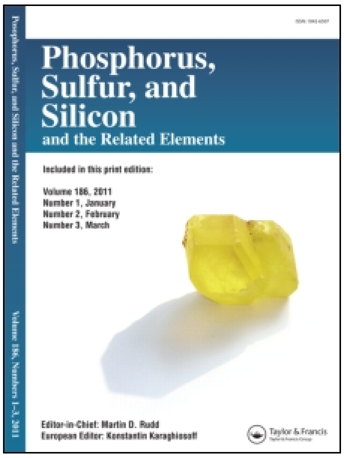

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Wolfgang Schnick; Stefan Horstmann; Marco Häser

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THE NOVEL TETRAAMINOPHOSPHONIUM ION - STRUCTURE, CHEMICAL BONDING AND REACTIONS

WOLFGANG SCHNICK and STEFAN HORSTMANN,
Laboratorium für Anorganische Chemie der Universität, D-95440 Bayreuth, Germany

MARCO HÄSER,
Theoretische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

Abstract: The first representatives of tetraaminophosphonium salts $[P(NH_2)_4]Cl$ and $[P(NH_2)_4]I$ were synthesized and structurally characterized by X-ray crystal structure determination and ab initio calculations on SCF and B3LYP level. According to the theoretical results a stable D_{2d} conformation and a significant distortion of the PN_4 tetrahedra were observed in the solid. The short P-NH_2 distances (~ 161 pm) are in agreement with the calculations. Tetraaminophosphonium salts emerged as versatile educts for condensation reactions forming P-N sceletons and frameworks.

Key Words: tetraaminophosphonium salts, crystal structure, ab initio calculations, phosphorus nitrogen compounds

INTRODUCTION

The characteristic building units of solid phosphorus(V) nitrides are PN_4 tetrahedra [1]. For the synthesis of defined P-N solids from solution soluble educts would be desirable, which contain "isolated" PN_4 building blocks. Because of their unusual high formal charge PN_4^{7-} ions, as in Li_7PN_4, are not appropriate for this purpose and no experimental evidence has been found that these anions would exist in solution. The salt Li_7PN_4 is derived from the hypothetical acid H_7PN_4, which is suspected to be an unstable monophosphazene intermediate during ammonolysis of PCl_5 [2]. However, due to its high basicity and tendency to undergo condensation reactions it has not yet proven possible to isolate imidophosphoric acid triamide, H_7PN_4.

SYNTHESES

By using excess liquid ammonia for the ammonolysis the condensation can be suppressed and, according to Equation (1), only the product of substitution, the tetraaminophosphonium chloride is obtained [3].

$$PCl_5 + 8\,NH_3 \longrightarrow [P(NH_2)_4]Cl + 4\,NH_4Cl \qquad (1)$$

The pure product is obtained by reacting the byproduct ammonium chloride with diethylamine and removing the formed diethylamine hydrochloride (Eq. (2)).

$$NH_4Cl + (C_2H_5)_2NH \longrightarrow NH_3 + (C_2H_5)_2NH_2Cl \qquad (2)$$

An alternative preparation starts from phosphorothionic triamide $SP(NH_2)_3$ and thus avoids any risk of condensation [4, 5]. A two step sequence (Eq.(3)) leads from the molecule $SP(NH_2)_3$ to an ionic solid $[P(NH_2)_4]I$.

$$SP(NH_2)_3 \xrightarrow{CH_3I} [CH_3SP(NH_2)_3]I \xrightarrow[-CH_3SH]{+3\,NH_3} [P(NH_2)_4]I \qquad (3)$$

STRUCTURE AND BONDING

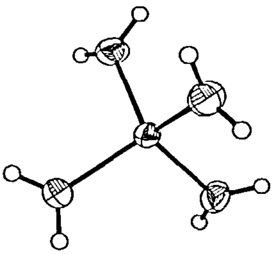


FIGURE 1 $[P(NH_2)_4]^+$ ion

According to the X-ray structure determination both salts contain the tetraaminophosphonium ion (Fig. 1). In $[P(NH_2)_4]I$ (P4/nbm, a = 842.6(2) pm, c = 486.7(2) pm, Z = 2, R = 2.23 %, wR = 1.34 %) the cations and anions resemble a CsCl analogous structure, while in $[P(NH_2)_4]Cl$ (Pbcn, a = 470.8(2) pm, b = 1622.3(3) pm, c = 756.3(2) pm, Z = 4, R = 2.94 %, wR = 1.64 %) a TlI analogous structure is found. In the tetraaminophosphonium cation (Table I) phosphorus and nitrogen form a markedly distorted tetrahedron with an unusual short P-N distance. Both, the distortion of the P-N tetrahedron as well as the short $P\text{-}NH_2$ distance have electronic reasons and can be explained using ab initio calculations on SCF or B3LYP level [6].

