

Stabilization of Cylindrical N_{12} and N_{18} by Phosphorus Substitution

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Abstract: Molecules consisting entirely or predominantly of nitrogen are the subject of much research for their potential as high energy density materials (HEDM). The problem with many such HEDM candidates is their instability with respect to dissociation. For example, a low-energy dissociation path has been shown for a cylindrical cage isomer of N_{12} . The instability is at least partially due to the ease of ring opening at triangles on either end of the molecule. In the current study, nitrogen cage molecules are examined to determine the stabilizing effect of substituting the triangle nitrogens with an element that more naturally forms triangles, namely phosphorus, which is valence isoelectronic with nitrogen. The cylindrical N_{12} , and a larger analogue N_{18} , form the structural basis for cage molecules of N_6P_6 and $N_{12}P_6$. Theoretical calculations using Hartree–Fock theory and perturbation theory (MP2 and MP4), along with the correlation-consistent basis sets of Dunning, have been carried out to determine dissociation energies along various pathways. The energies are discussed in terms of low-energy dissociation and the ability of the molecules to resist dissociation.

Introduction

Nitrogen molecules have been the subject of many recent studies because of their potential as high energy density materials (HEDM). An all-nitrogen molecule N_x can undergo the reaction $N_x \rightarrow (x/2)N_2$, a reaction that can be exothermic by 50 kcal/mol or more per nitrogen atom.^{1,2} To be a practical energy source, however, a molecule N_x would have to resist dissociation well enough to be a stable fuel. Theoretical studies^{3–7} have shown that numerous N_x molecules are not sufficiently stable to be practical HEDM, including cyclic and acyclic isomers with 8–12 atoms. Cage isomers of N_8 and N_{12} have also been shown^{7–10} by theoretical calculations to be unstable. Experimental progress in the synthesis of nitrogen molecules has been very encouraging, with the N_5^+ and N_5^- ions having been recently produced^{11,12} in the laboratory. More recently, a network polymer of nitrogen has been produced¹³ under very high-pressure conditions. Experimental successes have sparked theoretical studies^{14,15} on other potential all-nitrogen molecules. More recent

developments include the experimental synthesis of high energy molecules consisting predominantly of nitrogen, including azides^{16,17} of various heteroatoms and polyazido isomers¹⁸ of compounds such as 1,3,5-triazine. Future developments in experiment and theory will further broaden the horizons of high energy nitrogen research.

The stability properties of N_x molecules have also been extensively studied in a computational survey¹⁹ of various structural forms with up to 20 atoms. Cyclic, acyclic, and cage isomers have been examined to determine the bonding properties and energetics over a wide range of molecules. A more recent computational study²⁰ of cage isomers of N_{12} examined the specific structural features that lead to the most stable molecules among the three-coordinate nitrogen cages. Those results showed that molecules with the most pentagons in the nitrogen network tend to be the most stable, with a secondary stabilizing effect due to triangles in the cage structure. A recent study²¹ of larger nitrogen molecules N_{24} , N_{30} , and N_{36} showed significant deviations from the pentagon-favoring trend. Each of these molecule sizes has fullerene-like cages consisting solely of pentagons and hexagons, but a large stability advantage was found for molecules with

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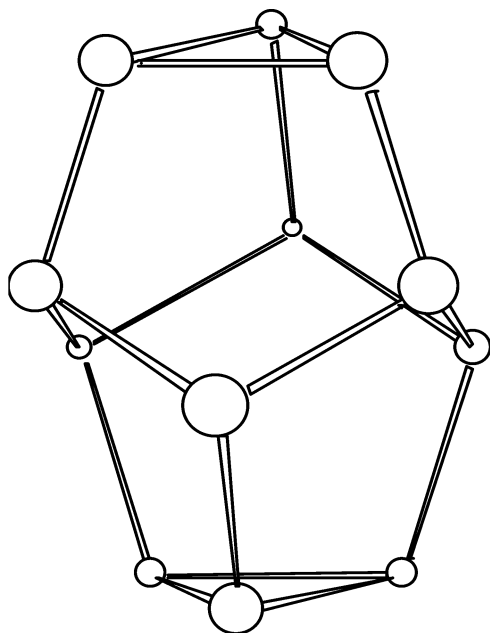


Figure 1. Cage isomer of N_{12} (designated 2060, ref 20). This is the most stable cage isomer of N_{12} .

fewer pentagons, more triangles, and an overall structure more cylindrical than spheroidal. Studies^{22,23} of intermediate-sized molecules N_{14} , N_{16} , and N_{18} also showed that the cage isomer with the most pentagons was not the most stable cage, even when compared to isomer(s) containing triangles (which have 60° angles that should have significant angle strain). For each of these molecule sizes, spheroidally shaped molecules proved to be less stable than elongated, cylindrical ones.

