Heteroatom Chemistry
Volume 2, Number 3, 1991

2-Aminopyridiniomethylphosphonite: A Hydrogen-Bonded Polymer from the Hydrolysis of 1,3,4-Diazaphospholo[1,2-a]pyridine†

Igor A. Litvinov*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Arbuzov Str. 8, Kazan 420083, USSR

Konstantin Karaghiosoff and Alfred Schmidpeter

Institut für Anorganische Chemie, Universität München, Meiserstr. 1, D-800 München 2, Germany

Elena Y. Zabotina and Evelina N. Dianova

A. M. Butlerov Chemical Research Institute, Kazan University, Lenin Str. 18, Kazan 420008, USSR

Received 27 November 1990.

ABSTRACT

Condensation of 2-aminopyridine and chloromethyldichlorophosphane yields 1,3,4-diazaphospholo[1,2-a]pyridine **2**. *Methanol adds to* **2** *while diethylamine does not; with additional elemental sulfur, in both cases the sulfides* **4**, **6** *of the respective adducts are formed. Hydrolysis of* **2** *specifically opens the PN-bond and gives the zwitterionic 2-aminopyridiniomethylphosphonite* **7**. *The compound crystallizes with one molecule water in the monoclinic space group* $P2_1/c$ *with* $a = 25.490(7)$ Å, $b = 7.365(4)$ Å, $c = 9.088(3)$ Å, $\beta = 100.06(3)°$, *and* $Z = 8$ *with two independent molecules of* **7** *and of water. In the crystal hydrogen bonds connect the molecules of* **7** *to form double-chain structured polymers. The individual double-chains are linked to each other by hydrogen-bonded water molecules.*

RESULTS AND DISCUSSION

A phosphorus atom is isoelectronic and similar in electronegativity to a CH group. It can substitute a CH unit in a delocalized ring system with the resulting heterocyclic system [1, 2] resembling the parent system. This is found to be true, for example, for the synthesis and part of the behavior of imidazo[1,2-a]pyridine **1** [3] and its 2-phosphaanalogue, the 1,3,4-diazaphospholo[1,2-a]pyridine **2** [4]. The two differ, however, in their sensitivity to hydrolysis and to protic nucleophiles in general.

Azaphospholes may behave rather differently against water. Some of them are inert, some add water to the ring, open the ring, or eliminate the phosphorus completely in the form of phosphorous acid [5, 6]. Compound **2** gives a ring-opened product that provides the possibility for a variety of hydrogen bonds to link the molecules to a polymer.

1,3,4-Diazaphospholo[1,2-a]pyridine

Imidazo[1,2-a]pyridine **1** is commercially available; it is prepared by reacting 2-aminopyridine with chloro- or bromoacetaldehyde and sodium bicarbonate as a base in aqueous–alcoholic solution [3, 7]. 1,3,4-Diazaphospholo[1,2-a]pyridine **2** can be synthesized according to the same scheme. In place of the haloacetaldehyde, chloromethyldichloro-

---

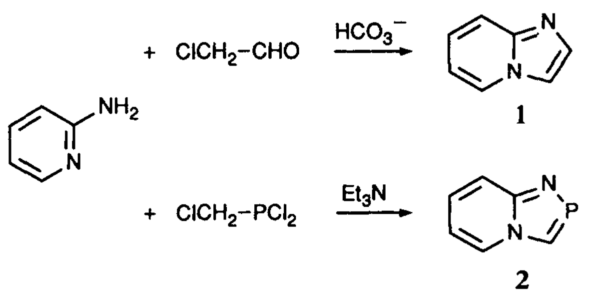
Dedicated to Professor Dr. Marianne Baudler on the occasion of her seventieth birthday.

*To whom correspondence should be addressed.

†Four- and Five-membered Phosphorus Heterocycles, Part 78. Part 77: Ref. [6].

1042-7163/91/$3.50 + .25

phosphane is used for the condensation with 2-aminopyridine. The reaction must be performed in an aprotic solvent such as acetonitrile with triethylamine acting as base. That only the 2-phospha derivative (and not also the 3-phospha derivative) is formed is ascribed to the intermediacy of a diazadiphosphetidine [4] from the initial reaction of the NH_2 and PCl_2 groups.



The phosphorus chemical shift of **2** (Table 1) is found in a range characteristic for azaphospholes of this type [8]. Together with the chemical shift of C-2 in **1** ($\delta^{13}C = 133.2$ [9]) it fits well into the linear $\delta^{13}C/\delta\,^{31}P$ correlation for azoles and the corresponding azaphospholes [10]. It also obeys the more general linear $\delta^{14,15}N/\delta^{31}P$ correlation for analogous dicoordinate nitrogen and phosphorus compounds [11].

The proton chemical shifts of **2** compare well to those of **1** [12] except for 3-H. In **2**, where this proton is adjacent to phosphorus, its resonance is found at much lower field than in **1** ($\delta^1H = 7.60$).

For the ^{13}C-NMR of **2** see Table 2. The introduction of a two-coordinate phosphorus in place of the 2-CH unit of **1** affects the shielding of the carbon atoms primarily in the five-membered ring. C-3 of **1** ($\delta^{13}C = 112.9$ [9]), which is adjacent to phosphorus in **2**, experiences a strong downfield shift, while C-9 ($\delta^{13}C = 145.0$ [9]) experiences a lesser one. The other carbon chemical shifts induced by the CH/P exchange are also positive but hardly significant.

The ^{15}N-NMR spectrum has been measured by use of a natural abundance sample of **2** by applying the INEPT pulse sequence and gave $\delta^{15}N = -127.6$, $^1J_{PN} = 89.1$ Hz for N-1 and $\delta^{15}N = -161.7$, $^2J_{PN} = 2.0$ Hz for N-4 (nitromethane as external reference).

