Heteroatom Chemistry
Volume 3, Number 4, 1992

# Aminophosphaethyne ($PCNH_2$) and Its Isomers

Ludmila Ermolaeva* and Alexey Ionkin

*Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of USSR, Arbuzov str. 8*
*420083 Kazan, USSR*

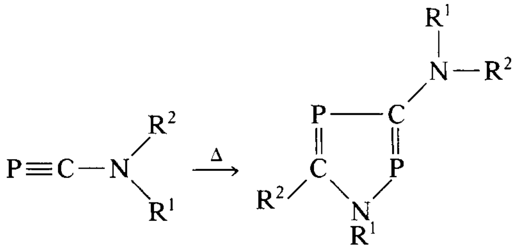
*Received 25 July 1991.*

## ABSTRACT

*The potential energy hypersurface of the conversion of aminophosphaethyne* (**1**) *to 1-aza-3-phosphaallene* (**2**) *has been studied with the MNDO method. The interconversion includes five intermediate species. The structure and energy of* **1** *and its isomers produced by a hydrogen shift have been calculated also with ab initio molecular orbital theory by a split valence basis set including a polarization function at the P atom. The results reveal that all the isomers are equilibrium structures. The ab initio calculation predicts the carbenaazaphosphirane* **3** *to be the intermediate lowest in energy. It is suggested that a carbene* (**3**), *phosphinidene* (**4**) *or azaphosphirene* (**5**) *are responsible for the 1-aza-2,4-diphosphole formation.*

## INTRODUCTION

One coordinated phosphorus compounds with a P≡C triple bond have been of great interest during the past few years [1]. The most natural types of reactivity of the P≡C triple bond are the cycloaddition reactions and the subsequent evolution of the primary and intermediate adducts. In particular, the mechanism of such reactions, especially with C-aminophosphaalkynes [2], has not been widely studied. The latter is a good model for the investigation of [3 + 2] cycloaddition and intermolecular rearrangements. It has been found that C-aminophosphaalkynes dimerize to novel organophosphorus compounds [3–4]:



$R^1$ = t-Bu $R^2$ = H
$R^1$ = i-Bu $R^2$ = $SiMe_3$
$R^1$ = cyc. Hexyl $R^2$ = $SiMe_3$

To explain this, the authors assumed that the formation of 1-aza-2,4-diphosphole involves a [1,2]hydrogen shift in the C-aminophosphaethyne followed by its cyclization to intermediate species. To elucidate the details of the above process $R^1$ and $R^2$ were replaced with hydrogen atoms and the relative stabilities of the possible $PCNH_2$ isomers were calculated by the MNDO [5] and *ab initio* methods.

## RESULTS AND DISCUSSION

First, we have studied with the MNDO method the two-parameter hypersurfaces for the isomerization of $P{\equiv}C{-}NH_2$ (**1**) to $HP{=}C{=}NH$ (**2**). The energy profiles for possible rearrangements of **1** and a section of the two-parameter MNDO hypersurface are given in Figures 1 and 2. According to these data, **1** may transform to **2** via a [1,3]-H shift or through two subsequent [1,2]-H shifts. The [1,3]-migration of a hydrogen from the nitrogen atom to the phosphorus proceeds through the carbene **3**.

---

*To whom correspondence should be addressed.

