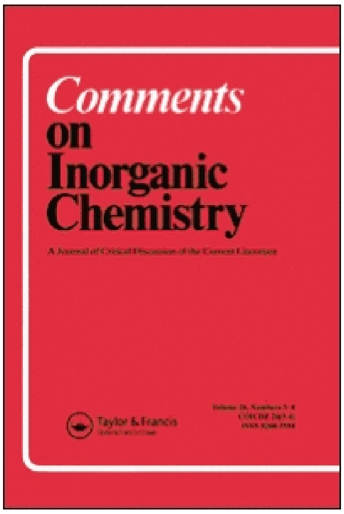

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

From Molecules to Solids: Novel Nitrido Compounds

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To cite this Article Schnick, Wolfgang(1995) 'From Molecules to Solids: Novel Nitrido Compounds', Comments on Inorganic Chemistry, 17: 4, 189 — 211

To link to this Article: DOI: 10.1080/02603599508033857
URL: http://dx.doi.org/10.1080/02603599508033857

From Molecules to Solids: Novel Nitrido Compounds

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Received November 24, 1994

The combination of the elements phosphorus and nitrogen in molecular compounds results in the versatile chemistry of the phosphazenes. Pure inorganic solid state P–N-compounds are accessible, starting from simple molecular phosphazenes. According to the isosteric behaviour of Si/O and P/N these phosphorus nitrides show distinct structural analogies to the silicate class of compounds. Potential applications of the new compounds as ceramic materials, ionic conductors, sintering additives, or pigments seem to be possible. Synthetic strategies like precursor routes or molecular preorganization are promising approaches, starting from molecules and leading to solid state P–N-compounds.

Key Words: *phosphazenes, phosphorus nitrides, nitrido zeolites, precursor compounds, molecular preorganization*

1. INTRODUCTION

One of the great challenges of modern chemistry is the design and the synthesis of novel compounds exhibiting useful and profitable properties. In inorganic chemistry during the last few decades several

Comments Inorg. Chem.
1995, Vol. 17, No. 4, pp. 189–211
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solid state compounds have appeared to be specifically useful, like superconductors, superionic conductors, zeolites, pigments, or advanced ceramic materials. The characteristic properties of these different compounds are due to the respective complex and collective interactions of the atoms in the solid state.

In molecular chemistry—especially in the organic field—modern synthetic strategies and retrosyntheses directly make possible the design of new compounds exhibiting the demanded specific properties. However, up to now such a planned synthetic approach has seemed to be rather difficult in inorganic solid state chemistry. Here complex mutual interrelations between structure determinating factors are to be considered. Together these factors control the formation of a stable solid. For these reasons the search for novel and interesting compounds in the area of inorganic solid state chemistry turns out to be an exciting voyage of discovery, which also has been called "exploratory" solid state chemistry.[1] In contrast to molecular chemistry, kinetic control of the reaction path often seems to be difficult in solid state chemistry where, due to high reaction temperatures, thermodynamics usually rules what is happening.[2]

In this article a class of compounds based on a specific combination of elements will be presented, which allows the synthesis of both molecules and extended solids. In this system the molecules always represent the starting point, and a main task is the development of synthetic strategies leading from molecules to solids. As will be outlined at the end of this article, molecular pre-organization seems to be a feasible strategy.

At the beginning of our work we had to decide in which class of compounds the experiments would have to be performed. In practice we had to select particular chemical elements. Aiming at the development of new inorganic materials, we focused our work on the synthesis of new nitrides—compounds containing nitrogen as electronegative element. Only a few hundred nitrides have so far been characterized, although, for example, the neighbouring element oxygen has been shown to form more than 10,000 oxides. This lack of knowledge might be caused by the fact that nearly without exception the chemical bonding of elements to oxygen is more stable than the respective chemical bonding to nitrogen. Accordingly, in several cases the standard heats of formation of simple oxides are significantly larger than the values of the respective nitrides.[3] However, due to their differing compositions (e.g., SiO_2 and Si_3N_4) a quantitative comparison seems to be rather difficult.

In selecting the electropositive elements to be bonded to nitrogen, the follow aspects seemed to be important: with respect to the demanded properties of the materials, the constituting elements should exhibit a relatively low specific weight. Furthermore, rather stable covalent chemical bonding should occur in combination with nitrogen. At the same time polymeric cross-linked structures should be possible in the solid. And last but not least, the respective chemical elements should exhibit a sufficient availability. Particularly, the following light main-group elements are meeting the requirements: boron, aluminum, carbon, silicon, and phosphorus. The binary nitrides of boron, aluminum, and silicon are well known for several applications. Silicon nitride Si_3N_4 has become an important non-oxidic material. Applications of Si_3N_4 range from ceramic turbochargers to integrated semiconductor modules.[4] Because of its unusually high thermal conductivity (285 $Wm^{-1}K^{-1}$), aluminum nitride is predestined for use as a substrate material in semiconductor manufacture.[5] Boron nitride is used as a high-temperature crucible material, as a lubricant (hexagonal (*h*)-BN), and in the abrasive sector (cubic (*c*)-BN). In recent years *h*-BN has also become increasingly important in the manufacture of composite materials.

We began our efforts to develop new inorganic solid materials with the synthesis and structure determination of the phosphorus nitrides. New solid materials based on the combination phosphorus/nitrogen seem to be particularly attractive because numerous molecular compounds with this combination have been synthesized and investigated in the past.[6] The knowledge available concerning these molecular compounds has been very useful in designing tailored syntheses from molecules to solids. Molecular, oligomeric, and polymeric phosphazenes are a well investigated class of compounds. Their characteristic structural element is a framework of alternating phosphorus and nitrogen atoms. Starting with the observation of Stokes[7] that $(PNCl_2)_3$ polymerizes to a long chain poly-phosphazene in the temperature range 230–300°C (chain lengths between 3 and 15,000), the substance class of polyphosphazenes has been studied thoroughly during the last one hundred years.[8] Choosing suitable substituents at the phosphorus atoms as well as controlling the cross-link between the polyphosphazene chains, the synthesis of new materials with specific properties has become possible. Perhaps the most important feature of polyphosphazene chemistry is the method of synthesis that allows the side groups to be varied over a very broad range. Due to different side groups, different properties arise such that the characteristics may vary from those of elastomers to glasses, from water-soluble to hydrophobic polymers, from bioinert to bioactive materials, and from electrical insulators to conductors.[8] Typical applications of these materials are solvent resistant elastomers, foam rubber materials for heat- and sound insulation, or non-burning textile fibres.[8]