TABLE 1 ^{31}P- and ^1H-NMR Data of 1,3,4-Diazaphospholo[1,2-a]pyridine **2** and Its Derivatives (in $CDCl_3$ except **7** in CD_3OD)

δ J[Hz]	**2**	**3**	**4**	**6**	**7**[a,b]
P	195.0	113.6	100.0	84.6	8.8
3-H(A)	8.87	3.53[c]	4.35[c]	3.99[c]	4.38
^2J(P,H)	29.8[d]	36.9	11.5	8.5	9.3
3-H(B)		3.99[c]	4.13[c]	3.85[c]	
^2J(P,H)		1.0	3.0	6.3	
^2J(H,H)		15.1	15.5	15.5	
5-H	8.14	7.37	7.61	7.42	7.83
^4J(P,H)	1.2		0.6		
^3J(H,6-H)	6.8	6.6	6.7	6.7	6.8
^4J(H,7-H)	1.4	1.8	1.8	1.8	1.7
^5J(H,8-H)	1.0				0.7
6-H	6.73	6.03	6.36	6.09	6.94
^5J(P,H)			1.3	1.2	
^3J(H,7-H)	6.8	6.6	6.7	6.9	7.1
^4J(H,8-H)	1.2	1.2	0.9	0.8	1.2
7-H	7.17	7.09	7.40	7.13	7.85
^5J(P,H)			1.8	1.8	0.7
^3J(H,8-H)	9.2	9.0	9.1	9.1	8.8
8-H	7.52	6.67	6.74	6.59	7.10
OCH_3,NCH_2		3.20	3.75	2.98[e]	
^3J(P,H)		10.5	14.2	14.0	

[a] The positions in **7** are numbered as in **2**.
[b] P–H: $\delta = 7.23$ (dt, ^1J(P,H) = 543.0 Hz, ^3J(H,H) = 1.2 Hz).
[c] The two methylene protons are diastereotopic and represent the AB part of an ABX spin system. The signal listed as A is assigned to the proton cis to the phosphorus lone pair or sulfur atom due to its larger ^2J(P,H) coupling [19, 20].
[d] ^5J(H,6-H) = 1.2 Hz.
[e] CH_3: $\delta = 0.90$ (t, ^3J(H,H) = 7.1 Hz).

TABLE 2 ^{13}C-NMR Data of 1,3,4-Diazaphospholo[1,2-a]pyridine and its Derivatives (in $CDCl_3$ except **7** in CD_3OD)

δ J[Hz]	**2**	**3**	**4**	**6**	**7**
C-3	151.2	55.6	52.4	52.6	55.3[a]
^1J(P,C)	65.5	42.0	76.2	65.2	83.4
^1J(C,H)	181.9	143.2	146.7	146.2	139.8
^3J(C,H)	1.7	2.2	3.3	1.8	3.3
C-5	127.8	136.1	135.9	135.9	141.0
^3J(P,C)	2.3		15.8	14.7	1.4
^1J(C,H)	181.9	180.6	183.2	184.3	190.0
^2J(C,H)		4.8	5.4	5.5	4.3
^3J(C,H)		6.2	8.4	8.8	7.1
C-6	112.7	107.7	108.5	107.9	115.0
^4J(P,C)	1.5		1.1	<1.0	
^1J(C,H)	166.9	168.9	171.1	170.7	174.9
^2J(C,H)	3.4, 1.7	2.8	2.9	2.2	2.8
^3J(C,H)	8.9	8.8	8.1	8.1	8.1
C-7	126.5	139.0	140.3	139.7	143.5
^4J(P,C)			2.9	2.9	1.4
^1J(C,H)	163.3[b]	161.9	163.0	163.0	168.7
^3J(C,H)	7.8	7.7	8.4	7.3	7.6
C-8	119.3	117.6	117.1	116.7	116.2
^3J(P,C)	8.6	6.3	24.9	23.4	
^1J(C,H)	167.2	169.4	164.9	171.5	172.7
^2J(C,H)	2.6		1.1	0.7	0.9
^3J(C,H)	8.4[c]	6.6	6.8	7.0	7.1
C-9	152.1	162.6	161.1	160.2	155.5
^2J(P,C)	14.2[d]	13.6	5.5	5.1	1.9
OCH_3,CH_2		51.5	52.4	39.2[e]	
^2J(P,C)		7.3	6.6	4.4	
^1J(C,H)		143.6	147.7	136.6[f]	

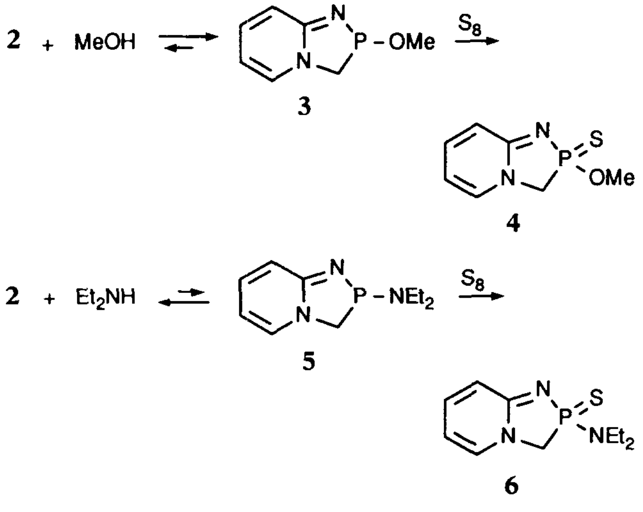
[a] ^2J(C,H) = 25.6 Hz.
[b] ^2J(C,H) = 1.2 Hz.
[c] ^4J(C,H) = 1.5 Hz.
[d] ^2J(C,H) = 4.4 Hz, ^3J(C,H) = 13.2 Hz, 8.5 Hz.
[e] CH_3: $\delta = 14.0$ (qtd, ^1J(C,H) = 126.0 Hz, ^2J(C,H) = 2.7 Hz, ^3J(P,C) = 2.2 Hz).
[f] ^2J(C,H) ≈ ^3J(C,H) ≈ 4.4 Hz.

