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A Theoretical Study of Nitrogen-Rich Phosphorus Nitrides $P(N_n)_m$

Lijie Wang, Peter L. Warburton, and Paul G. Mezey*

Department of Chemistry, Scientific Modeling and Simulation Laboratory (SMSL), Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada

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Ab initio calculations predict that structures $P(N_n)_m$ ($n = 3, 4$; $m = 1-4$; with linear N_3, tetrahedral N_4, and square N_4) correspond to local energy minima characterized by having real frequencies for all eigenvectors of the Hessian matrix. The central P atom often prefers having an odd number of bonds, although we also found some stable structures where P is evenly bonded. The special role of the phosphorus atom in the geometrical arrangements of the $P(N_n)_m$ systems was investigated. The low barriers of $P(N_4)_m$ in the gas-phase decomposition reactions mean that these nitrogen-rich systems require external stabilization if they are to be used as high-energy density materials or starting materials for further syntheses.

Introduction

For the storage of large amounts of chemical energy, nitrogen clusters are exceptionally useful; however, they are not the only compounds of high N content suitable for this purpose. Heteroatomic nitrides with high nitrogen content are also potential high-energy-density materials (HEDMs). For example, other elements such as sulfur provide convenient molecular centers[1] for stabilizing a large number of nitrogen atoms within a relatively small overall molecular volume. In the present paper we follow this principle and the results on a set of possible molecular structures of phosphorus nitrides $P(N_n)_m$ ($n = 3, 4$; $m = 1-4$; with linear N_3, tetrahedral N_4, and square N_4) are reported.

In experiments based on neutralization−reionization mass spectrometry, the molecule tetranitrogen N_4 was obtained from the N_4^+ cation as a gaseous metastable molecule with a lifetime exceeding 1 μs.[2] Both the geometrical structure and the dissociation reaction pathway of the N_4 cluster have been investigated theoretically.[3,4] According to the complete active space-self consistent field (CASSCF) results, the calculated barrier of tetrahedral N_4 dissociating into two N_2 molecules is 64.5 kcal/mol.[5] In addition to pure nitrogen clusters, other nitrogen-rich compounds have also attracted interest because of their possible use as HEDMs.[6−10] Bartlett suggested some nitrogen-rich compounds formed by N, O, and H as HEDMs[3]. The nitrogen-rich clusters CN_x have been studied by Hammerl and Klapötke[6] both experimentally and theoretically. Gagliardi and Pyykkö[11,12] designed and calculated the structures of ScN_7 and N_5−metal−N_7 and their dissociation pathways. Some nitrogen-rich sulfides $S(N_3)_m$ and $S(N_4)_m$[13,14] and possible reaction pathways for synthesizing nitrogen-rich ionic compounds HN_8^+, $N_4H_2F^+$, and $N_7H_2^+$[15−17] have been studied as well.

The PN species is the first phosphorus-containing molecule found in the interstellar medium,[18,19] and its properties have been studied experimentally.[20,21] The structure of PN and its ions have been studied by ab initio electronic structure methods.[22−25] Structure and properties of starting materials P_3N_5,[26−30] a high-pressure polymorph of binary phosphorus nitride built up from distorted PN_5 square pyramids, and PN_4 tetrahedra[31] were studied by Schnick's group.

The special properties of phosphorus with its large atomic radius and available M-shell (valence shell) d orbitals (unoccupied in the atomic ground state) make it a good candidate to link well with nitrogen clusters. On the basis of this expectation, in the present study, several $P(N_n)_m$ ($n = 3, 4$; $m = 1-4$) model systems were designed, their geometries were optimized, and their stabilities were analyzed with respect to thermodynamics and kinetics.

In this paper, our main goal is to model nitrogen-rich compounds $P(N_n)_m$ ($n = 3, 4$; $m = 1-4$), which can store large amounts of energy and yet are stable enough for potential applications as HEDMs or starting materials for further syntheses. Structural features and stabilities of these systems are discussed in the context of special properties of the phosphorus atom and the constituent tetrahedral N_4, square N_4, and linear N_3 clusters. In particular, compounds with linear N_3 units are expected to have distinct energy storage properties compared to more interconnected tetrahedral N_4 and square N_4 clusters.