2. PHOSPHORUS NITRIDE P_3N_5

Starting from molecular polyphosphazenes we worked out our plan to extend the one-dimensional chain of alternating phosphorus and nitrogen atoms to purely inorganic and three-dimensional cross-linked framework structures. Following this plan we focused our interests in the binary compound P_3N_5. For reasons of analogy this nitride should show structural and property analogies to other non-metal nitrides which, like BN or Si_3N_4, exhibit a polymeric and highly cross-linked structure in the solid.[3] At the beginning of our work, no reliable information concerning the synthesis and structure of P_3N_5 was available in the literature. However, elaborating an experimental procedure leading to pure, defined, and crystalline phosphorus nitride, the foundation has been laid for a systematic investigation of ternary and higher phosphorus nitrogen solid compounds. The synthesis of P_3N_5 is possible[3] by substitution of the chlorine atoms in $(PNCl_2)_3$ by NH_2-groups, followed by condensation of the resulting intermediates. At the very end of these condensation reactions, which proceed via oligo- and polyphosphazenes, the desired product P_3N_5 is formed. For the practical realization several synthetic procedures, including the heterogeneous ammonolysis of $(PNCl_2)_3$ with gaseous ammonia as well as a homogeneous chemical vapour deposition of these educts, have been tested.[3] Pure, defined, crystalline, colourless, and hydrogen-free phosphorus(V) nitride P_3N_5 finally became available by the reaction of PCl_5 with ammonium chloride in closed quartz ampoules by evolution of HCl (Eq. (1)):

$$3\ PCl_5 + 5\ NH_4Cl \xrightarrow{780\,^\circ C,\ 2d} P_3N_5 + 20\ HCl. \qquad (1)$$

The main difficulties in the synthesis of pure and crystalline P_3N_5 lie in the fact that this nitride has a significant lower thermal stability than BN or Si_3N_4. The thermal decomposition of P_3N_5 starts around 850°C by evolution of nitrogen (Eq. (2)):

$$2\ P_3N_5 \rightarrow 6\ PN + 2\ N_2 \rightarrow 3\ P_2 + 5\ N_2. \qquad (2)$$

During this reaction, brown coloured undefined and amorphous phosphorus(III) nitride is formed. Unlike the synthesis of boron or silicon nitride, an increase of the reaction temperature is not suitable for the elimination of contaminations (e.g., H, Cl, or S). The synthesis of crystalline and pure P_3N_5 starting from molecular phosphorus components therefore results in a tightrope walk between thermal decomposition and sufficient activation of the P–N-bonds (bond cleavage and reformation) while building an ordered and crystalline solid.[3] As thermal activation is not sufficient for this purpose, the required P–N-bond cleavage and reformation necessitates chemical support at the reaction path from the molecule to an ordered and crystalline solid. Accordingly, HCl, which in a pure state at higher temperatures leads to a chemical decomposition of P_3N_5 forming volatile molecular compounds, induces the reversible and reconstructive formation of crystalline P_3N_5. Despite manifold variation of the reaction parameters, the preparation of sufficiently large single crystals of P_3N_5 for a conventional X-ray crystal structure analysis has not been possible in the past. Structural characterization of this compound has therefore been performed by using several complementary investigation techniques. According to IR, EXAFS, ED, HRTEM, and ^{15}N and ^{31}P solid state MAS NMR spectroscopic studies, phosphorus(V) nitride P_3N_5 has a three-dimensional network consisting of corner-sharing PN_4-tetrahedra (d(P–N) = 160 pm). The solid, formulated as $^3_\infty[P_3^{[4]}N_2^{[3]}N_3^{[2]}]$, contains two types of nitrogen atoms, in a molar ratio of 2:3, which are linked to 3 and 2 atoms, respectively.[3] The PN_4-tetrahedra form dreier-rings. Via common P–N-bonds these P_3N_3-rings are condensed to one-dimensional infinite double-chains. Additionally, these double-chains via dreier-rings are condensed, resulting in a three-dimensional framework structure.[9]

3. ALKALINE AND ALKALINE-EARTH METAL PHOSPHORUS(V) NITRIDES

Realizing a preparative access to pure and crystalline P_3N_5 as well as performing the crystal structure determination results in a state of knowledge which is comparable to the fictitious situation that up to now only silicon dioxide SiO_2 was well known but no information would be available about the silicate group of compounds. This technical and scientifically important substance class contains such well known compounds as feldspars, zeolites, layer silicates, and pyroxenes.[10]

Accordingly, ternary phosphorus(V) nitrides which are derived from metals should be accessible from the corresponding binary nitrides. The analogy with oxo chemistry suggests that a reaction between an “acidic” non-metal nitride (P_3N_5) and a “basic” metal nitride should be successful. For various reasons the quasibinary Li_3N/P_3N_5 system appeared to be particularly suitable for the systematic study of the ternary phosphorus(V) nitrides: among the alkali metals only lithium forms a binary nitride with a composition M_3N (M = Li, Na, K, Rb, Cs). Lithium nitride is readily available from its constituent elements;[11] in addition its thermodynamic stability is sufficient to permit reactions with phosphorus(V) nitride to be carried out in the temperature range 600–850°C.

The quasibinary Li_3N/P_3N_5 system has so far afforded four lithium phosphorus(V) nitrides which have been prepared in a pure form and characterized both structurally and with respect to their properties: Li_7PN_4, $Li_{12}P_3N_9$, $Li_{10}P_4N_{10}$, and $LiPN_2$ can in each case be prepared (Eqs. (3)–(6)) in solid state reactions between stoichiometric amounts of the binary nitrides Li_3N and P_3N_5:[12–15]

$$7\ Li_3N + P_3N_5 \xrightarrow[\text{W-crucible, } N_2]{620\ ^\circ C,\ 4d} 3\ Li_7PN_4, \tag{3}$$

$$4\ Li_3N + P_3N_5 \xrightarrow[\text{W-crucible, } N_2]{750\ ^\circ C,\ 5d} Li_{12}P_3N_9, \tag{4}$$

$$10\ Li_3N + 4\ P_3N_5 \xrightarrow[\text{W-crucible, } N_2]{720\ ^\circ C,\ 5d} 3\ Li_{10}P_5N_{10}, \tag{5}$$

$$Li_3N + P_3N_5 \xrightarrow[\text{W-crucible, } N_2]{800\,^\circ\text{C, 4d}} 3\ LiPN_2. \tag{6}$$

Besides reactions between the binary nitrides, it is also possible to react the lithium phosphorus(V) nitrides themselves with Li_3N or P_3N_5 to obtain the corresponding ternary phases (Eqs. (7)–(10)):

$$2\ Li_3N + LiPN_2 \xrightarrow[\text{W-crucible, } N_2]{620\,^\circ\text{C, 14d}} Li_7PN_4, \tag{7}$$

$$2\ Li_3N + 4\ LiPN_2 \xrightarrow[\text{W-crucible, } N_2]{700\,^\circ\text{C, 5d}} Li_{10}P_4N_{10}, \tag{8}$$

$$6\ P_3N_5 + 10\ Li_7PN_4 \xrightarrow[\text{W-crucible, } N_2]{630\,^\circ\text{C, 10d}} 7\ Li_{10}P_4N_{10}, \tag{9}$$

$$3\ Li_3N + 3\ LiPN_2 \xrightarrow[\text{W-crucible, } N_2]{770\,^\circ\text{C, 4d}} Li_{12}P_3N_9. \tag{10}$$

The lithium phosphorus(V) nitrides are obtained from these syntheses as colourless powders or transparent single crystals. The sensitivity of the compounds towards hydrolysis increases with increasing lithium content, while their thermal stability decreases. All the lithium phosphorus(V) nitrides referred to have an ionic structure consisting of Li^+-ions and complex P–N-anions.[3] The common structural features are the PN_4 tetrahedra, which can be linked in different ways through common vertices: Li_7PN_4 contains "isolated" $[PN_4]^{7-}$ ions, which are isoelectronic with orthosilicate $[SiO_4]^{4-}$ and orthophosphate $[PO_4]^{3-}$ building blocks. The crystal structure (Fig. 1) of Li_7PN_4 can be considered as an anti-fluorite type.[12] Thus, the nitrogen atoms adopt a distorted cubic close packing, in which Li^+-ions and phosphorus atoms occupy all the tetrahedral holes in an ordered manner.