This means that the nitrogen chemical shifts in **2** also are found at lower field than in **1**: $\delta^{15}N = -140$ (N-1) and -179 (N-4) [13]. This has been found to be true for other pairs of azoles/azaphospholes as well [11, 14].

Compound **2**, like **1**, alkylates at N-1 and undergoes electrophilic substitution reactions at the 3-position [4]. Unlike **1**, it also reacts with alcohols and water, adding them to the PC bond.

2,3-Dihydro-1,3,4-diazaphospholo[1,2-a]pyridines and Their 2-Sulfides

Methanol adds immediately and quantitatively to **2**. The adduct **3** can be isolated and may be converted to the sulfide **4**. No reaction is detected by ^{31}P-NMR with diethylamine at ambient temperature or at 60°C. Nevertheless the adduct **5** must be present in a small equilibrium concentration. With elemental sulfur the mixture quantitatively yields the sulfide **6**. Compound **2** alone under the same conditions does not react with sulfur. Compounds **3**, **4**, and **6** are identified by their NMR spectra (Tables 1, 2), particularly by the *AB*X-signal of the protons in the 3-position with their characteristically different AX- and BX-coupling constants ^2J(P,H). The shielding of 5-, 6-, 7-, and 8-H varies in an almost parallel way and obviously reflects the charge of the pyridine ring. The positive charge of the latter is accordingly highest in **2** and is strongly lowered in **3**. It is increased again by the oxidation to **4** and decreased by the OMe/NEt$_2$ exchange.



3

4

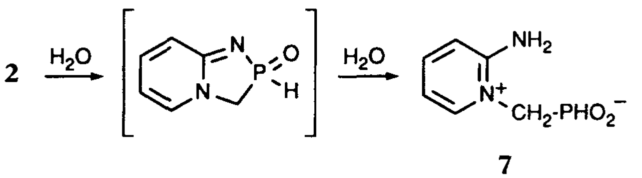
5

6

2-Aminopyridinio-methylphosphonite

If water is added to a solution of **2** the product immediately precipitates. It contains three moles of water per mole of **2**. The use of less water leaves some **2** unreacted. No intermediate can be detected spectroscopically. In the product two water molecules have been added to the PC and PN bond with cleavage of the latter to give **7**. A third water molecule is contained as such in the crystal (see below).

Compound **7** is a zwitterion consisting of a cationic 2-aminopyridinium and an anionic methylphosphonite moiety. Its identity results from the NMR spectra (Tables 1, 2). A low-field chemical shift of all the aromatic hydrogen atoms reflects the pyridinium character.



7

An X-ray analysis of slowly grown single crystals shows them to contain equal numbers of discrete molecules of **7** and of water. Both of them are found in two crystallographically independent positions. The two sets are however almost identical both in molecular dimensions and in intermolecular contacts (Tables 3, 4).

TABLE 3 Distances (Å) with Estimated Standard Deviations in Parentheses for **7**·H$_2$O

	Covalent Bonds		
P1–O1	1.493(2)	P2–O22	1.497(3)
P1–O2	1.500(2)	P2–O21	1.495(3)
P1–C7	1.832(4)	P2–C27	1.823(4)
C7–N1	1.474(4)	C27–N21	1.484(3)
N1–C2	1.371(5)	N21–C22	1.360(5)
C2–N2	1.327(4)	C22–N22	1.338(4)
C2–C3	1.423(4)	C22–C23	1.428(5)
C3–C4	1.351(5)	C23–C24	1.345(6)
C4–C5	1.402(6)	C24–C25	1.400(6)
C5–C6	1.350(6)	C25–C26	1.369(6)
C6–N1	1.371(5)	C26–N21	1.375(5)
	Hydrogen Bonds		
P1H–O1′	3.357(3)	P2H–O22′	3.400(3)
N2H–O1′	2.782(4)	N22H–O22′	2.753(3)
N2H–O2″	2.959(4)	N22H–O21″	3.091(4)
O32H–O31	2.704(4)	O31H–O32	2.722(5)
O32H–O2	2.776(3)	O31H–O21	2.791(3)

TABLE 4 Bond Angles (°) with Estimated Standard Deviations in Parentheses for **7**·H$_2$O.

O1–P1–O2	117.2(2)	O22–P2–O21	117.2(2)
O1–P1–C7	108.3(1)	O22–P2–C27	107.7(1)
O2–P1–C7	107.4(2)	O21–P2–C27	108.1(1)
P1–C7–N1	112.5(2)	P2–C27–N21	112.5(2)
C7–N1–C2	121.5(3)	C27–N21–C22	121.1(2)
N1–C2–N2	121.4(3)	N21–C22–N22	121.0(2)
N1–C2–C3	116.8(3)	N21–C22–C23	117.4(3)
N2–C2–C3	121.8(3)	N22–C22–C23	121.6(3)
C2–C3–C4	121.4(3)	C22–C23–C24	120.7(4)
C3–C4–C5	120.1(3)	C23–C24–C25	121.4(4)
C4–C5–C6	118.5(4)	C24–C25–C26	117.3(4)
C5–C6–N1	122.0(4)	C25–C26–N21	121.9(4)
C6–N1–C2	121.1(3)	C26–N21–C22	121.2(3)
C6–N1–C7	117.4(3)	C26–N21–C27	117.7(3)

Structure of 7·H_2O

In the crystal the molecules of **7** are found in the expected geometry. The NH_2 group is coplanar with the ring, while the NCP plane is roughly perpendicular to it.