Computational Method

The geometry of nitrogen-rich $P(N_n)_m$ ($n = 3, 4$; $m = 1-3$) and a number of their ions were optimized using ab initio and density functional theory methods. The MP2/6-31G*, B3LYP/6-31G*, and B3LYP/6-311+G* levels are applied for singlet even-electron species and doublet odd-electron ground states. The B3LYP is a hybrid functional method based on the Becke's three-parameter nonlocal exchange functional[32] with the nonlocal correlation due to Lee, Yang, and Parr,[33] and the MP2 stands for the second-order Mϕller−Plesset perturbation theory.[34] The basis designation 6-31G* refers to a split-valence double-ζ polarization basis set, whereas the 6-311+G* basis is a standard split-valence triple-ζ polarization basis set augmented with diffuse functions.[35] To characterize the stationary points and determine the zero-point vibrational energy (ZPVE) corrections, harmonic vibrational frequency calculations are performed at the corresponding levels of the theory. To confirm that a given transition structure connects reactants and products, minimum energy path calculations[36,37] were performed at the correspond-

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* Corresponding author. Phone: 1 709 737 8768. Fax: 1 709 737 3702. E-mail: pmezey@mun.ca.

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TABLE 1: Relative Energies (kcal/mol) of the Species on the PES of $P(N_4)_m$ ($m = 1-3$) at the Levels of B3LYP/6-31G*, B3LYP/6-311+G*, and MP2/6-31G*

species	B3LYP/6-31G*	B3LYP/6-311+G*	MP2/6-31G*
1 (PN_4)	0.0	0.0	0.0
TS1	4.327158	4.151054	25.484938
2 (PN_4)	−35.265108	−40.592668	−18.703915
TS2	−6.907931	−5.258383	
3 (PN_4^-)	−30.979767	−42.413401	−25.814406
TS3	−26.665962	−38.620028	−21.161746
4 ($P(N_4)_2$)	0.0	0.0	0.0
5 ($P(N_4)_2$)	−5.200050	−6.7491964	1.679869
TS5	−3.326456	−5.2282126	23.039908
6 ($P(N_4)_2^-$)	−80.253860	−90.0179159	−77.732324
TS6	−66.035287	−78.4488906	−75.572084
7 ($P(N_4)_3$)	0.0	0.0	0.0
8 ($P(N_4)_3^-$)	−99.961735	−107.342814	−106.001399
TS8	−83.867375	−92.558930	−92.402454

ing levels of theory with a coordinate size step of 0.1 $(amu)^{1/2}$ bohr. All calculations were carried out using the *Gaussian 98* program package.[38]

Results and Discussion

Structures **1**−**3** of the phosphorus nitrides $P(N_4)_m$ ($m = 1$) are formed by a P atom connected to a nonplanar N_4 tetranitrogen cluster. The relative energies of these structures obtained at the B3LYP/6-31G*, B3LYP/6-311+G*, and MP2/6-31G* levels are listed in Table 1. The geometrical structures optimized at the B3LYP/6-311+G* level are presented in Figure 1.

Structure **1** corresponding to PN_4 (C_{2v}, $^2A_2$) is formed by a phosphorus atom linked to a tetra-nitrogen N_4 cluster by two P−N single bonds. The P−N bond length is longer than those found experimentally for the molecule PN (1.4909 Å)[39] and ion PN^+ (1.4941 Å).[40] There are two types of single N−N bonds (1.507 and 1.394 Å), where the first value is larger than the experimental value for a single N−N bond of 1.449 Å.[41] For structure **2** (PN_4, C_s, $^2A''$), two bonds of the N_4 cluster are broken, and the P atom is bound to a single nitrogen atom and the triangular nitrogen cluster. The total energy of structure **1** is higher than that of structure **2** by 40.6 kcal/mol at the B3LYP/6-311+G* level. **TS1** and **TS2**, characterized by single imaginary vibrational frequencies of 688i and 554i cm^{-1} at the B3LYP/6-311+G* level, respectively, are transition states in dissociation paths of structures **1** and **2**; where $\mathbf{1} \rightarrow (PNN)^* + N_2$ and $\mathbf{2} \rightarrow (NPN)^* + N_2$, where the star symbol indicates the radical. Structure **1** has a barrier to dissociation of only 4.2 kcal/mol, while structure **2** shows kinetic stability with a dissociation barrier of 35.3 kcal/mol. Compared to the corresponding structure[1] of sulfur nitride SN_4, structure **1** is more reactive, while structure **2** is more kinetically stable. Actually, one can consider structure **2** as a quasi-complex $NPN...N_2$ because of the large N−N bond length of 1.576 Å. Attachment of an electron to PN_4 at the geometry of structure **1** results in the PN_4^- anion (structure **3**, C_{2v}, $^1A_1$). However, it is kinetically nearly unstable because of possessing a small barrier to dissociation of 3.8 kcal/mol. **TS3** is a transition state of structure **3** with respect to dissociation into $PN_2^- + N_2$ and has an imaginary frequency of 510i cm^{-1} at the B3LYP/6-311+G* level. The PN_4^- anion has a P−N bond of 1.876 Å length compared to the P−N bond of 1.809 Å in the neutral PN_4.