At the quasibinary Li_3N/P_3N_5 intersection, $LiPN_2$ is found as the compound with the lowest lithium content.[15] PN_4 tetrahedra are again the characteristic building blocks of the P–N substructure (Fig. 2). However, because of the molar ratio P:N = 1:2 they are not isolated but form a three-dimensional infinitely linked network ${}^3_\infty[PN_{4/2}]$, which is topologically equivalent to and isolelectronic with β-cristo-

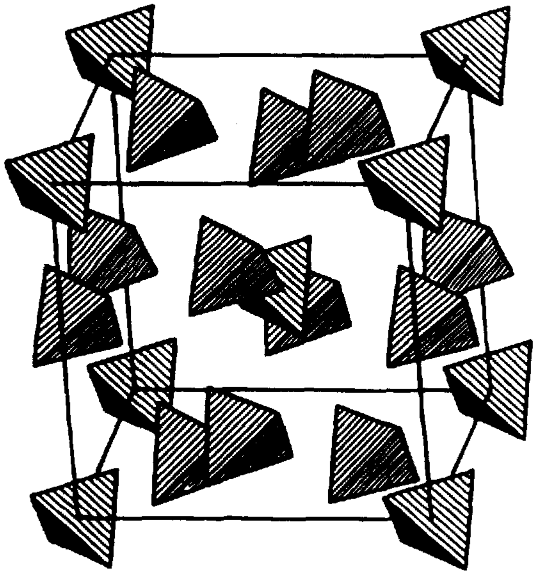


FIGURE 1 Packing of the PN_4 tetrahedra in Li_7PN_4.

balite (SiO_2). As compared with the idealized β-cristobalite structure, $LiPN_2$ is clearly distorted; all the PN_4 tetrahedra are rotated by an angle $\pi = 34.2°$ about their axes of inversion. This results in a structure which is equivalent to the chalcopyrite type, which is a superstructural variant of sphalerite. Thus, the crystal structure of $LiPN_2$ can also be explained on the basis of the concept of sphere packing: Li^+ ions and phosphorus atoms systematically occupy half of the tetrahedral holes in a distorted cubic closest packing of nitrogen atoms in an ordered manner. The Li^+ ions and phosphorus atoms in $LiPN_2$ and Li_7PN_4 appear not to be influenced by the significantly different bonding situations of P and N on the one hand and of Li and N (mainly covalent and ionic, respectively) on the other. Thus, it is surprising to find such extreme structural similarities.[3]

Two further ternary compounds within the Li_3N/P_3N_5 system, Li_4PN_3 and $Li_5P_2N_5$, have both been prepared in a pure state and structurally characterized.[13,14] In comparison with Li_7PN_4 and $LiPN_2$, both of these lithium phosphorus(V) nitrides have an intermediate lithium content. Accordingly, intermediate degrees of condensation

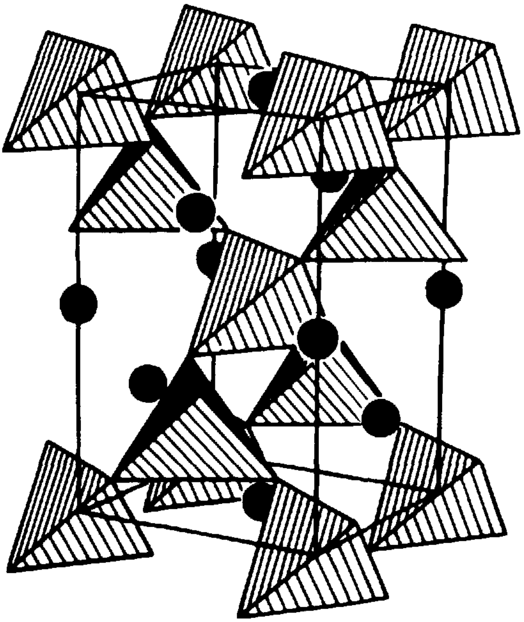


FIGURE 2 Crystal structure of $LiPN_2$.

of the corner-sharing PN_4-tetrahedra have been found. In analogy to cyclotrisilicate $[Si_3O_9]^{8-}$, complex anions with three corner-sharing PN_4-tetrahedra have been found in Li_4PN_3. Thus, the formula for this lithium phosphorus nitride is 3 (Li_4PN_3) = $Li_{12}P_3N_9$. The cyclic anions exist in a chair conformation (Fig. 3).

In $Li_5P_2N_5$, cage-like $[P_4N_{10}]^{10-}$-ions have been found, which are thus the first nitrido analogue of molecular phosphorus(V) oxide P_4O_{10}. Accordingly, the formula for this lithium phosphorus nitride is 2 $(Li_5P_2N_5)$ = $Li_{10}P_4N_{10}$. In the solid state, the complex anions in $Li_{10}P_4N_{10}$ have ideal T_d symmetry; the ten nitrogen atoms form an almost undistorted section from cubic closest packing. In comparison with the situation in molecular phosphorus(V) oxide, a much more favourable packing of the complex building units is attained in the solid state; molecular P_4O_{10}, like urotropine, has a distorted body-centered structure (with respect to the center of gravity of the molecule), while the packing of the $[P_4N_{10}]^{10-}$ units is derived from the

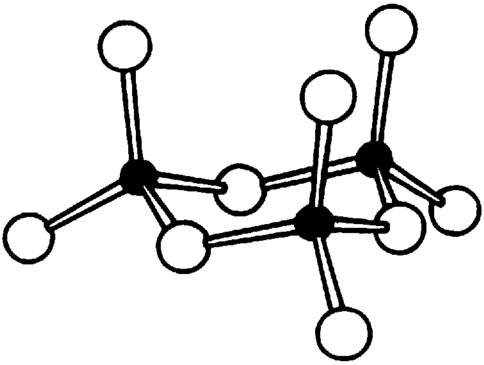


FIGURE 3 Cyclotrisilicate-like $[P_3N_9]^{12-}$ (chair-form) in $Li_{12}P_3N_9$.

cubic face-centered zinc blende-type structure. In the solid the neighbouring $[P_4N_{10}]^{10-}$ ions, which themselves have an almost completely regular tetrahedral structure, are arranged in a manner (Fig. 4) such that they face each other with their triangular surfaces parallel and rotated by 60°.