The two tetrahedral units make a staggered conformation. Bond lengths (Table 3) and bond angles (Table 4) are normal. All the molecules are joined together by hydrogen bonds forming a three-dimensional polymer. The bonds originate from the five hydrogen atoms of the PH and NH_2 group in **7** and of a water molecule. They are directed toward the oxygen atoms of the PO_2 group in **7** and of a water molecule, each increasing its coordination number to three. The polymer can be viewed to result from three steps of aggregation:

1. *Dimers of* **7**. Two molecules of **7** are joined to each other by two P–H· · ·O bonds and two N–H· · ·O bonds to the same phosphonite oxygen atoms to form a centrosymmetrical dimer (Figures 1 and 2).
2. *Double Chains of* **7**. The formation of the dimers leaves one NH linkage (H2.2, H22.2) and one PO linkage (O2, O21) per molecule of **7** unused. They enter into hydrogen bonding between symmetry-equivalent dimers, joining them to linear double chains. Each of them is made up of one of the two crystallographically independent molecules **7**. Figures 1 and 2 show two building blocks of each double chain.
3. *Three-dimensional Polymers of* **7**·H_2O. One of the two independent water molecules bonds to the remaining site of O2 (Figure 1) the other to that of O21 (Figure 2). In addition the two types of water molecules form hydrogen bonds between each other, which join them alternately to a zig-zag chain (Figure 3). This chain extends roughly perpendicular to the double chains of **7** and connects them to a three-dimensional structure.

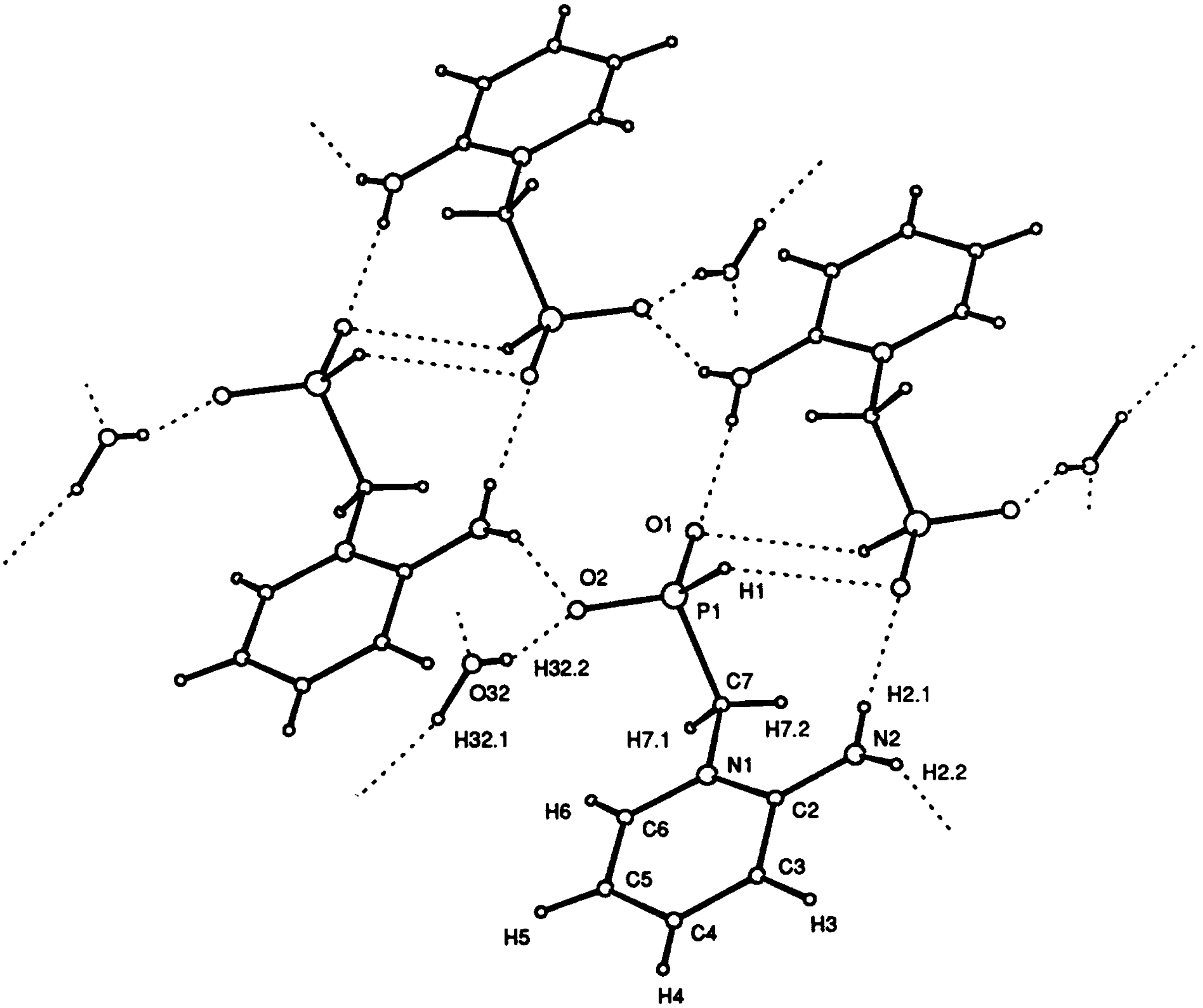


FIGURE 1 Part of the Crystal Structure of 7·H_2O: Two Units of One of the Double-Chains of **7** with One Sort of Linking Water Molecules.

Hydrogen Bonds in **7**·H_2O

The crystal structure of **7**·H_2O is unmistakably determined by the almost perfectly cooperating hydrogen bonds, although the single hydrogen bond may be relatively weak. To avoid uncertainties regarding the hydrogen position, we use for their discussion only the distances of the nonhydrogen atoms involved (Table 3). The most interesting one is the P–H· · ·O bond. The literature provides only conflicting evidence that P–H linkages participate in hydrogen bonds [15]. In the present structure, the distance beween P and O of the two molecules **7** in a dimer again is not shorter than the sum of their van der Waals radii (3.3 Å). Moreover, the assumed hydrogen bond is extremely bent. When the hydrogen atoms are included in such a manner, a chair-shaped six-membered ring results (Figures 1, 2). Analogous dimers from double hydrogen bonding were suggested earlier for dialkyl phosphites [15]; however, straightforward structural evidence seems to be lacking.

