Phosphorus Nitrides

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The First Structural Characterization of a Binary P–N Molecule: The Highly Energetic Compound $P_3N_{21}^{**}$

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Dedicated to Professor Karl Otto Christe on the occasion of his 70th birthday

Compounds of the elements phosphorus and nitrogen can exist either as molecular species or as three-dimensional polymeric solids. Examples of known solid-state compounds include the structurally well-characterized phases of the binary compound P_3N_5 , which were reported by Schnick et al.^[1] In contrast, none of the four binary P–N molecules described in the literature, namely P_4N_4 ,^[2] $P(N_3)_3$,^[3] $P(N_3)_5$,^[4] P_3N_{21} ,^[5] and the ionic compound $(N_5)P(N_3)_6$, have been structurally characterized.^[6] As shown by Christe et al. for $(N_5)P(N_3)_6$,^[6] the difficulties in the isolation and handling of these compounds arise from their highly endothermic character and their extremely low energy barriers, which lead to an often uncontrollable, explosive decomposition.^[7]

Herein, we report the single-crystal X-ray structure of $P_3N_{21}(1)^{[8]}$ and, thereby, the first structural characterization of a binary P–N molecule. Although the synthesis of this compound was first reported over 50 years ago through the reaction of hexachlorophosphazene with sodium azide,^[5a] compound **1** has only been characterized by elemental analysis,^[5a] and vibrational^[5b,c] and NMR spectroscopy.^[5c] The experimental difficulties involved in the structural characterization of P_3N_{21} are a consequence of its high energy content; our calculated gas-phase enthalpy of formation is $+ 341.4 \text{ kcal mol}^{-1}$.

To obtain as pure a product as possible, a new synthetic strategy for P_3N_{21} , in which the azide (N_3) group is introduced using trimethylsilylazide, was chosen [Eq. (1)]. The trime-

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$$P_{3}N_{3}Cl_{6} + 6(CH_{3})_{3}SiN_{3} \rightarrow P_{3}N_{21}(1) + 6(CH_{3})_{3}SiCl$$

(1)

thylsilylchloride by-product formed was continuously removed from the equilibrium under the reaction conditions. Owing to its volatility, excess trimethylsilylazide could also be easily removed from the reaction mixture. After sublimation of the product, **1** was obtained in high purity.

The appearance of only one signal at $\delta = 13.6 \text{ ppm} (\Delta v_{1/2} = 10 \text{ Hz})$ in the ³¹P NMR spectrum of **1** indicates that a complete chloride–azide exchange occurred. The ¹⁴N and ¹⁵N NMR spectra of **1** are shown in Figure 1. The ¹⁵N NMR



Figure 1. ¹⁴N NMR (top) and ¹⁵N NMR (bottom) spectra of P₃N₂₁ in C₆D₆. An enlargement of the broad signal at $\delta = -300$ ppm in the ¹⁴N NMR spectrum is also shown.

signal at $\delta = -305.4$ ppm is assigned to the ring nitrogen atoms, by comparison with the chemical shifts of hexasubstituted cyclophosphazenes.^[9] The ¹⁵N NMR signals of the covalent azide groups are assigned according to the typical chemical shifts reported for covalent azides:^[10] $\delta = -152.7$ (N_{β}), -166.8 (N_{γ}), and -291.3 ppm (N_{α}). In the ¹⁴N NMR spectrum, the signals of the ring nitrogen atoms and the N_{α} atoms appear as a broadened peak at -300 ppm.

The Raman and IR spectra of **1** are shown in Figure 2, and a comparison of the experimental and calculated (unscaled) vibrational frequencies is given in Table 1. If standard scaling factors are applied for both calculation methods^[11] (BLYP/6-



Figure 2. IR (top) and Raman (bottom) spectra of P_3N_{21} .

Table 1: Comparison of the experimental and calculated (C_1 point group) vibrational frequencies [cm⁻¹] and intensities^[a] of P_3N_{21} .