TABLE I Calculated and measured length and angles in $[P(NH_2)_4]^+$

Method	d (P-N)	HNH	NPN (2x)	NPN (4x)
SCF/SV	166.5 pm	115.3°	121.4°	103.9°
SCF/SVP	162.7 pm	114.2°	122.6°	103.3°
B3LYP/SV	168.5 pm	115.9°	124.4°	102.6°
B3LYP/SVP	164.6 pm	114.1°	124.6°	102.5°
$[P(NH_2)_4]I$	160.7(2) pm	114(4)°	124.3(1)°	102.7(1)°
$[P(NH_2)_4]Cl$	161.8(1) pm (2x) 160.6(1) pm (2x)	116(2)°-118(2)°	123.8(1)°	102.2(1)° (1x) 102.8(1)° (1x) 103.1(1)° (2x)

The D_{2d} conformation found in the crystal structures, is according to these calculations the most stable conformation of $[P(NH_2)_4]^+$. The enlargment of two NPN angles may be explained by a generalized anomeric effect, nitrogen lone pairs donate into antiperiplanar σ^* orbitals on phosphorus. The short P-N distances result from a significant charge transfer from phosphorus to nitrogen, corresponding to an electrostatic contraction of the P-N bonds, together with nearly planar amino groups and $d\pi p\pi$ -interactions [6].

REACTIONS

Depending on the reaction conditions, the tetraaminophosphonium cation may be used as a versatile educt for condensation reactions. By the influence of bases, the tetraaminophosphonium salts condense to triaminophosphazo-triaminophosphonium salts (Eq. (4)).

$$2\,[P(NH_2)_4]Cl \xrightarrow[\text{RT, 8 bar}]{NH_{3,\,liq.}} [(NH_2)_3PNP(NH_2)_3]Cl + NH_4Cl \qquad (4)$$

The crystal structure of this compound ($P\bar{1}$, a = 584.7(1) pm, b = 732.1(1) pm, c = 1092.0(2) pm, α = 71.05(3)°, β = 76.36(3)°, γ = 89.83(3)°, Z = 2, R = 4.75 %, wR = 2.47 %) shows a cation built up by two corner sharing PN_4 tetrahedra (Figure 2).

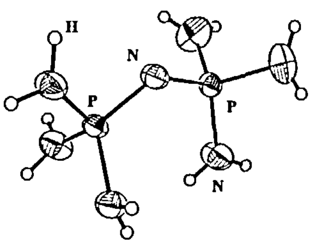
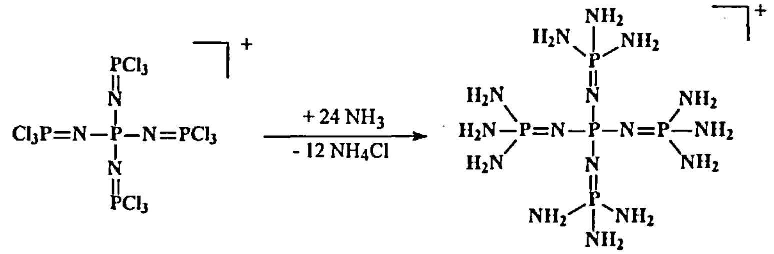


FIGURE 2 $[(NH_2)_3PNP(NH_2)_3]^+$ ion

Thermal condensation of tetraaminophosphonium salts leads dependend on the reaction conditions to linaer aminophosphazene polymers, HPN_2 or P_3N_5. The syntheses of P-N sodalites is possible by using this thermal condensation under influence of metal halides, e.g. $CoCl_2$ (Eq.(5)).

$$12\,[P(NH_2)_4]Cl + 7\,CoCl_2 \xrightarrow{800°C} Co_7[P_{12}N_{24}]Cl_2 + 24\,NH_4Cl \qquad (5)$$

By reaction of tetraaminophosphonium salts with phosphorus pentachloride $[P(NPCl_3)_4]^+$ is obtained, a product, which makes doubly branched phosphazenes accessible [7]. A dendrimeric structure is built up by ammonolysis of this product (Eq. (6)).



(6)

An extended dendrimer may be synthesized by repeated reaction with PCl_5 and subsequent ammonolysis. These results show, that $[P(NH_2)_4]^+$ is a useful educt to form P-N structures in solid state reactions or in solution.

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