TABLE 2: Charge Distribution of Mulliken and Natural Population Analysis

species		Mulliken	NBO
4	P	0.67098	0.97954
	N	−0.32186	−0.51214
	N	−0.32179	−0.51217
	N	−0.01353	0.02248
	N	−0.01380	0.02230
7	N	−0.23991	−0.39850
	N	0.02164	0.02801
	N	0.01364	0.03965
	N	−0.23371	−0.39880
	P	1.08068	1.80697
	N	−0.01976	0.01037
	N	0.04377	0.03365
	N	0.03881	0.03270
	N	−0.27274	−0.41750
	N	−0.23328	−0.40586
	N	0.01684	0.03872
	N	0.02801	0.03206
	N	−0.24401	−0.40144

The N_4 fragments in structures **4**−**6** of $P(N_4)_2$ are nonplanar tetranitrogens N_4 as well. When comparing them to the N_4 molecule, one finds that one bond is broken in the N_4 cluster that allows two nitrogen atoms to be singly bonded to the phosphorus atom. The P−N bonds are elongated, and structural parameters of the N_4 component are rather different from those in molecular N_4. This large structural difference, considered as a distortion of the structure of free N_4, suggests that $P(N_4)_2$ is likely of high energy. On the other hand, phosphorus is expected to form an odd number of bonds because of its number of valence electrons and location in the periodic table. Therefore, the radical structures of $P(N_4)_m$ formed by a phosphorus atom and singly bonded nitrogen clusters are not likely to have significant kinetic stability.

Two $P(N_4)_2$ isomers with structures **4** (C_2) and **5** (C_1) were optimized and found to correspond to the minima. Structure **4**, a radical, formed by the P atom connected to two N_4 clusters with a total of four single bonds is 6.7 kcal/mol less stable than asymmetric structure **5** formed by a P atom connected to two N_4 clusters with a total of three single bonds. Two types of P−N bond lengths (1.793 and 1.900 Å) are found for structure **4**, while there are three types of P−N bonds in structure **5** with nearly equal bond lengths of 1.818, 1.816, and 1.816 Å, respectively. When the P atom is connected to the first cluster by a single bond and to the second cluster by two single bonds as in **5**, one of the P−N bonds is shortened while the other one is lengthened compared to the corresponding bonds in structure **4**. **TS5**, with an imaginary vibrational frequency of 571i cm^{-1} obtained at the B3LYP/6-311+G* level, is the transition state for structure **5** toward dissociation into $2N_2 + PN_4$. Structure **5** has a small barrier height of only 1.5 kcal/mol. According to a Mulliken population analysis, the atomic charge on phosphorus is +0.498 e, while for each N_4 fragment, the charge is −0.249 e in structure **4**. Even though Mulliken charges are to be taken with caution, in the present case, their values are consistent with electronegativity considerations. For structure **5**, the Mulliken charge on phosphorus is +0.436, while the charges on the N_4 fragments are −0.266 and −0.170 e. The negative charge of smaller absolute value is found on the fragment connected to the phosphorus atom by only one single bond. The latter N_4 fragment is able to retain more “autonomy” within the overall structure than the first N_4 fragment. In some instances, the natural bond order (NBO) charges are considered more relevant for drawing chemical conclusions; therefore, we compare them with Mulliken charges. The differences between the results of Mulliken and NBO population analyses are given in Table 2 for structure **4**. As is seen, both schemes provide similar trends, although the NBO scheme produces a far more polarized description than the Mulliken one.