Assignment	Experiment		Calculation	
-	IR	Raman	BLYP	B3LYP
$v_{as}N_3 + v_sN_3$	3406 (w)			
$2\nu_s N_3$	2511 (w)			
$v_{as}N_3$	2162 (vs)	2181 [26]	2189 (128) [196]	2318 (172)
			2181 (701) [30]	2308 (1016)
			2180 (567) [72]	2306 (624)
			2178 (940) [50]	2304 (1101)
			2175 (303) [25]	2303 (251)
			2173 (83) [8]	2300 (37)
$\nu_s N_3$		1291 [21]	1275 (13) [51]	
			1257 (22) [18]	
$\nu_s N_3$	1256 (s)		1268 (175) [1]	1336 (191)
			1265 (99) [6]	1333 (103)
			1258 (661) [3]	1324 (848)
$v_{as}(PN)_{Ring}$	1201 (vs)		1149 (1536) [1]	1220 (1793)
-			1114 (1069) [2]	1185 (1191)
$v_{as}(PN)_{Ring}$	910 (w)		1048 (88) [0]	1120 (96)
δN₃	786 (m)		727 (421) [0]	779 (517)
δN₃	739 (m)		679 (175) [0]	729 (232)
			672 (191) [1]	721 (239)
$\delta_{bend}(PN)_{ring}^{[b]}$		712 [100]	638 (1) [63]	
$\delta_{wag}(PN)_{ring} \delta N_3$	614 (m)		582 (222) [1]	617 (222)
$\delta_{rock}(PN)_{ring}$, $[b] \delta N_3$	564 (m)		562 (11) [15]	567 (137)
			533 (148) [0]	558 (99)
			526 (116) [1]	
$\delta_{bend}(NPN)^{[b]}$	456 (w)	454 [63]	410 (0) [47]	
		220 [21]	298 (2) [1]	
$\delta_{twist}(NPN)^{[b]}$		160 [26]	215 (1) [11]	

[a] The intensities of the calculated IR and Raman spectra are given in (km mol^{-1}) and $[\text{\AA}^4 \text{ amu}^{-1}]$, respectively. The IR frequencies calculated using the B3LYP method have very low intensities and are not given.

31G(d): 0.9940; B3LYP/6-31G(d): 0.9613), good agreement between the calculated and experimental frequencies is obtained. The vibrational frequencies observed for the liquid phase were assigned by comparison with the frequencies calculated for a molecule of C_1 point symmetry, in contrast to the approach reported in the literature,^[5b,c] where a D_{3h} molecular symmetry was assumed.

The lowest-energy conformation calculated for a free P_3N_{21} molecule in the gas phase corresponds to that detected in the solid state by single-crystal X-ray diffraction (Figure 3). The relative arrangement of the azide groups and the (noncrystallographic) C_1 symmetry of the molecule are consistent in both structures. P₃N₂₁ crystallizes in the space group $P\bar{1}$ with two formula units per unit cell. Three azide groups (N4-N5-N6, N10-N11-N12, and N19-N20-N21) are nearly parallel to the phosphazene ring, as is also found in the calculated gas phase structure. The three remaining azide groups (N7-N8-N9, N13-N14-N15, and N16-N17-N18) are nearly perpendicular to the ring. The N_{α} - N_{β}/N_{β} - N_{γ} bond lengths and the $N_{\alpha}\text{-}N_{\beta}\text{-}N_{\gamma}$ angles are in good agreement with those of other covalently bound azides.^[10] The six-membered ring in 1 is nearly planar, with a slight chair conformation, as observed for the phosphazene ring of the P₃N₃Cl₆ starting material.^[12] The P-N-P/N-P-N angles (120.8(2)-122.9(2)°/ 117.0(2)-118.2(1)°), as well as the P-N distances (1.556(2)-



Figure 3. ORTEP representation of the molecular structure of P₃N₂₁; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: P1–N1 1.558(2), P1–N2 1.576(2), P1–N4 1.666(2), P1–N7 1.671(2), N4–N5 1.218(3), N5–N6 1.117(3), N7–N8 1.203(3), N8–N9 1.114(3); N1-P1-N2 118.2(1), P1-N1-P2 122.1(1), N4-N5-N6 173.4(3), N7-N8-N9 173.5(3), P1-N4-N5 117.7(2), P1-N7-N8 119.2(2), N4-P1-N7 102.2(1), N1-P1-N4 104.5(1), N2-P1-N4 111.9(1), N1-P1-N7 108.9(1), N2-P1-N7 109.8(1).

1.576(2) Å), correspond well with the average values of 121.4/ 118.4° and 1.58 Å reported for $P_3N_3Cl_6$. In addition, the N_{α} -P- N_{α} angles (99.2(1)–102.2(1)°) also correspond well with the average Cl-P-Cl angle of 102°. However, the average P– N_{α} distance in **1** (1.67 Å) is significantly shorter than the corresponding average P–Cl distance in $N_3P_3Cl_6$ (1.97 Å). The P- N_{α} - N_{β} angles are all approximately 120°, suggesting an sp² hybridization of the N_{α} atoms.

