

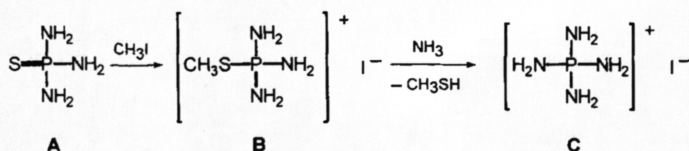
## Synthesis and Crystal Structure of the First Tetraaminophosphonium Salt $P(NH_2)_4I^{**}$

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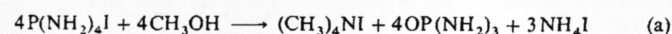
Dedicated to Professor Otto J. Scherer on the occasion of his 60th birthday

The characteristic building blocks in phosphorus(v) nitrides are  $PN_4$  tetrahedra. Linkage of these structural elements through common corners allows access to a large number of condensation degrees. This is reminiscent of the varied structural chemistry of the silicates and phosphates.<sup>[1]</sup> One of the extremes in the series of differently condensed phosphorus nitrides is the ionic compound  $Li_7PN_4$ , which comprises "isolated"  $PN_4^{7-}$  ions.<sup>[2]</sup> Due to its extremely high formal charge, no indications for the existence of this anion in solution have yet been found; therefore,  $Li_7PN_4$  is accessible only by solid-state reaction of the corresponding binary nitrides. Thus, the certainly high synthetic potential of isolated  $PN_4$  groups in solution for the formation of well-defined P–N solid compounds has remained unexplored.

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  $PCl_5$ .<sup>[3]</sup> However, due to its high basicity and tendency to undergo condensation reactions it has not yet proven possible to isolate imidophosphoric acid triamide,  $H_7PN_4$ . With  $P(NH_2)_4I$  (C) we report the first successful synthesis and structural proof of a tetraaminophosphonium salt, which can be regarded as a hydroiodide of  $H_7PN_4$ . The synthesis followed the modification of a procedure<sup>[4]</sup> that starts from phosphorothionic triamide (A).<sup>[5]</sup> Methylation of the sulphur atom in A with methyl iodide and careful subsequent ammonolysis of B readily yields the desired product C. As the last



reaction step is a heterogeneous solid–liquid reaction, C is obtained as a sparingly-soluble, fine-crystalline powder. The crystal growth of tetraaminophosphonium iodide was severely hampered by the fact that C is insoluble in most solvents and that, due to its reactivity, it easily undergoes hydrolysis and condensation reactions. In the past methanol had been suggested as a solvent for C. However, according to our investigations prolonged exposure of C to methanol leads to the formation of tetramethylammonium iodide [Eq. (a)]. Sufficiently large single crystals of C were obtained by crystallization from dry acetonitrile employing a temperature gradient between 70 °C and room temperature. Obviously, tetraaminophosphonium iodide is sufficiently soluble at the higher temperature.



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Unprecedented in chemistry, the acid–base pair  $H_7PN_4^+/PN_4^{7-}$  enables structural comparison over a range of eight successive dissociation steps: According to the results of the X-ray structure analysis,<sup>[6]</sup>  $P(NH_2)_4^+$  and  $I^-$  ions form a CsCl-analogous arrangement in the solid. The P–N bond length (160.7(2) pm) (Fig. 1) represents the shortest P–NH<sub>2</sub> bond distance reported to date. The valence sum for the phosphorus center (5.56), calculat-

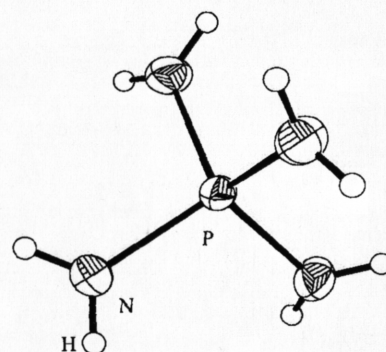


Fig. 1. Structure of the tetraaminophosphonium cation in  $P(NH_2)_4I$ . Distances [pm] and angles [°]: P–N 160.7(2), N–H 74.9(26), N–P–N 124.2(2) and 102.7(1), H–N–H 114(3), P–N–H 120(2).