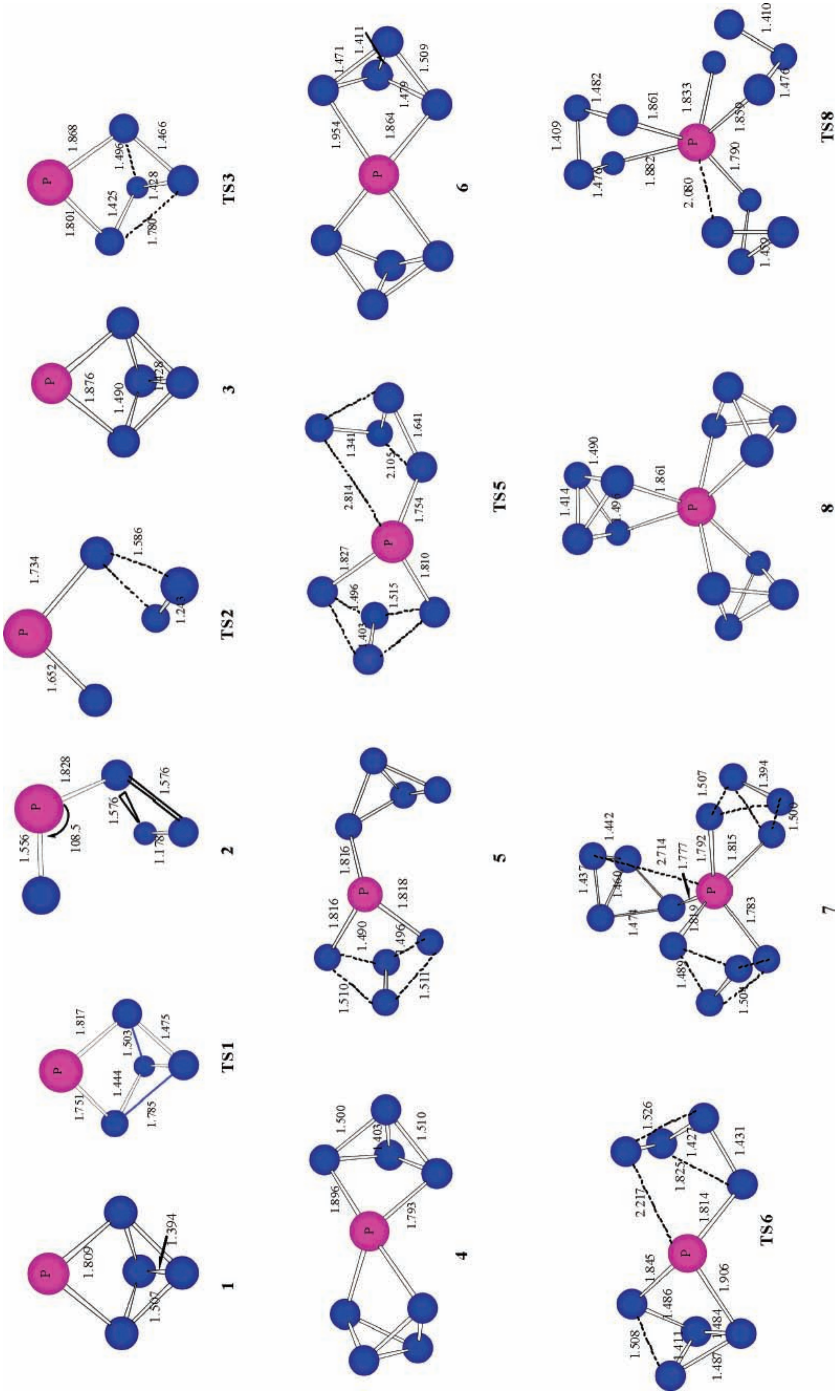

Figure 1. The geometrical structures of P(N$_4$)$_m$ at the B3LYP/6-311+G* level.