However, in terms of absolute stability with respect to dissociation processes, even the most stable N_{12} (see Figure 1) has been shown⁷ to have a low-energy path to dissociation. The low-energy dissociation involves the opening of the triangles on each end of the molecule. Nitrogen–nitrogen single bonds become double bonds, which are energetically very favorable compared to single bonds, and become triple bonds (yielding isolated N_2 molecules, the ultimate product of the dissociation processes). In the current study, nitrogen atoms in the triangles are substituted by phosphorus, an element that more naturally forms stable triangles²⁴ and is valence isoelectronic with nitrogen. This substitution is made on the most stable N_{12} and an analogous N_{18} cage (shown in Figure 2). The resulting molecules have molecular formulas of N_6P_6 and $N_{12}P_6$ and are illustrated in Figures 3 and 4, respectively. The issue to be examined in this study is whether the nitrogen–phosphorus molecules are stable enough to be good candidates for HEDM.

Computational Methods

Geometry optimizations are carried out using Hartree–Fock (HF) theory and perturbation theory²⁵ (MP2). Single energy points are calculated with fourth-order perturbation theory²⁵ (MP4(SDQ)). Single energy points for N_6P_6 have also been calculated with coupled-cluster theory²⁶ (CCSD(T)). Vibrational frequencies and zero-point energies (ZPE) have been calculated for N_6P_6 with MP2 theory. Geometries and

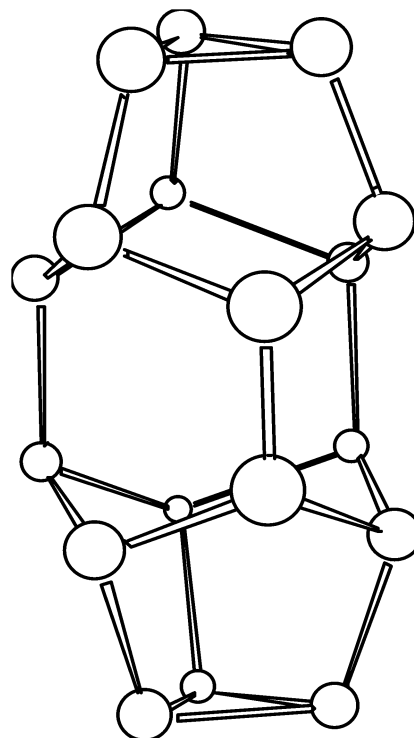


Figure 2. Cage isomer of N_{18} (designated 2063A, ref 22). This is the most stable cage isomer of N_{18} .

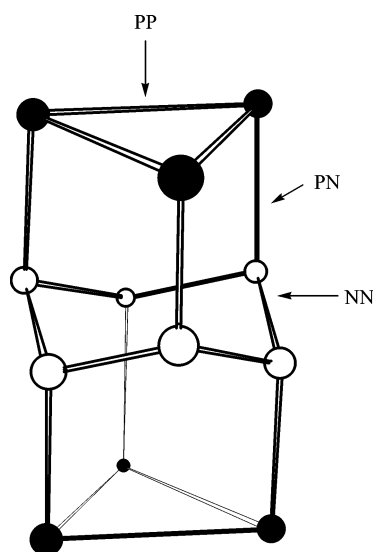


Figure 3. N_6P_6 molecule, with nitrogen atoms in white and phosphorus atoms in black. The molecule has D_{3d} point group symmetry, and symmetry-independent bonds have been labeled.

energies of the intact molecules are calculated in the singlet state, while dissociation intermediates, which have one broken bond, are calculated in the triplet state. The basis sets are the polarized valence double- ζ (cc-pVDZ) and augmented polarized valence double- ζ (aug-cc-pVDZ) sets of Dunning.²⁷ The Gaussian 03 computational chemistry software package²⁸ is used for all calculations in this work.

