pm 0{\cdot}02\ \text{Å}\,.$$

Reflexions observed to be systematically absent were those of type $\{h00\}$ when h was odd, and $\{0k0\}$ when k was odd, which indicated space group $P2_12_12$. A distinct pyroelectric effect was observed in the crystals, thus confirming the space group as belonging to a non-centrosymmetrical Laue class. The observed crystal density of 1·95 g.cm.$^{-3}$ indicated that the unit cell contained two molecules of $P_4N_4(OH)_8.2\,H_2O$.

Space group $P2_12_12$ requires four asymmetric units in general positions or two twofold axially symmetric units situated on twofold axes. The foregoing crystallographic data are therefore consistent with two 8-membered rings having at least twofold symmetry, lying with their centres on the twofold axes of the unit cell, with their planes perpendicular to these axes.

With intensities obtained from Weissenberg photographs, a Patterson synthesis of type $P(X, Y, 0)$ has been computed and the approximate x and y co-ordinates of the phosphorus and nitrogen atoms have been derived. This, together with preliminary trial-and-error work followed by a Fourier synthesis, has confirmed the existence of a puckered 8-membered ring similar to that found in the parent chloride. Tetraphosphonitrilic chloride (Ketelaar & de Vries, 1939) is tetragonal with $a = 10{\cdot}82$, $c = 5{\cdot}95$ Å, the tetragonal axis being perpendicular to, and passing through, the centre of the ring.

The presence of the two water molecules in the acid structure presumably prevents it assuming full tetragonal symmetry.

The dipotassium and dirubidium salts were prepared, and rotation and Weissenberg photographs showed them to be closely isomorphous with the acid (Table 1). A brief examination of the diammonium salt revealed that it was isomorphous with this series, the shortest axis being $c = 5{\cdot}08$ Å.

The water molecules in the acid structure presumably occupy roughly the same positions as the corresponding metal atoms in the isomorphous salts. This suggests the metal atoms may be equivalent to H_3O^+ in the former, with charged water molecules acting as cations in the structure. The acid dihydrate is very insoluble and exceptionally stable compared with other members of the phosphonitrilic series (Audrieth, Steinman & Toy, 1943); moreover, the two water molecules are removed only with difficulty.

From general structural considerations, an extensive hydrogen-bonding system seems highly probable. This is supported by evidence from infra-red absorption spectra. No absorption was observed in any of the compounds near 3620 cm.$^{-1}$ which usually corresponds to free OH vibrations. On the other hand strong absorptions were observed in the region 2600–3000 cm.$^{-1}$, which indicates hydrogen bonded P–OH groups (Daasch & Smith, 1951; Bellamy & Beecher, 1952).

Detailed structural work is proceeding and will be published in full at a later date.

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Table 1.

	a (Å)	b (Å)	c (Å)	ϱ_o (g.cm.$^{-3}$)	ϱ_c (g.cm.$^{-3}$)	n
$P_4N_4(OH)_8.2\,H_2O$	13·92	8·34	5·05	1·95	1·97	2
$P_4N_4(OH)_6(OK)_2$	13·89	8·07	5·03	2·31	2·31	2
$P_4N_4(OH)_6(ORb)_2$	14·03	8·24	5·06	2·74	2·75	2