

Acta Cryst. (1974). B30, 522**Tetrasodium Imidodiphosphate Decahydrate**

BY M. L. LARSEN* AND R. D. WILLETT

Department of Chemistry, Washington State University, Pullman, Washington 99163, U.S.A.

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Abstract. $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$, monoclinic, $C2/c$, $a=17.069$ (7), $b=6.905$ (5), $c=4.752$ (12) Å, $\beta=110.34$ (4)°; $\mu(\text{Mo } K\alpha)=4.6$ cm⁻¹. The N-P distance of 1.678 (5) Å and the P-N-P angle of 127.2 (5)° differ significantly from the corresponding P-O and P-O-P values in the isomorphous pyrophosphate, $\text{Na}_4(\text{P}_2\text{O}_7) \cdot 10\text{H}_2\text{O}$. Bond distances and angles are reported with e.s.d.'s of about 0.005 Å and 0.4°. The calculated density for $Z=4$ is 1.81 g cm⁻³.

Introduction. A small (<0.1 mm in largest dimension) crystal was selected for data collection from a sample supplied by Professor R. Yount of the Washington State University Chemistry Department. Systematic absences were observed when $h+k=2n+1$ for all reflections and $l=2n+1$ for $h0l$ reflections, indicating the space group $C2/c$ or $C2$. Intensity data were collected on a Picker diffractometer equipped with a Gen-

eral Electric quarter-circle single-crystal orienter at 22°C using a take-off angle of 3.0° with Zr-filtered Mo $K\alpha$ radiation. A θ - 2θ scan was employed, scanning 1.62° in 2θ at a rate of 1.0° min⁻¹. Background counts of 10 s duration were taken immediately before and after each scan. A standard reflection monitored periodically showed no systematic drift in intensity. The intensities of the 1065 reflections within the sphere of reflections for Mo $K\alpha$ radiation with $\theta < 22.5^\circ$ were measured. Of these, 989 had intensities which were at least 1% of the background count.

The distribution of normalized structure factors clearly indicated that the centrosymmetric space group, $C2/c$, was the correct space group. The location of all of the non-hydrogen atoms in the $\text{PO}_3\text{NHPO}_3^-$ ion was established from the Patterson map. At this point, the isostructural nature of $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_7) \cdot 10\text{H}_2\text{O}$ was clearly established, and the locations of the oxygen atoms of the water molecules were taken from the structure investigation of the latter compound (MacArthur & Beevers, 1957).

* Present address: United Medical Laboratories, Inc., P.O. Box 3932, Portland, Oregon 97208, U.S.A.

Table 1. *Final parameters for* $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$

Standard deviation on the least significant digit is given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.0674 (1)	0.2688 (1)	0.3480 (1)	0.0011 (1)	0.0059 (2)	0.0013 (1)	0.0001 (1)	0.0004 (1)	-0.0002 (1)
Na(1)	0.2395 (1)	0.6916 (3)	0.6071 (1)	0.0021 (1)	0.0158 (5)	0.0034 (1)	-0.0009 (2)	0.0010 (1)	-0.0008 (2)
Na(2)	0.3850 (1)	0.9103 (3)	0.7967 (1)	0.0023 (1)	0.0119 (4)	0.0027 (1)	-0.0003 (2)	0.0009 (1)	-0.0001 (1)
O(1)	0.0249 (2)	0.4470 (4)	0.3707 (2)	0.0016 (1)	0.0082 (7)	0.0026 (2)	0.0005 (2)	0.0009 (1)	-0.0006 (3)
O(2)	0.0844 (2)	0.1127 (4)	0.4249 (2)	0.0025 (1)	0.0086 (7)	0.0016 (2)	0.0006 (3)	0.0006 (1)	0.0007 (3)
O(3)	0.1448 (2)	0.3279 (4)	0.3265 (2)	0.0013 (1)	0.0106 (7)	0.0025 (2)	-0.0006 (3)	0.0009 (1)	-0.0010 (3)
N	0.0000	0.1621 (7)	0.25	0.0018 (2)	0.0059 (11)	0.0024 (3)	0.0000	0.0006	0.0000
H ₂ O(1)	0.1009 (2)	0.3943 (5)	0.0556 (2)	0.0018 (1)	0.0198 (9)	0.0027 (2)	0.0007 (3)	0.0009 (1)	0.0003 (3)
H ₂ O(2)	0.2430 (2)	0.0172 (5)	0.0226 (2)	0.0020 (1)	0.0132 (8)	0.0032 (2)	-0.0006 (3)	0.0004 (1)	0.0001 (3)
H ₂ O(3)	0.2311 (2)	0.0902 (5)	0.2515 (3)	0.0027 (2)	0.0164 (9)	0.0045 (2)	0.0003 (3)	0.0016 (2)	-0.0030 (4)
H ₂ O(4)	0.3914 (2)	0.2717 (5)	0.1619 (2)	0.0023 (1)	0.0106 (8)	0.0027 (1)	0.0002 (3)	0.0010 (1)	-0.0002 (3)
H ₂ O(5)	0.4156 (2)	0.3863 (5)	0.3890 (2)	0.0034 (2)	0.0158 (9)	0.0030 (2)	-0.0001 (3)	0.0015 (2)	-0.0005 (3)