ed from the four P–N bonds according to O'Keeffe et al.,<sup>[7]</sup> is indicative of significant polar bonding or multiple bonds between the phosphorus and nitrogen atoms. The electrostatic repulsion between the nitrogen atoms in  $PN_4^{7-}$  (P–N: 171 pm<sup>[2]</sup>) is obviously compensated by the interaction between the nitrogen atoms and the terminal protons of the tetraaminophosphonium ion. This results in a marked shortening of the P–N bonds by approximately 10 pm. In accord with these short P–N bond lengths the H–N–H and H–N–P bond angles (114(3)° and 120(2)°, respectively) in the tetraaminophosphonium ion indicate a significant P–N double-bond character. Even though there are no N–H···N hydrogen bonds present between the cations, the  $NH_2$  groups are fixed with regard to rotation around the P–N bonds. Accordingly, it was possible to locate the positions of the hydrogen atoms unambiguously<sup>[8]</sup> during X-ray structure analysis by difference-Fourier synthesis.

### Experimental Procedure

$SP(NH_2)_3$  (4.53 g, 0.04 mol) was treated with  $CH_3I$  (8.17 g, 0.06 mol) in dry acetonitrile (25 mL) for 6 days at room temperature. The resulting solid B (yield: 76%) was separated and washed with diethyl ether. <sup>31</sup>P NMR (36.9 MHz,  $CDCl_3$ , 25 °C):  $\delta = 48.1$  (s). B (4.82 g, 0.02 mol) was suspended in 100 mL of dichloromethane and treated at room temperature (duration: 3 h) with a vigorous stream of  $NH_3$  (KOH drying column). The resulting solid C was separated off and washed with diethyl ether (yield: 96%). For purification and crystal growth, 1.0 g of C in 25 mL acetonitrile was transferred to a Schlenk tube, and a temperature gradient (bottom: 70 °C, top: 25 °C) was applied to the supernatant. Coarse-crystalline, colorless C deposited at the cooler end. According to X-ray powder diffraction studies and <sup>31</sup>P NMR MAS measurements the product was obtained as a single phase. IR(KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] = 3378 (NH), 3280 (NH), 3097 (NH), 1078 (PN), 946 (PN).  $T = 180$  °C ( $10^{-3}$  mbar, decomposition). All reactions were carried out in dry solvents under an inert argon atmosphere.

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- [6] X-ray structure analysis of **C**:  $\text{H}_8\text{PN}_2\text{I}$ .  $M = 221.9 \text{ g mol}^{-1}$ , space group  $P4/nbm$ ,  $Z = 2$ ,  $a = 842.6(2)$ ,  $c = 486.7(2) \text{ pm}$ ,  $V = 345.5 \times 10^6 \text{ pm}^3$ ,  $\rho_{\text{calcd}} = 2.133 \text{ g cm}^{-3}$ ,  $F(000) = 208$ ,  $\lambda = 71.073 \text{ pm}$ ,  $T = 173 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 4.76 \text{ mm}^{-1}$ , Siemens P4 diffractometer, crystal dimensions (mm):  $0.24 \times 0.20 \times 0.20$ ,  $2\theta$ - $\theta$  scan,  $4.0^\circ \leq 2\theta \leq 60.0^\circ$ , 1260 observed reflections, 282 symmetry-independent reflections ( $R_{\text{int}} = 0.007$ ), structure solution with direct methods, H-atoms by difference-Fourier synthesis, structure refinement with full matrix by the least-squares method (16 parameters), all atoms anisotropic, H-atoms isotropic,  $R = 0.022$ ,  $wR = 0.013$ . Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-400461 and the journal citation.
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- [8] The X-ray structure analysis gave a N-H bond length of  $74.9(26) \text{ pm}$ .