The dimer is also (and probably more effectively) held together by the NH· · ·O hydrogen bonds between N2 and O1 (Figure 1) or N22 and O22 (Figure 2) of the two molecules **7**. They are significantly shorter (average 2.77 Å) than the sum of N and O van der Waals radii (2.9 Å) and nearly linear (angle at hydrogen around 170°), and they seem to be primarily responsible for the geometry of the dimer. The N–H· · ·O hydrogen bonds between the dimers are longer (average 3.03 Å).

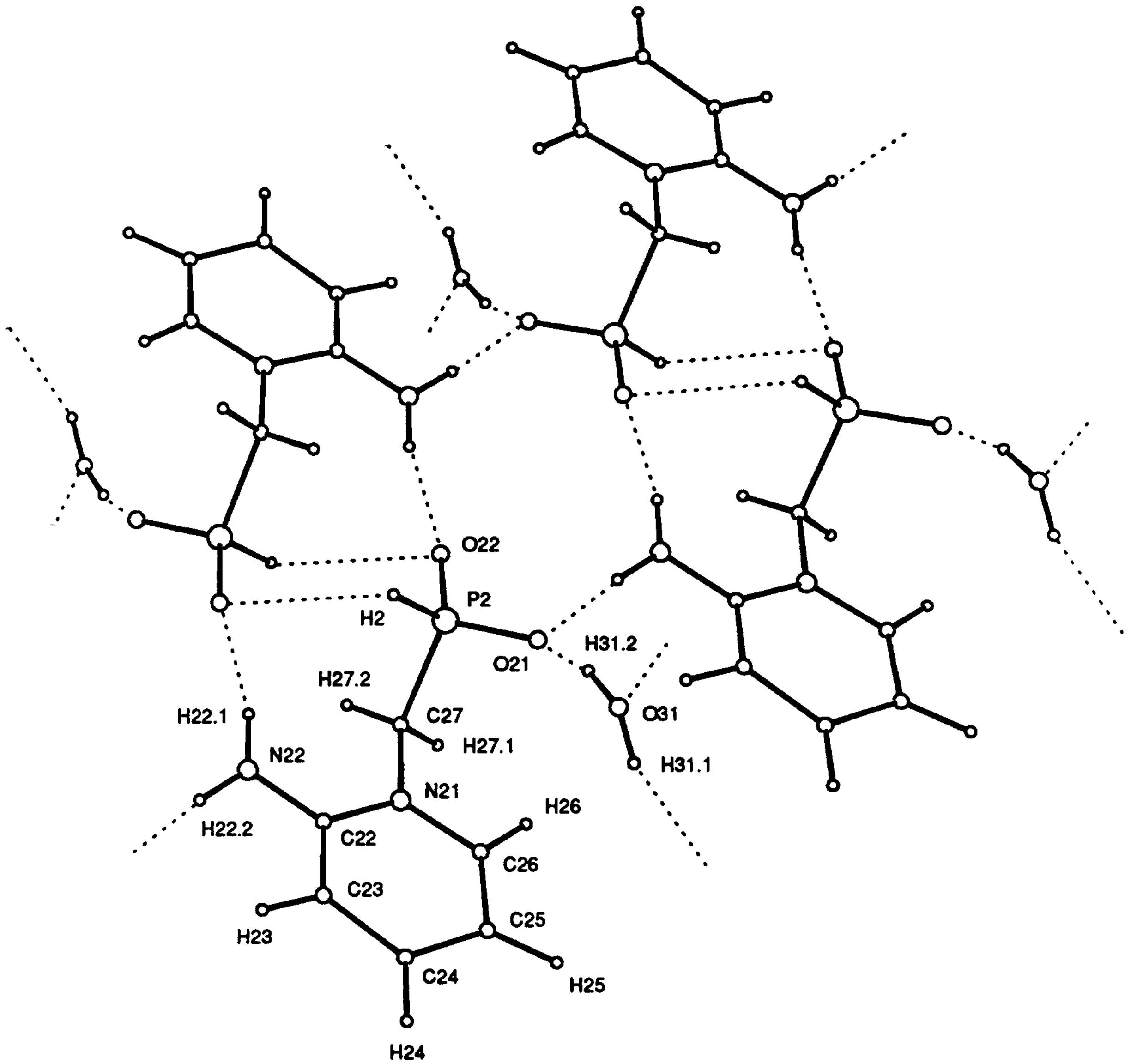


FIGURE 2 Part of the Crystal Structure of **7**·H_2O: Two Units of the Other Double-Chain of **7** with the Other Sort of Linking Water Molecules.