1042-7163/92/$3.50 + .25

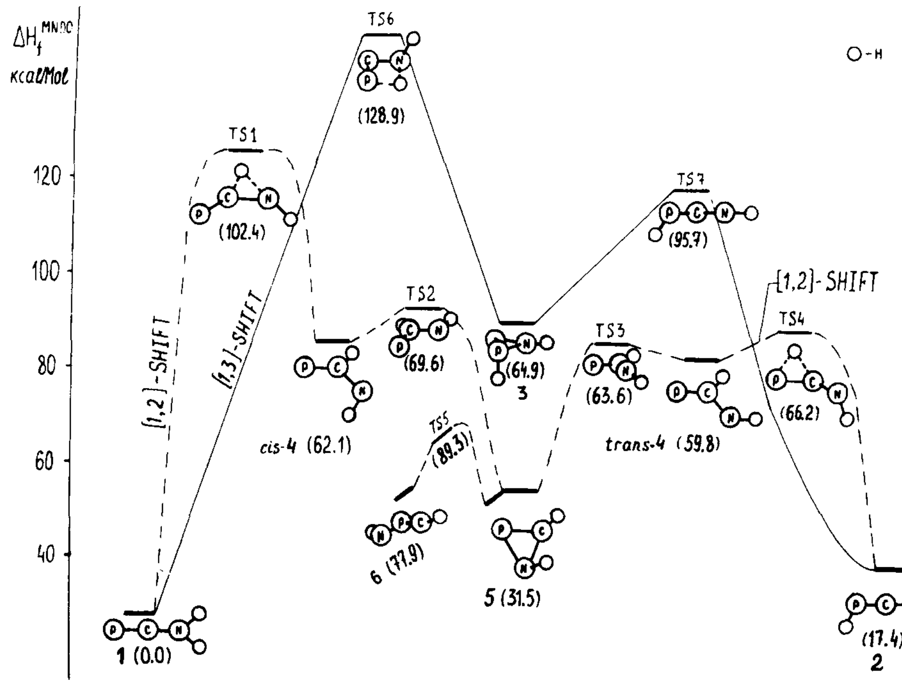


**FIGURE 1** The MNDO reaction profiles corresponding to transformation of **1** to **2** (relative energies are in parentheses).

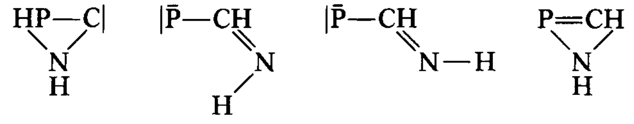
$P{\equiv}C{-}NH_2$

**1**

$HP{=}C{=}NH$

**2**

The [1,2]-H shift in **1** leads to the intermediate *cis*-phosphinidene **4**.



**3** *cis*-**4** *trans*-**4** **5**

The latter may convert to **2** in a subsequent [1,2]-H shift [6], but the cyclization of **2** to azaphosphirene (**5**) is more kinetically preferable. An opening of **5** results in the formation of *cis/trans*-**4** or the carbene HN=P—C̄—H (**6**). Thus, there are electron-deficient intermediates (**3**, **4**, **6**) which are the precursors of **2**.

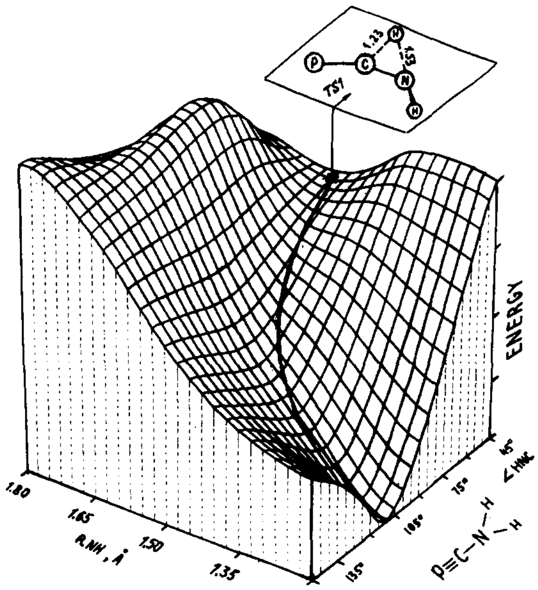


**FIGURE 2** Section of the two-parameter MNDO hypersurface for the [1,2] hydrogen shift in $P{\equiv}C{-}NH_2$. The reaction profile (⇒) via the transition states TS1 is represented.

In the second step, we have investigated the structures of possible isomers (**1**–**6**) with *ab initio* molecular quantum mechanical methods. The standard split valence basis set 3-21G [7] and 4-31G [8] with additional P diffuse functions was chosen. The d polarization exponent $\alpha_d(P)$ was 0.55. The Hartree-Fock optimized geometries were used to compute the force constant matrices by finite difference of the analytical first derivatives at the 3-21G (d(P)) level. All structures are equilibrium structures. The *ab initio* molecular orbital calculations were performed with the MICROMOL program constructed by the Cambridge group [9].

The theoretical geometries of the isomers **1**–**6** by *ab initio* treatment are shown in Figure 3. The total and relative energies are given in Table 1. The structure with the P≡C triple bond has been predicted theoretically to be the most stable. The 1-aza-3-phosphallene **2** lies 11.3 and 11.8 kcal/mol higher than **1** at the 3-21G (d(P)) and 4-31G (d(P)) levels, respectively. The former have been studied at the *ab initio* level by S. Nagase *et al.* [10]. Further discussion is carried out on the assumption that the topology of the potential energy surface does not depend on the method of calculation. Compound **2** can convert to **3** and the latter to **1**.