The extension of this packing principle to a three-dimensional infinite solid leads to the formation of "free" layers, which extend in all directions in space because of the cubic symmetry of the crystal. The lithium ions, on the other hand, occupy these layers. According to this highly symmetric arrangement the relatively high number of cations are not coordinated in a uniform manner by nitrogen atoms of the complex anions. The Li^+-ions are coordinated either in a trigonal planar manner, tetrahedrally, or with a distorted octahedral nitrogen environment; the molar ratio of these arrangements is 6:1:2. And the remaining 10% of the lithium ions are distributed with disorder on a site with higher multiplicity.[3] Lattice-energy and point-potential calculations confirm this arrangement.[3] A systematic study of the lithium phosphorus nitrides is also of interest because the covalent and polarizable P–N-substructures in these compounds, in combination with their ionic Li–N contacts, should lead to a considerable mobility of the Li^+ ions in the solid state, so that they could form a new class of ionic conductors. Impedance-spectroscopic measurements on $LiPN_2$ and Li_7PN_4 confirm this prediction (Fig. 5).[16]

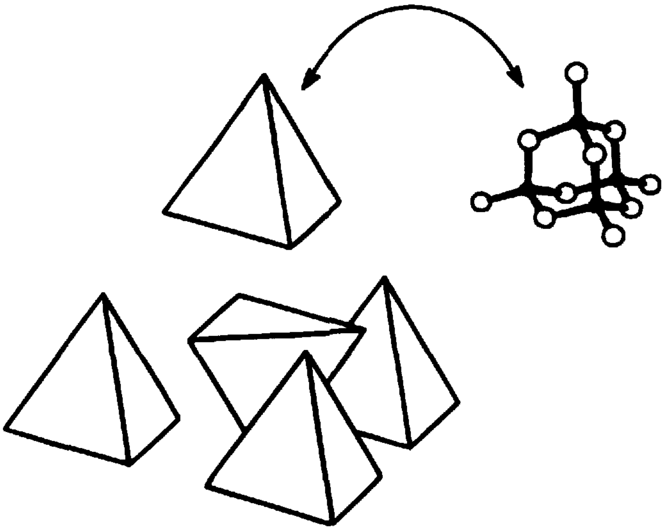


FIGURE 4 Packing of the $[P_4N_{10}]^{10-}$ ions in the solid state.

The lithium phosphorus(V) nitrides discussed above contain either discrete complex P–N anions (Li_7PN_4, $Li_{12}P_3N_9$, $Li_{10}P_4N_{10}$) or a three-dimensional network of PN_4 tetrahedra ($LiPN_2$). In the silicate family, the cyclosilicates are less stable than the corresponding chain like compounds. Hard cations (e.g., Li^+, Mg^{2+}) increase this effect while soft cations (e.g., Ca^{2+}, K^+) stabilize the rings.[10] The replacement of the monovalent Li^+ ions by bivalent alkaline-earth metal ions, while the P:N ratio is kept at 1:3, leads, in contrast to the observations made for the silicates, to a surprising result: while $[P_3N_9]^{12-}$ rings are present in $Li_{12}P_3N_9$, the alkaline-earth metal phosphorus nitride Ca_2PN_3 contains infinite chains ${}^1_\infty[PN_2N_{2/2}{}^{4-}]$ of corner-sharing PN_4 tetrahedra (Fig. 6).[17] The calcium phosphorus nitride Ca_2PN_3 is accessible by solid state reaction between the corresponding binary nitrides (Eq. (11)):

$$2\ Ca_3N_2 + P_3N_5 \xrightarrow[\text{W-crucible, } N_2]{800\ ^\circ\text{C, 14d}} 3\ Ca_2PN_3. \tag{11}$$

As well as the calcium compound, magnesium phosphorus nitride

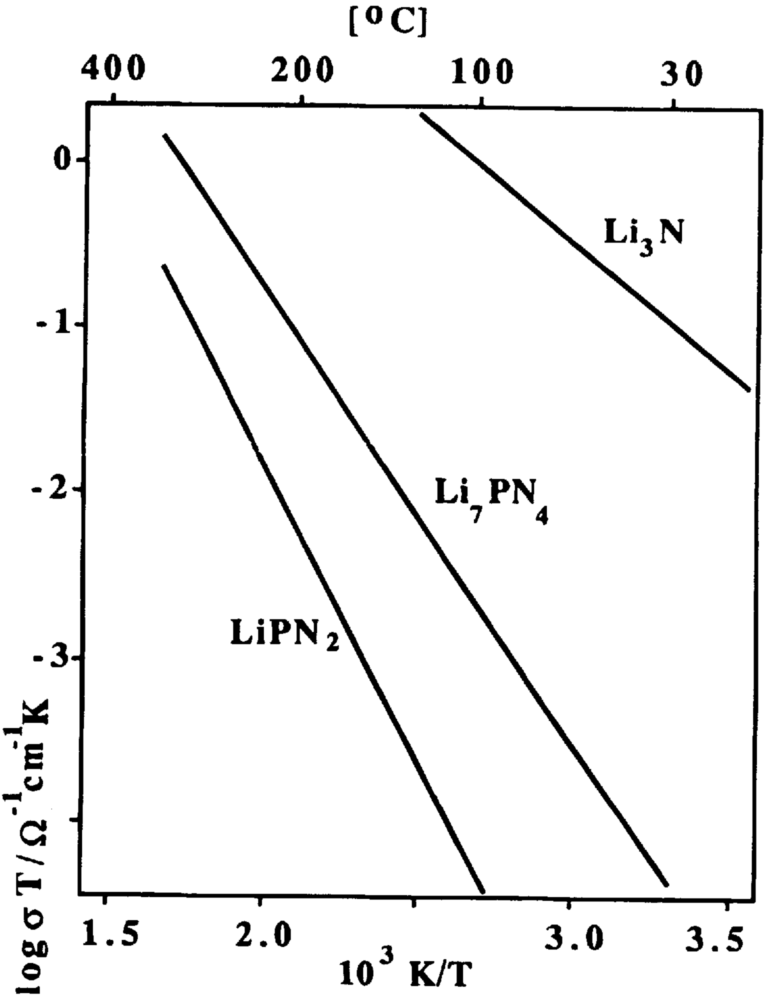


FIGURE 5 Temperature dependence of the Li^+ ion conductivities in Li_3N, $LiPN_2$, and Li_7PN_4.