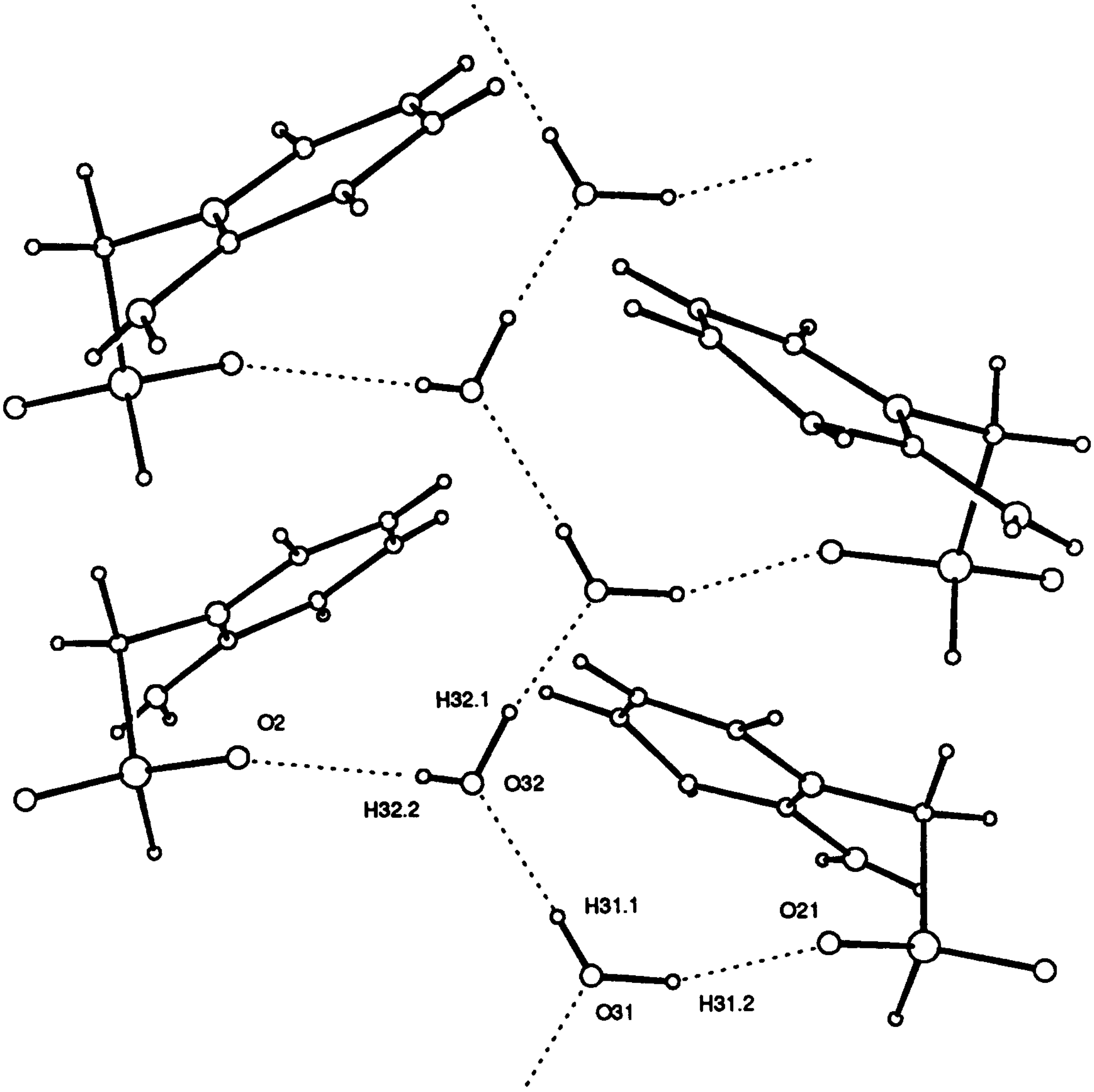


FIGURE 3 Part of the Crystal Structure of 7·H_2O: Chain of the Water Molecules Linking the Two Different Double-Chains of 7.

Four O–H· · ·O hydrogen bonds originate from the two nonequivalent water molecules (Figure 3). The ones between them are somewhat shorter (average 2.71 Å) than those to the PO groups (average 2.78 Å); they are to be compared to a van der Waals radius of 1.4 Å for oxygen.

The coordination of the oxygen atoms including the hydrogen bonds is pyramidal in the case of the oxygen that is part of the dimeric structure (O1, O22; average angular sum 335°) but close to planar in all other cases.

EXPERIMENTAL

1,3,4-Diazaphospholo[1,2-a]pyridine **2**

To a stirred solution of 10.0 g (106.3 mmol) 2-aminopyridine in 250 mL of acetonitrile 16.1 g (106.3 mmol) of (chloromethyl)dichlorophosphine was added dropwise during 10 min at ambient temperature. A white precipitate was formed. While the reaction mixture was stirred and cooled in an ice bath, 32.3 g (318.9 mmol) of triethylamine was added dropwise during 15 min. The mixture was stirred for two more hours at ambient temperature. The precipitated triethylammonium chloride was filtered off, the solvent removed from the filtrate under vacuum, and the yellow solid residue extracted by stirring it with 300 mL of diethyl ether for 12 h. The ether was removed from the filtrate *in vacuo*, leaving 9.7 g (67%) of **2** as a pale yellow microcrystalline powder (mp 44–46°C). Compound **2** exhibits a characteristic naphthalene-like odor. Anal. Calcd. for $C_6H_5N_2P$: C, 52.95; H, 3.70; N, 20.58 (136.09). Found: C, 52.42; H, 4.10; N, 20.42.

TABLE 5 Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **7**·H_2O. ($B_{eq} = \frac{4}{3}(a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + a \times b \times \cos\gamma \times B(1,2) + a \times c \times \cos\beta \times B(1,3) + b \times c \times \cos\alpha \times B(2,3))$ [Å^2]).