TABLE 3: Geometrical Parameters of Structures $P(N_4)_m$ Optimized With or Without d Orbitals

with d orbitals		P and N	P	N	
without d orbitals			N	P	P and N
1	P−N	1.814	1.820	1.894	1.937
	N−N	1.400−1.512	1.486-1.613	1.404−1.504	1.492−1.600
2	P−N	1.562	NPN + N_2	PN + N_3	NPN + N_2
	N−N	1.189−1.571			
3	P−N	1.886	1.880	1.960	1.981
	N−N	1.432−1.496	1.528−1.589	1.434−1.490	1.528−1.575
4	P−N	1.796−1.892	1.813−1.926	1.903−2.583[a]	1.933−2.681[a]
	N−N	1.408−1.510	1.491−1.604	1.414−1.490	1.502−1.595
5	P−N	1.818−1.833	1.748−1.849	1.903−1.928	1.935−1.953
	N−N	1.407−1.517	1.492−1.551	1.412−1.504	1.502−1.595
6	P−N	1.867−1.946	1.871−1.978	1.967−2.010	1.988−2.062
	N−N	1.415−1.515	1.500−1.614	1.421−1.497	1.508−1.593
7	P−N	1.777−1.819	1.750−1.838	1.908−1.922	1.916−1.971
	N−N	1.394−1.515	1.482−1.613	1.415−1.502	1.507−1.590
8	P−N	1.861	1.874	1.950	1.993
	N−N	1.414−1.490	1.499−1.581	1.424−1.490	1.515−1.571

[a] Structure **4** is broken (one P−N) when d orbitals were not considered on P, and the symmetry also changed.

Structure **6** ($P(N_4)_2^-$, C_2) corresponds to the negative ion obtained by adding an extra electron to the wavefunction of structure **4**. In comparison to structure **4**, the two types of P−N bonds are elongated by 0.058 and 0.071 Å, respectively. According to the Mulliken population analysis for structure **6**, the atomic charge on phosphorus is +0.274 e and 0.637 e on each N_4 fragment. Although the P−N bonds are elongated, structure **6** is more stable than **TS6** with a slightly higher energy barrier of 11.6 kcal/mol. Here, **TS6** is the transition state for dissociation of structure **6** into $PN_4^- + 2N_2$ and has an imaginary frequency of 607i cm^{-1} obtained at the B3LYP/6-311+G* level.

The third set ($m = 3$) of the first family of structures includes structure **7** corresponding to $P(N_4)_3$, formed by the P atom anchoring three N_4 clusters by five nonequivalent single bonds. The corresponding ionic structure **8** of $P(N_4)_3^-$ is found to correspond to a local minimum of C_3 symmetry with real frequencies found at all three computational levels. In structure **8**, the Mulliken atomic charge on P is +0.746 e, and the charge on each N_4 fragment is −0.582 e. Comparison of the Mulliken and NBO charges given in Table 2 shows that the NBO scheme again provides a more polarized description. Structure **8** is kinetically unstable and has a 14.8 kcal/mol barrier for dissociation into $P(N_4)_2^- + 2N_2$ via transition state **TS8**.

To test the special role of phosphorus d orbitals in the structural preferences involving the PN bonds of $P(N_4)_m$, we have carried out formal structure optimizations both with and without inclusion of d orbitals. The role of sulfur d orbitals[1,42,43] has been proven in a similar manner, and it was found that inclusion of d orbitals of both the S and N atoms in the basis sets plays a crucial role. As is seen from Table 3, the role of d functions is dramatic in the $P(N_4)_m$ compounds. Here, a lack of d orbitals on both the phosphorus and nitrogen atoms results in not only a a significant elongation of the P−N bond but also in a major change in the nature of the critical points and dissociation (in structures **2** and **4**). By contrast, if the d orbitals are included in either of the following three different ways:

(i) on the P atom but not on the N atoms, or

(ii) on the N atoms but not on the P atom, or

(iii) included on the P and all N atoms,

then the optimized structures appear stable (except **2** and **4**) but with much shorter bonds of N−N and P−N. These bonds will shorten much more when d orbitals are included on the P atom only as compared to having d orbitals on N only. Structure **2** formally dissociated when optimization was carried out without d orbitals on either of the P or on all of the N atoms. According to these models, structure **4** dissociates if the d orbitals are not included on the P atom. The computed bond shortening in the presence of d orbitals is almost as dramatic as in the extreme case found for the S=O bonds in DMSO (dimethyl sulfoxide), in an early study on the propagation of basis set errors.[42,43] Because of the special actual geometries of the fragments of N_4 in these structures, the d polarization functions of N have a natural role to play because of the geometrical distortions of the bond angles from an ideal sp^3 hybridization on the N atoms.