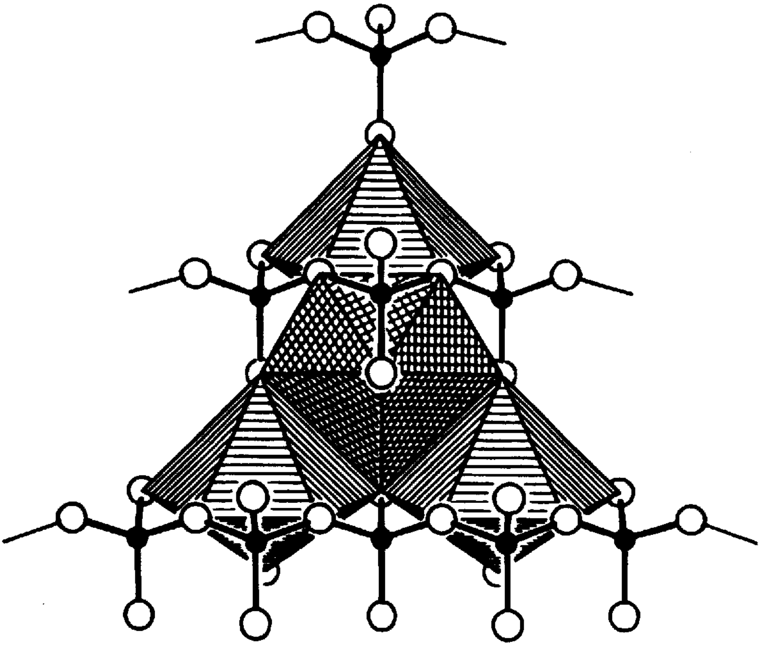


FIGURE 6 Crystal structure of Ca_2PN_3.

Mg_2PN_3 is also known, and its crystal structure is an ordered wurtzite variant.[18] More recent studies indicate that this phosphorus nitride also contains chains made up of corner-sharing PN_4 tetrahedra.

4. PHOSPHORUS NITRIDE IMIDE AND P–N-SODALITES

A typical reaction, which starts from a single molecule and leads to an infinite solid, proceeds during the ammonolysis reaction of phosphorus pentachloride. In principle the first intermediate of this reaction could be the corresponding pentaamide $P(NH_2)_5$. In fact, however, condensation reactions occur when only a fraction of the chlorine atoms have been replaced by NH_2 groups; during the whole reaction path only tetracoordinated phosphorus atoms occur. During these condensation reactions oligocyclo- and polyphosphazenes are formed. Product formation is influenced both by the reaction temperature and the ratio of NH_3PCl_5, so that either chlorine-rich compounds, such as $[NPClNH_2]_x$, or completely substituted compounds, such as $[NP(NH_2)_2]_x$, are obtained.[19] Already 150 years ago a polymeric compound $^3_\infty[PN_{2/2}(NH)_{2/2}] = HPN_2$ was postulated as the final product of substitution and condensation during the ammonolysis reaction of PCl_5.[20] However, starting from phosphorus pentachloride, the reaction with ammonia leads to a vast number of different oligomeric and polymeric phosphazenes; thus a homogeneous reaction product HPN_2 is not easily obtained. More advantageous seems to be a reaction path starting from the completely substituted compound $[P(NH_2)_4]I$ which directly converts into crystalline and defined HPN_2 (cf. Section 5). Pure and crystalline HPN_2 can also be obtained from the heterogeneous ammonolysis of pure phosphorus(V) nitride under pressure.[21] A particularly useful procedure involves the in situ preparation of the ammonia required, starting from the corresponding amounts of ammonium chloride and magnesium nitride (Eqs. (12) and (13)):

$$P_3N_5 + NH_3 \xrightarrow{580\,^\circ C,\ 14d} 3\ HPN_2, \qquad (12)$$

$$Mg_3N_2 + 6\ NH_4Cl \xrightarrow{400\,^\circ C} 8\ NH_3 + 3\ MgCl_2. \qquad (13)$$

Analogously to $LiPN_2$, phosphorus(V) nitride imide HPN_2 has a network structure $^3_\infty[PN_{4/2}{}^{1-}]$ consisting of PN_4 tetrahedra linked through all four vertices by corner-sharing.[21] This structure is derived from the isosteric β-cristobalite-type. The hydrogen atoms are covalently bonded to one half of the nitrogen atoms of the P–N-skeleton.

The phosphorus(V) nitrides so far discussed, that incorporate electropositive elements (hydrogen, alkali metals, or alkaline earth metals), mainly contain P–N structural elements with isosteric analogues in the silicate family. It thus seemed to be particularly interesting to treat Si–O compounds of particular interest, such as framework silicates and zeolites, as structural models for the preparation of new phosphorus(V) nitrides.

In recent years zeolites have gained great importance as catalysts, molecular sieves, adsorbents, and ion exchangers. Additionally, nonconventional applications for zeolites seem to be possible as pigments, luminophores, quantum-cutters, or hydrogen-storage materials. The specific properties of zeolites are based particularly on the characteristic topology of the tetrahedral skeletal structures, which have the general composition TO_2(T = Si,Al).[22] By exchanging aluminum or silicon for other elements such as B, P, Ga, Ge, As, Sb, Ti, Zr, Hf, Fe, Cr, it proved possible to tailor the catalytic properties of zeolites in a manner favorable for certain applications.[22,23] Substitution in the anion substructure of the framework, for example by replacing oxygen by other electronegative elements, has, in contrast, been almost completely neglected. During a systematic investigation on nonmetal nitrides, it appeared that the preparation of nitrido zeolites should be particularly interesting in view of the possibility of obtaining desirable material properties (stability) and modifying the chemical properties of known zeolites.

A zeolite-like framework structure $^3_\infty[PN_{4/2}{}^-]$ is obtained when, for the in situ preparation of ammonia (Eq. (14)) in the high-pressure ammonolysis of P_3N_5, Zn_3N_2 rather than Mg_3N_2 is treated with ammonium chloride. Analogously to HPN_2, a phosphorus(V) nitride is formed (Eq. (15)), with a molar ratio P:N = 1:2, while at the same time zinc and chlorine are incorporated into the solid through gaseous $ZnCl_2$, which is volatile under the experimental conditions. A hydrogen-free product is formed by subsequent reaction with additional $ZnCl_2$ in which HCl is liberated (Eq. (16)):[24]

$$Zn_3N_2 + 6\ NH_4Cl \xrightarrow{400\ ^\circ C} 8\ NH_3 + 3\ ZnCl_2, \tag{14}$$

$$4\ P_3N_5 + 4\ NH_3 + 5\ ZnCl_2 \xrightarrow{640\ ^\circ C,\ 3d} Zn_5H_4[P_{12}N_{24}]Cl_2 + 8\ HCl, \tag{15}$$

$$Zn_5H_4[P_{12}N_{24}]Cl_2 + 2\ ZnCl_2 \xrightarrow{700\ ^\circ C,\ 3d} Zn_7[P_{12}N_{24}]Cl_2 + 4\ HCl. \tag{16}$$

In $Zn_7[P_{12}N_{24}]Cl_2$ phosphorus and nitrogen form a sodalite-like three-dimensional network of PN_4 tetrahedra which are linked through all four vertices by corner-sharing (Fig. 7).[24] By combination of $[P_6N_6]$ as well as $[P_4N_4]$ rings, β-cages are formed, which are typical building units of sodalites and several zeolites. The β-cages are centered by halogen anions which are tetrahedrally coordinated by metal ions.