$R(1A)=0.062$ $R(1C)=0.061$
 $R(1B)=0.054$ $R(3)=0.060$

Table 2. *Bond distances and angles in* $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$

The standard deviation on the least significant digit is given in parentheses.

Bond distances (Å)		Bond angles (°)		Dihedral angles down the P-N bond (°)	
P-O(1)	1.524 (5)	P—N—P	127.2 (5)	O(1)—O(2)	119.8 (5)
P-O(2)	1.520 (9)	O(1)—P—O(2)	112.9 (6)	O(1)—O(3)	119.6 (4)
P-O(3)	1.518 (7)	O(2)—P—O(3)	113.3 (3)	O(2)—O(3)	120.5 (4)
P—N	1.678 (5)	O(1)—P—O(3)	109.9 (2)		
		N—P—O(1)	108.4 (3)		
		N—P—O(2)	102.9 (3)		
		N—P—O(3)	109.0 (4)		

Refinement of the structure model proceeded directly, first with isotropic and later anisotropic thermal parameters, to a value of R of 0.062 ($R = \sum |\Delta F| / \sum |F_{\text{obs}}|$). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). A difference synthesis at this point clearly revealed the presence of all hydrogen atoms (including the hydrogen atom in the $\text{PO}_3\text{NHPO}_3^{4-}$ ion) accounting for all peaks above about $0.5 \text{ e } \text{\AA}^{-3}$. Inclusion of the hydrogen atoms reduced the R value to 0.058 but attempts to refine their positions gave unrealistic O-H and N-H distances. Heavy-atom structural parameters are given in Table 1.* The hydrogen atom positions are not reported. The position of the hydrogen atoms associated with the water molecules are in qualitative agreement with those reported by McDonald & Cruickshank (1967) for $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$. The position of the imido hydrogen was on the twofold axis along the bisector of the P-N-P bond angle. Fig. 1 illustrates the $\text{PO}_3\text{NHPO}_3^{4-}$ ion and its surroundings. Observed and calculated structure factors are available. Distances and angles are given in Tables 2-5.

Discussion. This structural investigation was undertaken to determine the detailed geometry of the $\text{PO}_3\text{NHPO}_3^{4-}$ ion and compare it with the geometry of the pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$. The latter is important in under-

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30234 (5 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Hydrogen bonds in $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$*

The standard deviation on the least significant digit is given in parentheses.