Furthermore, the identity of P_3N_{21} was confirmed by highresolution mass spectrometry, which also demonstrated that the compound can be transferred into the gas phase without decomposition. Two signals were observed in the mass spectrum: the first mass peak corresponds to the molecular peak, and the second to a species in which one azide group has been removed from the P_3N_{21} molecule.

The thermal stability of P_3N_{21} was investigated using differential scanning calorimetry (DSC). At a heating rate of 2 °Cmin⁻¹, the compound decomposes explosively at an onset temperature of 220 °C. This relatively high decomposition temperature is in contrast with the very high impact sensitivity of the substance at room temperature (<1 J). Direct heating in a flame also results in an explosive decomposition of the compound with a loud noise and a flash of light.

Experimental Section

Caution! Phosphorus azides are highly endothermic compounds and decompose explosively under various conditions! P_3N_{21} is extremely impact sensitive. Owing to the high energy content of P_3N_{21} , explosions can cause substantial damage, even when quantities on the order of 1 mmol are used.^[5a] The use of suitable protective clothing, in particular a face shield, ear protectors, a bullet-proof vest, arm protectors, and kevlar gloves, as well as appropriate shoes for

protection from electrostatic charge, is mandatory. Ignoring these safety precautions can result in serious injury!

 $P_3N_3Cl_6$ and trimethylsilylazide were purchased from Aldrich. Propionitrile was dried over P_4O_{10} and distilled prior to use. The Raman spectra were measured using a Perkin Elmer Spectrum 2000R NIR FT-Raman instrument (Nd:YAG Laser (1064 nm)). The IR spectra were recorded using a Perkin Elmer Spectrum One FT-IR instrument. The ³¹P, ¹⁵N, and ¹⁴N NMR spectra were recorded using a Jeol EX 400 NMR spectrometer operating at 28.9 MHz (¹⁴N), 40.6 MHz (¹⁵N), or 162.0 MHz (³¹P); the chemical shifts are in ppm relative to nitromethane (^{14/15}N) or 85 % phosphoric acid (³¹P). The mass spectra were measured using a Jeol MStation JMS-700 spectrometer. The decomposition temperature was determined using a Pyris 6 DSC instrument. The impact sensitivity at room temperature was determined using a Bundesanstalt für Materialforschung und -prüfung (BAM) drop hammer.

P₃N₂₁: P₃N₃Cl₆ (224 mg, 0.644 mmol) was added to a flame-dried Schlenk flask under argon and dissolved in anhydrous propionitrile (20 mL) at room temperature. Trimethylsilylazide (893 mg, 7.750 mmol) was added dropwise to the stirred solution under a nitrogen purge. A bubbler was connected to the flask, and a slow stream of nitrogen gas was passed continuously through the apparatus. The colorless solution was warmed to 60°C and stirred for 3 h at this temperature. The now pale yellow solution was then stirred for 19 h at room temperature. The reaction mixture was subsequently concentrated using a rotary evaporator (30 °C, 50 mbar) and the remaining solvent was removed on a high-vacuum line (1 \times 10⁻³ mbar, room temperature, several minutes). The pale yellow liquid obtained was purified by sublimation $(1 \times 10^{-3} \text{ mbar}, 130 \,^{\circ}\text{C} \text{ oil})$ bath, -86°C cold finger), yielding a colorless liquid. Single crystals of 1 were obtained by the controlled cooling and warming of the substance near its melting point. The substance was repeatedly cooled to -78.5 °C with dry ice and slowly warmed to -17 °C in a cold room, while being monitored with a microscope. As soon as the liquid phase formed, it was again cooled with dry ice. The cycle was repeated until crystals formed. The single crystals of 1 must be handled with great care! Raman (neat, 25°C): see Table 1; IR (nujol, KBr, background subtracted): see Table 1; ³¹P NMR (C₆D₆, 25 °C): $\delta = 13.6$ ppm ($\Delta v_{1/2} =$ 10 Hz); ¹⁵N NMR (C_6D_6 , 25 °C): $\delta = -152.7$ (N_β), -166.8 (N_γ), -291.3 (N_{α}) , -305.4 ppm (N_{ring}) ; ¹⁴N NMR $(C_6D_6, 25$ °C): $\delta = -152.7$ $(N_{\beta}, \Delta \nu_{1/2})$ = 34 Hz), -166.8 (N_y, $\Delta v_{1/2}$ = 115 Hz), -300 ppm (N_a/N_{ring}, $\Delta v_{1/2}$ = 950 Hz); MS (DEI, 70 eV): m/z (%): 387 (39) $[M]^+$, 345 (100) $[M-N_3]^+$; MS (HR): m/z calcd for P_3N_{21} : 386.9858; found: 386.9851. DSC (2°C min⁻¹): 220°C (decomp); impact sensitivity: < 1 J.