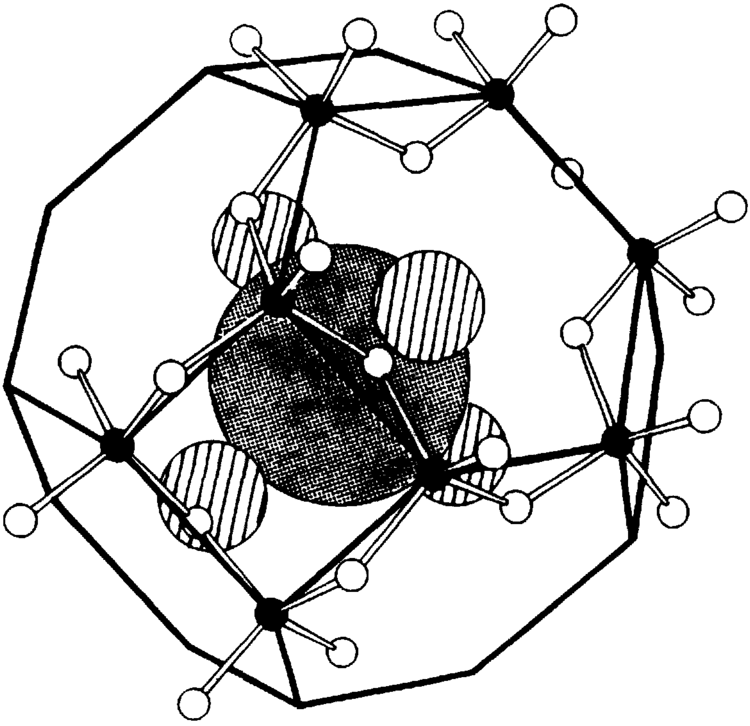


FIGURE 7 Section of the crystal structure of $Zn_7[P_{12}N_{24}]Cl_2$. The zeolite-like β-cage made up of condensed $[P_4N_4]$ and $[P_6N_6]$ rings is shown.

A fraction of the metal ions can be replaced by two protons each, which in turn are covalently bonded to nitrogen atoms of the P–N-skeleton. The P–N-sodalite has a phase width of $Zn_{(7-x)}H_{2x}[P_{12}N_{24}]Cl_2$ $(0 \leq x \leq 3)$.[25]

The synthetic method described previously is not suitable for the preparation of modified P–N-sodalites containing other metal cations or different halogen anions. For this reason we have developed more simplified synthetic procedures leading to P–N-sodalites. All these methods start from the respective metal halide and involve either a molecular phosphorus component (cyclic phosphazene) or polymeric HPN_2:[25,26]

$$5\ \mathrm{MCl_2} + 4(\mathrm{PNCl_2})_3 + 12\mathrm{NH_4Cl} \xrightarrow{700\,^\circ\mathrm{C},\ 2\mathrm{d}} \mathrm{M_5H_4[P_{12}N_{24}]Cl_2} + 44\ \mathrm{HCl}, \quad (17)$$

$$7\ \mathrm{MCl_2} + 4(\mathrm{PN(NH_2)_2})_3 \xrightarrow{700\,^\circ\mathrm{C},\ 2\mathrm{d}} \mathrm{M_7[P_{12}N_{24}]Cl_2} + 12\ \mathrm{NH_4Cl}, \quad (18)$$

$$5\ \mathrm{MX_2} + 12\ \mathrm{HPN_2} \xrightarrow{700\,^\circ\mathrm{C},\ 2\mathrm{d}} \mathrm{M_5H_4[P_{12}N_{24}]X_2} + 8\ \mathrm{HX}. \quad (19)$$

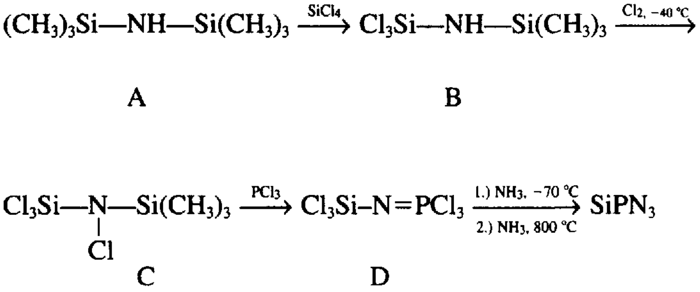
The former two reactions (Eqs. (17) and (18)) represent elegant synthetic approaches leading from molecules to solids. These synthetic methods are distinguished by high flexibility concerning the insertion of different metals or halogen atoms. The P–N sodalites exhibit remarkable properties: they are firmly stable up to about 800°C (in a nonoxidizing atmosphere) and are inert towards all common solvents as well as hot acids and alkalis. Of particular interest is the fact that, depending on the metal cation and the halogen present, some P–N sodalites are intensely colored (blue (Co/Cl, Ni/Cl), turquoise blue (Co/I), brown (Fe), dark green (Cr)), which suggests that they may find a use as pigments.

5. MOLECULAR PREORGANISATION AND MOLECULAR PRECURSORS

For the development of new high-performance materials it is particularly interesting to search for new covalent nitrides with highly cross-linked structures. The binary compounds BN, AlN, Si_3N_4, and P_3N_5 are now well known. For carbon(IV) nitride C_3N_4, interesting material properties have been postulated on the basis of high level ab initio calculations. Synthetic routes starting from molecular precursor compounds have been proposed.[27]

With respect to a systematic investigation of phosphorus nitrides and a search of new high-performance phosphorus(V) nitride ceramic materials, it appears attractive to search for novel ternary compounds containing both phosphorus and a second electropositive element, the latter also being able to form a stable nitride which is a known ceramic material (BN, AlN, Si_3N_4). The concrete task was the synthesis and investigation of mixed ternary nitrides in the systems B–Si–N, B–P–N, Si–P–N.

In the past, attempts to prepare such ternary nitrides by reaction of the respective binary nitrides always have failed because the binary nitrides do not melt congruently and also because of the low self-diffusion coefficients of these materials. However, for the synthesis of $SiPN_3$ a molecular precursor $Cl_3SiNPCl_3$ has been proven to be specifically useful.[28] In this compound the required structural element of two vertex sharing tetrahedra centered by phosphorus and silicon and connected via a common nitrogen atom is pre-organized on a molecular level. The precursor compound is obtained (Eq. (20)) in a three-step synthesis starting from $((CH_3)_3Si)_2H$ which is commercially available.



$$\underset{\textbf{A}}{(CH_3)_3Si{-}NH{-}Si(CH_3)_3} \xrightarrow{SiCl_4} \underset{\textbf{B}}{Cl_3Si{-}NH{-}Si(CH_3)_3} \xrightarrow{Cl_2,\ -40\ ^\circ C}$$

$$\underset{\textbf{C}}{Cl_3Si{-}\underset{\displaystyle Cl}{\underset{|}{N}}{-}Si(CH_3)_3} \xrightarrow{PCl_3} \underset{\textbf{D}}{Cl_3Si{-}N{=}PCl_3} \xrightarrow[2.)\ NH_3,\ 800\ ^\circ C]{1.)\ NH_3,\ -70\ ^\circ C} SiPN_3 \qquad (20)$$

Low temperature ammonolysis, followed by removal of the ammonium chloride formed and pyrolysis in a stream of ammonia, leads to $SiPN_3$.[28] During the reaction starting from molecules and leading to the $SiPN_3$ solid, the structural element of two corner-sharing PN_5 and SiN_4 tetrahedra is preserved. Accordingly, silicon phosphorus nitride $SiPN_3$ has a three-dimensional network structure of corner-sharing PN_4 and SiN_4 tetrahedra.[28] Analogous to the isosteric compounds Si_2N_2O and Si_2N_2NH,[29,30] the structure of $SiPN_3$ (Fig. (8)) is derived from a defect wurtzite modification.