O(1)-W(1 ^b)	2.803 (5)
O(1)-W(1 ^c)	2.744 (5)
O(3)-W(2)	2.715 (6)
O(2)-W(2 ^c)	2.734 (5)
O(3)-W(3)	2.682 (5)
O(1)-W(4 ^d)	2.785 (5)
O(2)-W(4 ^e)	2.778 (5)
O(2)-W(5 ^f)	2.754 (6)

Coordinate transformation

(b)	\bar{x}	y	$\frac{1}{2} - z$
(c)	x	\bar{y}	$\frac{1}{2} + z$
(d)	$\frac{1}{2} - x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$
(e)	$\frac{1}{2} - x$	$-\frac{1}{2} + y$	$\frac{1}{2} - z$
(f)	$\frac{1}{2} + x$	$-\frac{1}{4} + y$	z

Table 4. *Distances in the sodium octahedra in $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$*

Standard deviation in parentheses.

Distances in the Na(1) octahedron (Å)		Distances in the Na(2) octahedron (Å)	
Na(1)-H ₂ O(1 ^b)	2.301 (4)	Na(2)-O(1 ^d)	2.464 (4)
Na(1)-H ₂ O(2 ^c)	2.373 (5)	Na(2)-O(3 ^d)	2.488 (4)
Na(1)-H ₂ O(2 ^d)	2.368 (5)	Na(2)-H ₂ O(1 ^b)	2.495 (5)
Na(1)-H ₂ O(3 ^b)	2.655 (5)	Na(2)-H ₂ O(3 ^b)	2.486 (5)
Na(1)-H ₂ O(3 ^d)	2.772 (5)	Na(2)-H ₂ O(4 ^b)	2.390 (4)
Na(1)-H ₂ O(4 ^b)	2.440 (4)	Na(2)-H ₂ O(5 ^b)	2.407 (5)

Coordinate transformation

(b)	x	\bar{y}	$\frac{1}{2} + z$
(c)	x	$1 - y$	$\frac{1}{2} + z$
(d)	$\frac{1}{2} - x$	$\frac{1}{2} - y$	z

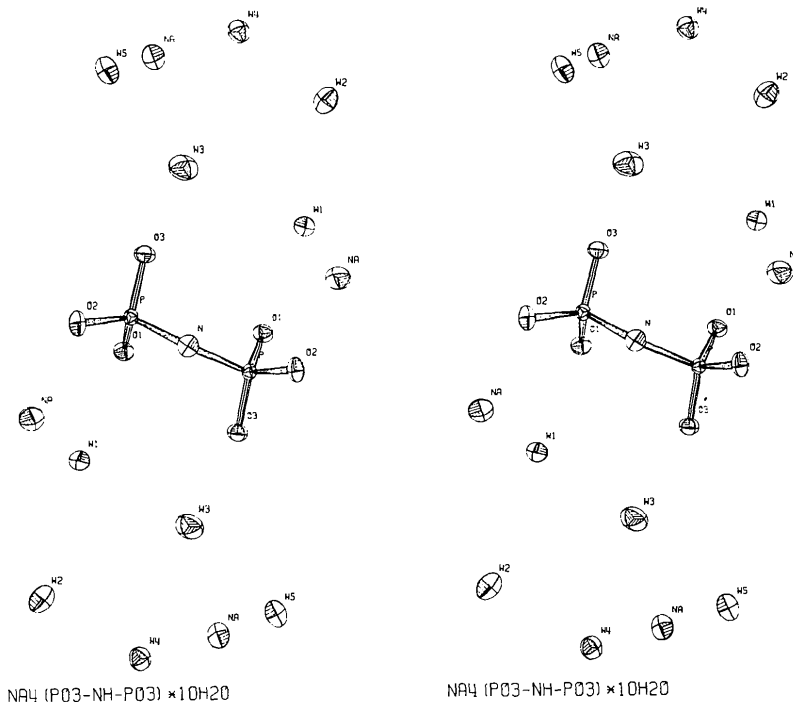


Fig. 1. Stereographic illustration of the surroundings of the $\text{PO}_3\text{NHPO}_3^{4-}$ ion in $\text{Na}_4(\text{PO}_3\text{NHPO}_3) \cdot 10\text{H}_2\text{O}$.

Table 5. *Other interatomic distances less than 3.5 Å in Na₄(PO₃NHPO₃).10H₂O*

The standard deviation on the least significant digit is given in parentheses.