Atom	*x*	*y*	*z*	B_{eq}
P1	0.43705(3)	0.1331(1)	0.9112(1)	1.23(2)
O1	0.4886(1)	0.2291(4)	0.9623(3)	1.64(5)
N1	0.3960(1)	−0.1176(4)	0.6966(4)	1.23(5)
O2	0.3886(1)	0.2486(4)	0.8633(3)	1.85(5)
N2	0.4277(1)	−0.3768(4)	0.8356(4)	1.60(6)
C2	0.3907(1)	−0.2952(5)	0.7368(4)	1.14(6)
C3	0.3442(1)	−0.3883(5)	0.6656(5)	1.73(7)
C4	0.3062(1)	−0.3031(5)	0.5674(5)	1.59(7)
C5	0.3118(2)	−0.1188(6)	0.5348(5)	1.73(7)
C6	0.3566(2)	−0.0319(6)	0.5993(4)	1.61(7)
C7	0.4446(1)	−0.0128(5)	0.7530(4)	1.04(6)
H1	0.429(1)	0.010(6)	1.024(5)	1.4(9)
P2	0.06463(4)	0.1291(1)	0.9769(1)	1.36(2)
O21	0.1144(1)	0.2381(4)	0.9825(3)	2.26(6)
N21	0.1046(1)	−0.1227(4)	0.8012(4)	1.16(5)
O22	0.0138(1)	0.2317(4)	0.9744(3)	2.07(5)
N22	0.0701(1)	−0.3753(4)	0.9100(4)	1.65(6)
C22	0.1084(1)	−0.2986(5)	0.8474(4)	1.29(7)
C23	0.1543(2)	−0.3982(5)	0.8240(5)	1.79(8)
C24	0.1922(2)	−0.3188(6)	0.7600(5)	1.75(7)
C25	0.1893(2)	−0.1348(6)	0.7207(5)	1.84(7)
C26	0.1445(2)	−0.0420(6)	0.7403(4)	1.64(7)
C27	0.0564(1)	−0.0131(5)	0.8102(4)	1.27(7)
O31	0.7762(1)	0.6943(5)	0.4219(4)	3.24(7)
O32	0.7205(1)	0.7129(6)	0.6488(4)	3.62(8)
H2	0.072(1)	0.024(5)	1.088(4)	0.4(7)
H3	0.340(2)	−0.523(7)	0.688(6)	3(1)
H4	0.281(2)	−0.355(6)	0.520(5)	1.8(9)
H5	0.286(1)	−0.037(5)	0.470(4)	0.5(7)
H6	0.366(1)	0.078(5)	0.574(4)	0.4(7)
H2.1	0.448(2)	−0.333(6)	0.893(5)	2.0(9)
H2.2	0.421(2)	−0.484(6)	0.871(4)	1.2(8)
H23	0.148(1)	−0.520(6)	0.857(4)	1.1(8)
H24	0.227(2)	−0.397(5)	0.744(5)	1.2(8)
H25	0.220(2)	−0.055(6)	0.682(4)	1.8(9)
H26	0.132(1)	0.087(5)	0.711(4)	0.6(7)
H7.1	0.453(2)	0.068(6)	0.662(5)	1.9(9)
H7.2	0.475(2)	−0.087(6)	0.769(5)	3(1)
H22.1	0.041(2)	−0.305(7)	0.934(6)	3(1)
H22.2	0.080(2)	−0.502(9)	0.927(7)	6(1)
H27.1	0.050(1)	0.063(5)	0.721(4)	−0.2(6)
H27.2	0.021(2)	−0.068(6)	0.807(5)	1.5(8)
H31.1	0.761(2)	0.673(8)	0.490(8)	5(2)
H31.2	0.814(2)	0.713(8)	0.433(6)	5(1)
H32.1	0.738(2)	0.728(7)	0.748(6)	3(1)
H32.2	0.698(2)	0.689(8)	0.646(7)	6(2)

2-Methoxy-2,3-dihydro-1,3,4-diazaphospholo[1,2-a]pyridine 3

To 850 mg (6.2 mmol) of **2** in 5 mL of acetonitrile 200 mg (6.2 mmol) of methanol was added at ambient temperature. After 5 min, the solvent was removed in vacuo from the clear yellow solution, and the yellow oily residue was stirred for 1 day with 10 mL of diethyl ether. Evaporation of the ether solution yielded 705 mg (65%) of **3** as a pale yellow solid that became oily around 30°C. Anal. Calcd. for $C_7H_9N_2PO$: C, 50.01; H, 5.40; N, 16.66 (168.13). Found: C, 50.17; H, 5.51; N, 17.35.

2-Methoxy-2,3-dihydro-1,3,4-diazaphospholo[1,2-a]pyridine 2-sulfide 4

To 63.8 mg (10.47 mmol) of **2** and 23.0 mg (0.72 mmol) of elemental sulfur in 0.3 mL of deuterochloroform contained in an NMR tube (15.0 mg 0.47 mmol) of methanol was added at ambient temperature. The ^{31}P-NMR spectrum of the solution after 30 min showed only the signal of **4**.

2-Diethylamino-2,3-dihydro-1,3,4-diazaphospholo[1,2-a]pyridine 2-sulfide 6

As described above, 67.4 mg (0.50 mmol) of **1** and 20.0 mg (0.62 mmol) of elemental sulfur were reacted with 36.2 mg (0.50 mmol) of diethylamine in 0.3 mL of deuterochloroform. The ^{31}P-NMR spectrum of the solution after 12 h at ambient temperature showed only the signal of **6**.

(2-Aminopyridinio-1)-methylphosphonite 7.

To a stirred solution of 1.0 g (7.3 mmol) of **2** in 10 mL of chloroform 132 mg (7.3 mmol) of H_2O was added. A precipitate immediately formed. The reaction mixture was stirred for 45 min at ambient temperature, the solid material was filtered off and dried *in vacuo*, giving 460 mg (quantitative yield with respect to H_2O) of pale yellow **7**·H_2O, mp 224–226°C, soluble in methanol and water; IR, νPH, 2300 cm^{-1} (m). The ^{31}P-NMR spectrum of the filtrate showed the signal of unreacted **2**. Anal. Calcd. for $C_6H_9N_2O_2P \cdot H_2O$: C, 37.90; H, 5.83; N, 14.73 (190.1). Found: C, 37.35; H, 5.91; N, 14.52

X-Ray Structure Investigation of 7·H_2O

Single crystals were obtained from an acetonitrile/hexane solution containing **2** to which moisture was admitted. The crystals became turbid when separated from the mother liquor and dried; mp 267–268°C. For the study, a clear yellow prismatic crystal of the dimensions 0.3 × 0.2 × 0.1 mm was used.

All the data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated MoKα radiation. The unit cell dimensions were obtained at −155°C from 25 high-angle reflections. Intensities were measured at −155°C between $4 < 2\theta < 60°$, $-35 < h < 35$, $0 < k < 10$, $0 < l < 11$, ω-($\frac{4}{3}\theta$) scan mode with scan width $\omega = 1.35 + 0.35 \times \mathrm{tg}\theta$. Two orientation control reflections and two intensity control reflections were checked every 200 measurements. Correction for Lorentz and polarization factors, but not for absorption or extinction, were performed. 3280 reflections were measured, 2381 with $I \geq 3\sigma$.