With respect to the structure and some properties, the ternary nitride $SiPN_3$ is a hybrid of both binary nitrides P_3N_5 and Si_3N_4. The thermal stability of $SiPN_3$ is significantly higher than that of P_3N_5. However, it does not reach the rather high stability of Si_3N_4. The

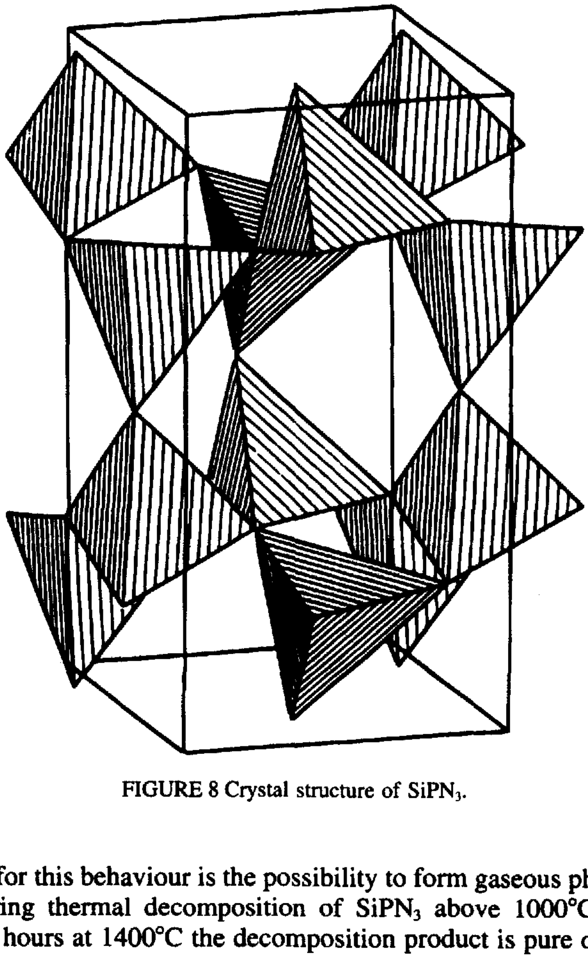


FIGURE 8 Crystal structure of $SiPN_3$.

reason for this behaviour is the possibility to form gaseous phosphorus during thermal decomposition of $SiPN_3$ above 1000°C. After several hours at 1400°C the decomposition product is pure α-Si_3N_4, which acts as a nucleus for crystallization. Calcination of commercially available amorphous Si_3N_4 by the addition of small amounts of $SiPN_3$ gives pure crystalline Si_3N_4 with a low oxygen content and a large amount of α-Si_3N_4, which is preferred for sintering processes.[28] For this reason $SiPN_3$ might be a valuable sinter additive.

At least the final reaction steps of the syntheses of the most nitrido solids mentioned in this article are performed during solid state reactions and high-temperature processes. However, for the synthesis of defined P–N solids from solutions, involving kinetic control of the reaction path, soluble educts, which contain "isolated" PN_4 building blocks, would be desirable. Because of their unusual high formal charge, PN_4^{7-} ions are not appropriate for this purpose, and no experimental evidence has been found that these anions would exist in solutions. 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.[31] 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.

By using excess liquid ammonia for the ammonolysis (Eq. (21)), the condensation can be suppressed and only the product of substitution, the tetraaminophosphonium chloride, is obtained:[32]

$$PCl_5 + 8\,NH_3 \xrightarrow[-50\,°C]{NH_3} [P(NH_2)_4]Cl + 4\,NH_4Cl. \qquad (21)$$

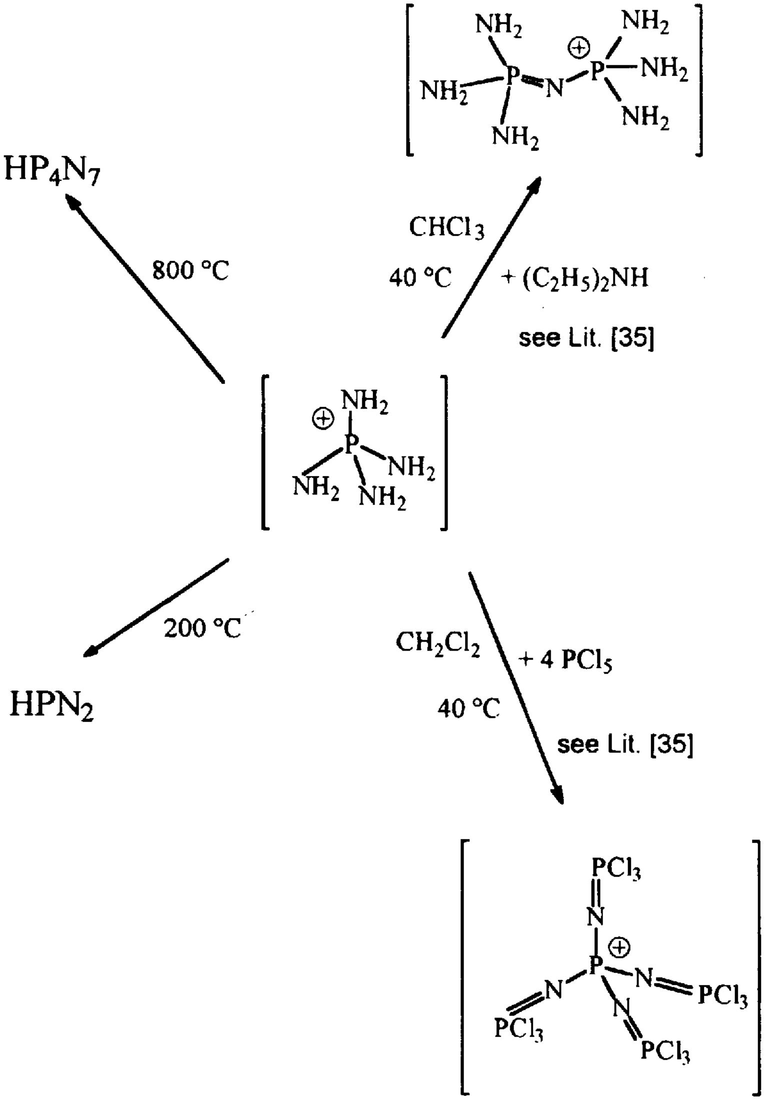
An alternative preparation starts from phosphorothionic triamide $SP(NH_2)_3$ and thus avoids any risk of condensation. A two step sequence (Eq. (22))[33,34] leads from the molecule $SP(NH_2)_3$ to an ionic solid $[P(NH_2)_4]I$:

$$SP(NH_2)_3 \xrightarrow{CH_3I} [CH_3SP(NH_2)_3]I \xrightarrow[-CH_3SH]{NH_3} [P(NH_2)_4]I. \qquad (22)$$

According to the X-ray structure determination, both salts contain the tetraaminophosphonium ion. In the cation phosphorus and nitrogen form a markedly distorted tetrahedron with a P–N distance of 160.7 pm being the shortest P–NH_2 bond ever reported. Both the distortion of the P–N tetrahedron and the short P–NH_2 distance have electronic reasons and may be explained by a significant d-orbital participation in the P–N bonds and by two 3c4e-bonds.[32]

An essential feature of the arrangement of the cations in both structures is the formation of N–H · · · X hydrogen bonds to Cl^- and I^-, respectively (Fig. 9).