Computational methods: BLYP and B3LYP density functional theory (DFT) calculations were carried out. The geometry, IR spectrum, and Raman spectrum of **1** were calculated with the Gaussian program,^[13] using 6-31G(d) basis sets.

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- a) S. Horstmann, E. Irran, W. Schnick, Angew. Chem. 1997, 109, 1938; Angew. Chem. Int. Ed. Engl. 1997, 36, 1873; b) K. Landskron, H. Huppertz, J. Senker, W. Schnick, Angew. Chem. 2001, 113, 2713; Angew. Chem. Int. Ed. 2001, 40, 2643.
- [2] E. H. Kober, H. F. Lederle, G. F. Ottmann, USA Patent US 32918645, 1966.
- [3] X. Zeng, W. Wang, F. Liu, M. Ge, Z. Sun, D. Wang, Eur. J. Inorg. Chem. 2006, 416.
- [4] P. Volgnandt, A. Schmidt, Z. Anorg. Allg. Chem. 1976, 425, 189.
- [5] a) C. Grundmann, R. Rätz, Z. Naturforsch. B 1954, 10, 116; b) F. Räuchle, M. Gayoso, Ann. Fis. 1970, 66, 241; c) J. Müller, H. Schröder, Z. Anorg. Allg. Chem. 1979, 450, 149.

Angew. Chem. Int. Ed. 2006, 45, 6037-6040

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- [6] R. Haiges, S. Schneider, T. Schroer, K. O. Christe, Angew. Chem. 2004, 116, 5027; Angew. Chem. Int. Ed. 2004, 43, 4919.
- [7] a) I. C. Tornieporth-Oetting, T. M. Klapötke, Angew. Chem.
 1995, 107, 559; Angew. Chem. Int. Ed. Engl. 1995, 34, 511;
 b) T. M. Klapötke, Chem. Ber. 1997, 130, 443; c) I. C. Tornieporth-Oetting, T. M. Klapötke in Combustion Efficiency and Air Quality (Eds.: I. Hargittai, T. Vidoczy), Plenum, New York, 1995, p. 51.
- [8] Crystal data for P_3N_{21} : Xcalibur S (Oxford Diffraction), $0.26 \times$ 0.22×0.13 mm, triclinic, space group $P\overline{1}$, a = 7.1953(9), b =7.3718(9), c = 12.994(1) Å, $\alpha = 87.41(1)$, $\beta = 78.95(1)$, $\gamma =$ 89.59(1)°, V = 675.8(1) Å³, Z = 2, $\rho_{calcd} = 1.902 \text{ g cm}^{-3}$, $2\theta_{max} =$ 52.12°, Mo_{Ka} radiation ($\lambda = 0.71073$ Å), graphite monochromator, ω scans, T = 200 K, 6941 measured reflections, 2657 independent reflections, 2207 with $F_{o} > 4\sigma(F_{o})$, 217 parameters, $R_{1} =$ 0.0375, $wR_2(\text{all data}) = 0.0944$, $\mu(\text{Mo}_{K\alpha}) = 0.486 \text{ mm}^{-1}$, programs used: SHELXS-97, SHELXL-97 (G. M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, Universität Göttingen, 1997; G. M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, Universität Göttingen, **1997**), refinement on F^2 , residual electron density: 0.334/-0.321 $e Å^3$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-416415.
- [9] B. Thomas, G. Seifert, G. Großmann, Z. Chem. 1980, 20, 217.
- [10] P. Geißler, T. M. Klapötke, H. J. Kroth, Spectrochim. Acta Part A 1995, 51, 1075.
- [11] J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd ed., Gaussian, Philadelphia, **1996**, p. 64.
- [12] G. J. Bullen, J. Chem. Soc. A 1971, 1450.
- [13] Gaussian 03 (Revision A.1): M. J. Frisch et al., see Supporting Information.