Because external stabilization of many of these structures may be required for practical applications, it is useful to consider charged species, suitable for forming ion pairs for additional stabilization. In addition, if the N_4 clusters change their shapes, this might allow more clusters to surround a single P atom, which may be an advantage for energy storage purposes. We have found that such geometrical rearrangement may occur for negative ions. To test these ideas, we have considered some examples for highly charged negative ions. The geometrical structures of multiply charged negative ions are rather different from those found for the neutrals. The second series of structures are ionic phosphorus nitrides $P(N_4)_m^{-3}$ ($m = 1-4$), formed by the P atom connecting to planar N_4 clusters. Total energies of these structures at the B3LYP/6-31G*, B3LYP/6-311+G*, and MP2/6-31G* levels are given in Table 4. The optimized geometrical structures obtained at the B3LYP/6-311+G level are presented in Figure 2. For this set of structures, one goal is to find how many N_4 clusters could be held by a single P, with an overall charge of −3 e. Symmetries of PN_4^{-3}, $P(N_4)_2^{-3}$, $P(N_4)_3^{-3}$, and $P(N_4)_4^{-3}$ are C_{2v}, C_{2v}, C_3, and C_4, respectively. Optimizations of $P(N_4)_5^{-3}$ result in $P(N_4)_4^{-3} + N_4$. Another interesting result is that the N−N bonds in planar square N_4 connecting to the P atom are all nearly of the same length in PN_4^{-3}, $P(N_4)_2^{-3}$, and $P(N_4)_4^{-3}$, but not in $P(N_3)_3^{-3}$.

The last series can be formally derived from a complete octet P^{+3} cation connected to $(N_3^-)_m$. The structures $P(N_3)^{+2}$ ($D_{\infty h}$), $P(N_3)_2^+$ (C_{2v}), $P(N_3)_3$ (C_3), and $P(N_3)_4^-$ (C_1) were optimized and found to be minima, having all the eigenvalues of the corresponding Hessian matrices as real. Total energies of these structures obtained at the B3LYP/6-31G*, B3LYP/6-311+G*,

TABLE 4: Total Energies (hartree)/ZPVE (kcal/mol) of Species on the PES of $P(N_4)_m^{-3}$ ($m = 1-4$) at the Levels of B3LYP/6-31G*, B3LYP/6-311+G*, and MP2/6-31G*

species	B3LYP/6-31G*	B3LYP/6-311+G*	MP2/6-31G*
9 (PN_4^{-3})	−559.67819/10.0	−559.92731/9.98	−559.54536/10.0
10 ($P(N_4)_2^{-3}$)	−778.75946/21.0	−778.99769/20.6	−777.07520/21.2
11 ($P(N_4)_3^{-3}$)	−997.73761/32.4	−998.01735/32.2	−995.49084/32.4
12 ($P(N_4)_4^{-3}$)	−1216.64672/44.1	−1216.97153/43.7	−1213.83319/44.3

TABLE 5: Total Energies (hartree)/ZPVE (kcal/mol) of Species on the PES of $P(N_3)_m$ ($m = 1-4$) at the Levels of B3LYP/6-31G*, B3LYP/6-311+G*, and MP2/6-31G*

species	B3LYP/6-31G*	B3LYP/6-311+G*	MP2/6-31G*
13 (PN_3^{+2})	−504.62461/8.6	−504.69502/8.5	−503.70904/7.8
14 ($P(N_3)_2^{+}$)	−669.43847/16.9	−669.55185/16.8	−668.08210/16.1
15 ($P(N_3)_3$)	−833.93848/25.3	−834.10345/25.1	−832.15805/25.2
16 ($P(N_3)_4^{-}$)	−998.16759/33.5	−998.38672/33.1	−995.96181/33.4