Crystal Data: Monoclinic $P2_1/c$, $a = 25.490(7)$, $b = 7.365(4)$, $c = 9.088(3)$ Å, $\beta = 100.06(3)°$, $V = 1679.7(9)$ Å^3 at -155°C, $Z = 8$ (two independent molecules), $D_x = 1.50$ g/cm^3, $\mu_{\mathrm{MoK}\alpha} = 2.9$ cm^{-1}.

The structure was solved by direct methods with MULTAN [16] using 2381 reflections with $I \geq 3\sigma$. All hydrogen atoms were found in the difference electron density maps. Full-matrix least-squares refinements (on F's) on all positional parameters were performed. Nonhydrogen atoms were refined anisotropically, hydrogen atoms isotropically; $\Sigma\omega(|F_o| - |F_c|)^2$ minimized with $\omega = 4|F_o|^2/\mathrm{SQRT}((\sigma(I))^2 + (0.07 \times |F_o|^2)^2)$. Convergence was reached at $R = 0.048$, $R_w = 0.072$, $S = 1.78$, $(\Delta/\sigma)_{\max} = 0.2$, for 305 variables using 2140 reflections with $|F_o|^2 \geq 8\sigma$ in the final refinement. The final difference fourier map reveals a maximum of 0.36 eÅ^{-3}. Atomic scattering functions were taken from ref. [17]. Enraf-Nonius SDP/V18 [18] was used. Refined parameters are given in Table 5; the atomic numbering scheme is given in Figures 1, 2, and 3.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-54965, the names of the authors, and the journal citation.

REFERENCES

[1] A. Schmidpeter, K. Karaghiosoff: Heterophospholes, in M. Regitz, O. J. Scherer (eds): *Multiple Bonds and Low Coordination in Phosphorus Chemistry,* Thieme Verlag, Stuttgart, p. 258 (1990).

[2] G. Märkl: λ^3-Phosphinines, in M. Regitz, O. J. Scherer (eds): *Multiple Bonds and Low Coordination in Phosphorus Chemistry,* Thieme Verlag, Stuttgart, p. 220 (1990).

[3] W. L. Mosby: Heterocyclic Systems with Bridgehead Nitrogen Atoms, Part One, in A. Weissberger (ed): *The Chemistry of Heterocyclic Compounds,* vol. 15, Interscience Publishers, New York, p. 460 (1961).

[4] K. Karaghiosoff, C. Cleve, A. Schmidpeter, *Phosphorus Sulfur, 28,* 1986, 289.

[5] A. Schmidpeter, K. Karaghiosoff: Azaphospholes, in H. W. Roesky (ed): *Rings, Clusters and Polymers of Main Group and Transition Elements,* Elsevier, Amsterdam, p. 308 (1989).

[6] R. K. Bansal, K. Karaghiosoff, Neelima Gupta, A. Schmidpeter, C. Spindler, *Chem. Ber.,* 1991, *124,* 1991, 475.

[7] A. M. Roe, *J. Chem. Soc.,* 1963, 2195; W. W. Paudler, H. L. Blewitt, *J. Org. Chem., 30,* 1965, 4081.

[8] K. Karaghisoff, A. Schmidpeter, *Phosphorus Sulfur, 36,* 1988, 217.

[9] R. J. Pugmire, J. C. Smith, D. M. Grant, B. Stanovnik, M. Tisler, B. Vercek, *J. Heterocycl. Chem., 24,* 1987, 805.

[10] K. Karaghiosoff: ^{31}P NMR Survey, in M. Regitz, O. J. Scherer (eds): *Multiple Bonds and Low Coordination in Phosphorus Chemistry,* Thieme Verlag, Stuttgart, p. 463 (1990).

[11] A. Schmidpeter, B. Wrackmeyer, *Z. Naturforsch. B, 41,* 1986, 553.

[12] H. L. Blewitt: Indolizine and Aza Derivatives with Additional Nitrogens in the 5-Membered Ring, in A. Weissberger, E. C. Taylor (eds): *The Chemistry of Heterocyclic Compounds,* vol. 30, Interscience Publishers, New York, p. 117 (1977).

[13] L. Stefaniak, J. D. Roberts, M. Witanowski, B. T. Hamdi, G. A. Webb, *Org. Magn. Reson., 22,* 1984, 209.

[14] M. Haddad, M. T. Boisdon, L. Lopez, C. Malavaud, G. Pelletier, J. Barrans, G. Pfister-Guillouzo, J. P. Legros, *J. Chem. Res., Synop.,* 1989, 250.

[15] D. E. C. Corbridge: *The Structural Chemistry of Phosphorus,* Elsevier Scientific Publishing Co., Amsterdam, 1974.

[16] P. Main, M. M. Woolfson, G. Germain: *MULTAN, A Computer Program for the Automatic Solution of Crystal Structures,* Univ. of York, England and Louvain, Belgium, 1975.

[17] D. T. Cromer, J. T. Waber: *International Tables for X-Ray Crystallography,* vol. 4, Tables 2.2A, The Kynoch Press, Birmingham, U.K., pp. 72–98, (1974).

[18] B. A. Frenz, in H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, G. C. Bassi (eds): *Computing in Crystallography,* Delft University Press, Delft, p. 64 (1978).

[19] W. Rösch, M. Regitz, *Phosphorus Sulfur, 21,* 1984, 97.

[20] W. G. Bentrude, W. N. Setzer: Stereospecifity in ^{31}P-Element Couplings: Proton–Phosphorus Couplings, in J. G. Verkade, L. D. Quin (eds): *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis,* VCH Publishers, Deerfield Beach, p. 380 (1987).