Results and Discussion

The N_6P_6 molecule has D_{3d} point group symmetry and has only three symmetry-independent bonds, marked in Figure

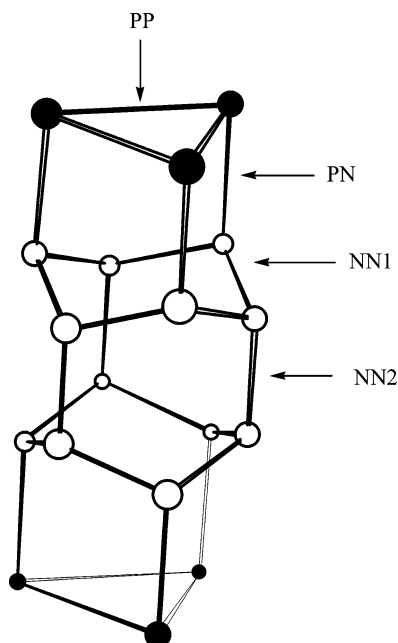


Figure 4. N₁₂P₆ molecule, with nitrogen atoms in white and phosphorus atoms in black. The molecule has *D*_{3h} point group symmetry, and symmetry-independent bonds have been labeled.

Table 1. Dissociation Energies for Each of the Symmetry-Independent Bonds in the N₆P₆ Molecule^a

method/basis set	symmetry-independent bonds (Figure 3)		
	PP	PN	NN
HF/cc-pVDZ	+26.6	+42.9	+9.5
MP2/cc-pVDZ	+53.9	+68.6	+45.3
MP2 (+ ZPE)/cc-pVDZ	+53.3	+67.5	+44.5
HF/aug-cc-pVDZ	+26.4	+42.6	+10.2
MP2/aug-cc-pVDZ	+54.4	+70.8	+47.2
MP4/cc-pVDZ // MP2/cc-pVDZ	+46.7	+61.1	+34.6
CCSD(T)/cc-pVDZ // MP2/cc-pVDZ	+47.4	+56.2	+32.1

^a Energies in kcal/mol. Zero-point energies (ZPE) have been calculated at the MP2/cc-pVDZ level of theory.

3 as PP, PN, and NN, denoting the phosphorus–phosphorus, phosphorus–nitrogen, and nitrogen–nitrogen bonds, respectively. Breaking any of these bonds results in a dissociation intermediate whose ground electronic state is a triplet. HOMO–LUMO gaps of the intact molecules and all dissociation intermediates are sufficiently large that there are no other low-lying states, and therefore the use of single-reference methods in this study is justified. The calculated energies of dissociation for each of the three bonds are shown in Table 1; each dissociation energy is the energy difference between the intact molecule and the corresponding dissociation intermediate. The Hartree–Fock numbers are consistently low, with a strong upward correction from MP2 and a moderate lowering effect from MP4. Coupled-cluster theory (CCSD(T)) bond dissociation energies for N₆P₆ are within a few kcal/mol of the MP4 results. Vibrational frequencies with MP2 theory confirm that the N₆P₆ and all of its dissociation intermediates are local minima, and the zero-point corrections to the MP2/cc-pVDZ energies are about 1 kcal/mol. Basis

Table 2. Energies (Relative to the N₆P₆ Molecule) of an Intermediate with Two PN Bonds Broken To Produce an N=N Double Bond^a

	HF	MP2	MP4//MP2
energy of breaking two PN bonds	+38.3	+61.5	+44.7

^a Energies in kcal/mol calculated with cc-pVDZ basis set.

Table 3. Energy Releases for N₁₂ and N₁₈ and the Phosphorus-Substituted Analogues^a

molecule	reaction	kJ/mol	kJ/g
N ₁₂	N ₁₂ → 6N ₂	2225	13.2
N ₁₈	N ₁₈ → 9N ₂	3449	13.7
N ₆ P ₆	N ₆ P ₆ → 3N ₂ + (3/2)P ₄	907	3.4
N ₁₂ P ₆	N ₁₂ P ₆ → 6N ₂ + (3/2)P ₄	2069	5.8

^a Calculated at MP2/cc-pVDZ level of theory.

set effects are minimal and tend toward a very slight increase in dissociation energy as the basis set increases.