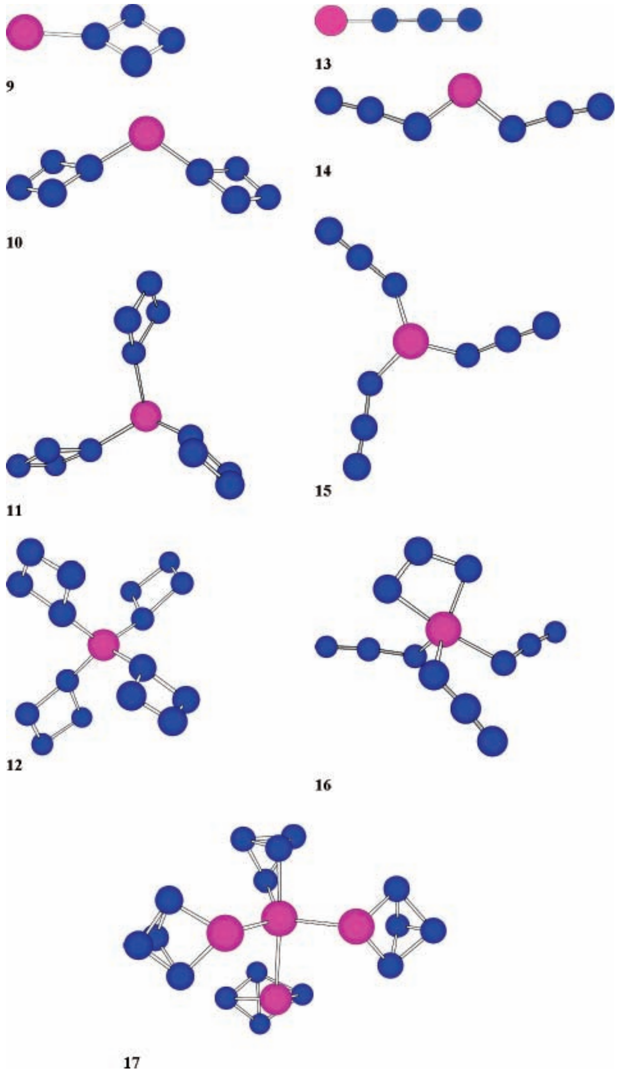

Figure 2. The geometrical structures of $P(N_4)_m^{-3}$, $P(N_3)_m$, and $P_4(N_4)_4$ at the B3LYP/6-311+G* level.

and MP2/6-31G* levels are listed in Table 5. Parameters of the optimized geometrical structures obtained at the B3LYP/6-311+G* level are presented in Figure 2. The geometrical structure of $P(N_3)_4^-$ is rather interesting. When four linear clusters of N_3 are placed around the central P atom, one N_3 cluster bends, and the P atom is attached to both ends of this N_3 fragment. As a result, the P atom forms five single bonds in $P(N_3)_4^-$.

One type of elemental phosphorus is the tetrahedral P_4 white phosphorus allotrope. Consequently, the configuration (structure **17** in Figure 2) formed by four P atoms forming the central tetrahedron P_4 unit might be able to anchor four tetrahedral N_4 clusters, with each P atom linking one N_4 cluster via two single bonds. Optimizations show that the P_4 cluster becomes highly distorted, and one P atom links to three other P atoms and to one of the N_4 clusters via two additional single bonds; that is, this P atom has five single bonds, whereas each of the remaining P atoms has two additional bonds, each to one of the N_4 clusters. In this optimized structure, the phosphorus atoms formed an odd number of single bonds, either five or three.

Summary

The results of calculations performed in this paper suggest that the series of $P(N_4)_m$ could exist as stable species, although some barriers to dissociation are critically low. The results confirm our initial conjecture that a phosphorus atom can "concentrate" several nitrogen clusters around itself because of the rather diffuse electron density around P. It is suggested that these molecules could provide a new approach for storing metastable nitrogen clusters or as starting materials for various syntheses.