P—P ^b	3.006 (3) Å	O(2)—W(5)	3.153 [*] (6) Å
Na(1)—Na(2)	3.382 (3)	N—W(4)	3.272 (6)
Na(1)—Na(1 ^c)	3.395 (5)	N—W(5)	3.446 (5)
P—Na(2)	3.368 (3)	O(3)—W(3)	3.292 _a (5)
P—O(1 ^b)	3.302 (4)	O(3)—W(4)	3.138 [*] (5)
N—O(1)	2.598 (6)	W(1)—W(2)	3.320 _a (5)
N—O(2)	2.503 (4)	W(2)—W(2')	3.309 (8)
N—O(3)	2.604 (4)	W(2)—W(3)	3.484 (6)
O(1)—O(2)	2.538 (5)	W(2)—W(4)	3.176 (5)
O(1)—O(3)	2.492 (5)	W(2)—W(4)	3.226 (5)
O(2)—O(3)	2.537 (5)	W(3)—W(5)	2.976 (6)
O(1)—O(1 ^b)	3.368 (7)	W(4)—W(5)	3.319 (6)
O(1)—O(3 ^b)	3.422 (5)		

Coordinate transformation

$$\begin{array}{l} (b) \quad \bar{x} \quad y \quad \frac{1}{2}-z \\ (c) \quad \frac{1}{2}-x \quad \frac{1}{2}-y \quad \bar{z} \end{array}$$

standing the similarities and differences between the behavior of adenosine triphosphate and its imido analog. This has been discussed in a previous communication (Larsen, Willett & Yount, 1971).

The similarities between this structure and that of Na₄P₂O₇.10H₂O are very striking. The only essential differences are in the bridging P—X—P geometry. The P—N distance of 1.678 (5) Å is significantly longer than the bridging P—O distance of 1.612 (5) Å. The presence of the N—H group in the bridging position decreases

the P—X—P angle by 3° (127.2° vs. 130.2°) but because of the longer P—X bonds, the P—P distance is longer in the imido compound (3.006 Å) than in the pyrophosphate ion (2.925 Å).

The details of the remainder of the structure are virtually indistinguishable from those of the pyrophosphate. In particular, the hydrogen-bonding scheme appears to be undisturbed. This indicates that the imido hydrogen is effectively 'buried' between the two PO₃ groups and blocked from participation in the hydrogen bonding scheme. This is borne out by the length of the closest intermolecular N—O distances, which, at 3.292 and 3.446 Å, are too long for effective hydrogen bonding.

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Tetrafluoro-*p*-benzoquinone (Fluoranil)

PAR ALAIN MERESSE, CHRISTIAN COURSEILLE ET NGUYEN BA CHANH

Laboratoire de Cristallographie et de Physique Cristalline, associé au CNRS, Université de Bordeaux I, 351 Cours de la Libération, 33405-Talence, France

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Abstract. C₆O₂F₄, monoclinic, *P*2₁/*c*, *a*=6.690 (5), *b*=5.405 (5), *c*=9.107 (6) Å, β=106.15 (8)°, *Z*=2, *D_c*=1.915, *D_m*=1.90 g cm⁻³, *R*=0.066. Fluoranil is not isotypic with the isomorphous compounds chloranil and bromanil.

Introduction. L'étude de ce dérivé s'insère dans le cadre des recherches effectuées au Laboratoire sur les conditions de miscibilité en phase solide entre composés organiques. Dans ce domaine, la connaissance de la structure cristalline de ces derniers apporte un argument décisif sur les possibilités de leur syncristallisation

(Chanh & Haget, 1972).* Dans la série des composés tétrahalogénés de la parabenzoquinone, on sait déjà que les dérivés chlorés (chloranil) et bromé (bromanil) sont isotypes comme le montre le Tableau 1.

Données expérimentales. Le cristal de fluoranil a été obtenu par recristallisation après dissolution dans le

* Selon Kitaigorodskii (1961), il est possible d'obtenir des solutions solides entre composés organiques si ceux-ci sont cristallographiquement isotypes (même groupe spatial et paramètres voisins) et que les molécules présentent un degré de ressemblance élevé.