The data suggest that the weakest bond in the molecule is the NN bond; this bond has the lowest dissociation energy at all levels of theory. However, even this bond has a dissociation energy over 30 kcal/mol, which implies that this molecule is stable and could be a viable HEDM. Breaking a bond anywhere in the molecule requires the input of a substantial amount of energy, but what about a concerted dissociation process whereby two or more bonds break simultaneously? Such a process is most likely to proceed at low energy if it leads to the creation of an N=N double bond, because an N=N double bond is an energetically favorable step toward the creation of free N₂. The N₆P₆ has only one pathway whereby the breaking of two bonds leads to an N=N double bond. If two PN bonds are broken such that the two nitrogen atoms are bonded to each other, the two nitrogen atoms will form a double bond. The intermediate with the double bond has a triplet ground state, and its energies are shown in Table 2. The energies are lower than for breaking one PN bond, which is due to the stabilizing effect of the N=N double bond, but the energies are still above 40 kcal/mol. The two-bond-breaking pathway is also a high energy dissociation route for the molecule.

N₆P₆ is a stable molecule, but the loss of half of the nitrogen atoms (relative to N₁₂) would result in a drastic loss of energy production from the molecule. The reaction N₆P₆ → 3N₂ + (3/2)P₄ would be a great deal less exothermic than N₁₂ → 6N₂. This loss of energy release power is quantified in Table 3. In designing a practical HEDM, maximizing the nitrogen content is a desirable goal. For that reason, calculations are carried out on the N₁₂P₆ molecule shown in Figure 4. Its structure is based on the N₁₈ shown in Figure 2, with phosphorus substitution similar to the N₆P₆. This molecule has *D*_{3h} point group symmetry and four symmetry-independent bonds, which are labeled in Figure 4. Two of the bonds are nitrogen–nitrogen and are labeled NN1 and NN2. Dissociation energies for each of the four bonds are shown in Table 4.

The N₁₂P₆ molecule is less stable than its N₆P₆ counterpart, due to lesser stability in the NN1 bond. The NN1 bond is the “weakest link” in the N₁₂P₆, with a dissociation energy of 25.1 kcal/mol at the MP4/cc-pVDZ level of theory,

Table 4. Dissociation Energies for Each of the Symmetry-Independent Bonds in the $N_{12}P_6$ Molecule^a

method/basis set	symmetry-independent bonds (Figure 4)			
	PP	PN	NN1	NN2
HF/cc-pVDZ	+27.5	+41.4	+2.4	+41.8
MP2/cc-pVDZ	+55.4	+67.9	+34.7	+58.0
MP4/cc-pVDZ // MP2/cc-pVDZ	+48.1	+59.6	+25.1	+62.1

^a Energies in kcal/mol.

compared with the 34.6 kcal/mol dissociation energy of the NN bond of N_6P_6 . This is an effect that has been previously shown²⁹ for hexagonal nitrogen tubes, namely a weakening in N–N bonds with increasing length of a nitrogen tube. Further lengthening of the tube to create $N_{18}P_6$, $N_{24}P_6$, etc., by incorporating additional hexagonal “layers” of nitrogen is similarly unlikely to result in strengthening of the molecule. Rather the opposite, not only in the weakening of individual nitrogen–nitrogen bonds but also in the proliferation of multiple-bond-breaking pathways that could expose an N=N double-bonded pair. Even one such low-energy pathway would render the molecule unstable with respect to dissociation. The $N_{12}P_6$ may be more stable than its N_{18} analogue, but the viability of $N_{12}P_6$ as a stable HEDM is questionable.

Conclusion

Nitrogen cages previously shown to be unstable with respect to dissociation can be stabilized with the substitution of appropriate atoms such as phosphorus. Such substitutions can lead to small molecules that are feasible as high energy density materials. It seems, however, that two limitations exist in the utility of phosphorus as a heteroatom: (1) phosphorus substitution on the triangular end-caps does not solve the problem of weakness in the interior of a lengthening nitrogen tube, and (2) the high mass and low energy release properties of phosphorus dilute the energy release properties of the HEDM. While tradeoffs between stability and energy release may be inevitable in HEDM design, other heteroatoms may provide stability with less loss of power. If, in fact, the goal of a 100% nitrogen HEDM is unattainable, then further heteroatom studies will be required to find the optimum balance between stability and energy production.

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