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References and Notes

(1) Wang, L. J.; Mezey, P. G. *Chem. Phys. Lett.* **2004**, *387*, 233.
(2) Cacace, F.; Petris, G.; Troiani, A. *Science* **2002**, *295*, 480.
(3) Bartlett, R. *Chem. Ind. (London)* **2000**, *21*, 140.
(4) Larson, Å.; Larsson, M.; Östmark, H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2963.
(5) Dunn, K. M.; Morokuma, K. *J. Chem. Phys.* **1995**, *102*, 4904.
(6) Hammerl, A.; Klapötke, T. M. *Inorg. Chem.* **2002**, *41*, 906.
(7) Hammerl, A.; Klapötke, T. M.; Nöth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 3570.
(8) Glukhovtsev, M. N.; Jiao, H.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 7124.
(9) Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. *Angew. Chem.* **2000**, *112*, 1861.
(10) Fraenk, W.; Haberader, T.; Hammerl, A.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Nöth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 1334.
(11) Gagliardi, L.; Pyykkö, P. *J. Am. Chem. Soc.* **2001**, *123*, 9700.
(12) Gagliardi, L.; Pyykkö, P. *J. Phys. Chem. A* **2002**, *106*, 4690.
(13) Wang, L. J.; Zgierski, M. Z.; Mezey, P. G. *J. Phys. Chem. A* **2003**, *107*, 2080.
(14) Wang, L. J.; Mezey, P. G.; Zgierski, M. Z. *Chem. Phys. Lett.* **2003**, *369*, 386.
(15) Wang, L. J.; Li, Q. S.; Warburton, P.; Mezey, P. G. *J. Phys. Chem. A* **2002**, *106*, 1872.
(16) Wang, L. J.; Mezey, P. G. *Chem. Phys. Lett.* **2002**, *363*, 87.
(17) Wang, L. J.; Mezey, P. G. *J. Phys. Chem. A* **2002**, *106*, 10391.
(18) Turner, B. E.; Bally, J. *Astrophys. J. Lett.* **1987**, *321*, L75.
(19) Ziurys, L. M. *Astrophys. J.* **1990**, *41*, 91.
(20) Ahmad, I. K.; Hamilton, P. A. *J. Mol. Spectrose.* **1995**, *169*, 286.

(21) Maki, A. G.; Lovas, F. J. *J. Mol. Spectrose.* **1981**, *85*, 75.

(22) Peterson, K. A.; Wood, R. C. *J. Chem. Phys.* **1988**, *89*, 4929.

(23) Glaser, R.; Horan, C. J.; Haney P. E. *J. Phys. Chem.* **1993**, *97*, 1835.

(24) Gutsev, G. L.; Jena, P.; Bartlett, R. J. *Phys. Rev. A* **1998**, *58*, 4972.

(25) Kemeny, A. E.; Francisco, J. S.; Dixon, D. A.; Feller D. *J. Chem. Phys.* **2003**, *118*, 8290.

(26) Schnick, W.; Lucke, J.; Krumeich, F. *Chem. Mater.* **1996**, *8*, 281.

(27) Horstmann, S.; Irran, E.; Schnick, W. *Angew Chem., Int. Ed. Engl.* **1997**, *36*, 1873.

(28) Horstmann, S.; Irran, E.; Schnick, W.; Anorg. Z. *Allg. Chem.* **1998**, *624*, 620.

(29) Landskron, K.; Huppertz, H.; Senker, J.; Schnick, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1465.

(30) Kroll**,** P.; Schnick, W. *Chem.—Eur. J.* **2002**, *8*, 3530.

(31) Landskron, K.; Huppertz, H.; Senker, J.; Schnick, W. *Angew Chem., Int. Ed.* **2001**, *40*, 2643.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* B **1988**, *37*, 785.

(34) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(35) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(36) Melissas, V. S.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1992**, *96*, 5758.

(37) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(39) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(40) Imajo, T.; Todieda, K.; Nakashima, Y.; Tanaka, K.; Tanaka, T. *J. Mol. Spectrosc.* **2000**, *204*, 21.

(41) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 73rd ed.; CRC press: Boca Raton, FL, 1992.

(42) Mezey, P. G.; Hass, E. C. *J. Chem. Phys.* **1982**, *77*, 870.

(43) Mezey, P. G.; Hass, E. C. *J. Comput. Chem.* **1983**, *4*, 482.