Depending on the reaction conditions, the tetraaminophosphonium cation may be used as a versatile educt for condensation reactions as summarized in Scheme 1.



SCHEME 1 Condensation reactions of the tetraaminophosphonium ion.

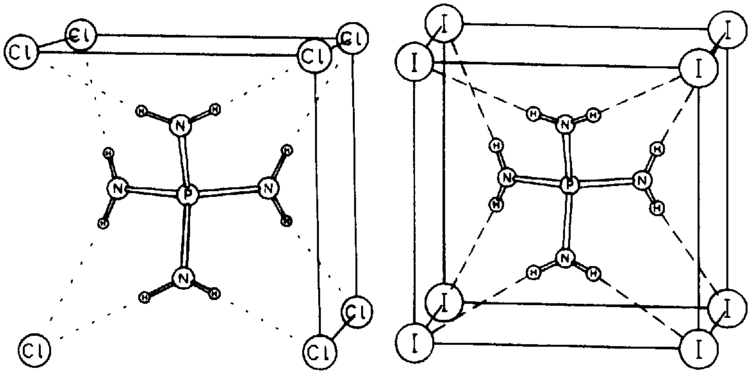


FIGURE 9 N–H · · · X hydrogen bonds in $[P(NH_2)_4]Cl$ (left) and $[P(NH_2)_4]I$ (right).

Thus, the tetraaminophosphonium ion is a promising reactive intermediate on the reaction path from molecules to solids leading to novel nitrido materials.

6. CONCLUSIONS

The results presented in this overview suggest that the chemistry of solid state P–N-compounds is just in its starting blocks. Not only do the phosphorus nitrides represent an interesting substance class with P–N-substructures analogous to the Si–O-arrangements in the silicate class of compounds. In addition, these compounds may also obtain practical applications in the fields of new ceramic materials, ionic conducturs, pigments, or microporous materials.

Molecules and extended solids seem to represent opposite sides in the large field of inorganic chemistry. Up to now only very few synthetic links have been elaborated between the two. However, the P–N class of compounds seems to be particularly suitable for the development of tailored synthetic procedures leading from molecules to solids.

Acknowledgments

This research project would never have been possible without the combined efforts of a group of enthusiastic co-workers. Special thanks go to Jan Lücke, Ute Berger, Verena Schultz-Coulon, Stefan Horstmann and Norbert Stock. Kind support by Martin Jansen and Frank Krumeich (Bonn University) is also appreciated. Generous support was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industre.

References

1. F. J. DiSalvo, Science **247**, 649 (1990).
2. H. Schäfer, Angew. Chem. Int. Ed. Engl. **10**, 43 (1971).
3. W. Schnick, Angew. Chem. Int. Ed. Engl. **32**, 806 (1993).
4. H. Lange, G. Wötting and G. Winter, Angew. Chem. Int. Ed. Engl. **30**, 1579 (1991).
5. G. A. Slack, J. Phys. Chem. Solids **48**, 641 (1987).
6. H. R. Allcock, *Phosphorus–Nitrogen Compounds* (Academic Press, New York, 1972).
7. H. N. Stokes, Am. Chem. J. **19**, 782 (1897).
8. H. R. Allcock, in *Inorganic Polymers,* eds. J. E. Mark, H. R. Allcock and R. West (Prentice Hall, New Jersey, 1992), p. 61.
9. W. Schnick, J. Lücke and F. Krumeich, unpublished.
10. F. Liebau, *Structural Chemistry of Silicates* (Springer-Verlag, Berlin, 1985).
11. A. Rabenau, Solid State Ionics, **6**, 277 (1982).
12. W. Schnick and J. Lücke, J. Solid State Chem. **87**, 101 (1990).
13. W. Schnick, Phosphorus, Sulfur, and Silicon **76**, 183 (1993).
14. W. Schnick and U. Berger, Angew. Chem. Int. Ed. Engl. **30**, 830 (1991).
15. W. Schnick and J. Lücke, Z. Anorg. Allg. Chem. **588**, 19 (1990).
16. W. Schnick and J. Lücke, Solid State Ionics **38**, 271 (1990).
17. W. Schnick and V. Schultz-Coulon, Angew. Chem. Int. Ed. Engl. **32**, 280 (1993).
18. R. Marchand and Y. Laurent, Mater. Res. Bull. **17**, 399 (1982).
19. A. Schmidpeter, C. Weingand and E. Hafner-Roll, Z. Naturforsch. **B24**, 799 (1969).
20. M. C. Gerhardt, Ann. Chim. Phys. **18**, 188 (1846).
21. W. Schnick and J. Lücke, Z. Anorg. Allg. Chem. **610**, 121 (1992).
22. J. V. Smith, Chem. Rev. **88**, 149 (1988).
23. W. Hölderich, M. Hesse and F. Näumann, Angew. Chem. Int. Ed. Engl. **27**, 226 (1988).
24. W. Schnick and J. Lücke, Angew. Chem. Int. Ed. Engl. **31**, 213 (1992).
25. W. Schnick and J. Lücke, Z. Anorg. Allg. Chem. **620**, 2014 (1994).
26. W. Schnick, N. Stock, J. Lücke, M. Volkmann and M. Jansen, Z. Anorg. Allg. Chem. **621** (1995), in press.
27. Cf. W. Schnick, Angew. Chem. Int. Ed. Engl. **32**, 1580 (1993).
28. H. P. Baldus, W. Schnick, J. Lücke, U. Wannagat and G. Bogedain, Chem. Mater. **5**, 845 (1993).
29. I. Idrestedt and C. Brosset, Acta Chem. Scand. **18**, 1879 (1964).
30. D. Peters and H. Jacobs, J. Less-Common Met. **146**, 241 (1989).
31. M. Becke-Goehring and K. Niedenzu, Chem. Ber. **90**, 2072 (1957).
32. M. Häser, St. Horstmann and W. Schnick, publication in progress.
33. W. Schnick, St. Horstmann and A. Schmidpeter, Angew. Chem. Int. Ed. Engl. **33**, 785 (1994).
34. St. Horstmann and W. Schnick, Z. Naturforsch. **B49**, 1381 (1994).
35. A. Schmidpeter and C. Weingand, Angew. Chem. Int. Ed. Engl. **8**, 615 (1969).