The carbene structure **3** is less stable than **2** by 38.1 kcal/mol at both of the *ab initio* levels. A ring opening followed by the migration of a hydrogen

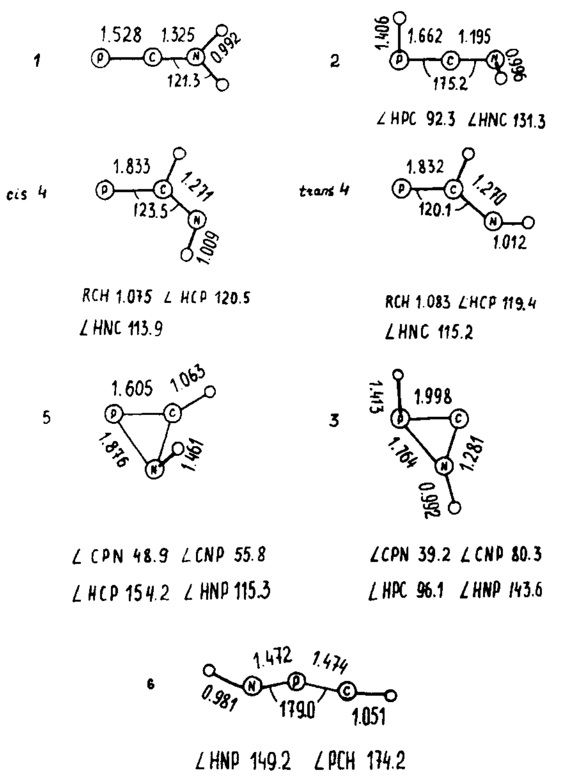


**FIGURE 3** Geometries for the various isomers of aminiphosphaethyne at the 4-31G (d(P)) level. All bonds are in Å.

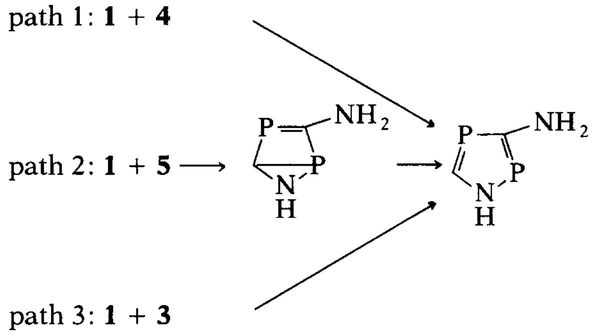
from phosphorus atom to nitrogen leads to the aminophosphaethyne **1** A[1,2]-hydrogen shift in **1** or **2** results in the phosphinidene structure **4**.

The *cis*-isomer is lower in energy than *trans*-**4** at the 4-31G (d(P)) level; at the 3-21G (d(P)) level, the result is vice versa. This is due to a different symmetry of the frontier orbitals localized at the phosphorus atom. According to the 4-31G (d(P)) data, the highest occupied molecular orbital (HOMO) in **4** possesses $\sigma$-symmetry, and the lowest unoccupied molecular orbital (LUMO) has $\pi$-symmetry. Thus, phosphorus and nitrogen lone pairs are located in the same plane, and the higher relative energy of the *trans* form may be attributed to the larger four-electron repulsion between the two lone pairs. The calculation at the 3-21G (d(P)) level shows that the phosphorus lone pair in **4** lies in the $\pi$-plane, and the destabilizing interaction is absent due to the different symmetry of the lone pairs.

**TABLE 1** Total Energies (hartrees) and Relative Energies (kcal / mol)

| *Species* | *RHF / 3-21G (d(P)* | | *RHF / 4-31G d(P)* | |
|---|---|---|---|---|
| **1** ($D_{2h}$) | −432.01136 | (0.0) | −433.65826 | (0.0) |
| **2** ($C_1$) | −431.9933 | (11.3) | −433.63950 | (11.8) |
| **3** ($C_1$) | −431.93260 | (49.4) | −433.57878 | (49.9) |
| **4** *cis* ($C_s$) | −431.91318 | (60.9) | −433.56286 | (59.8) |
| **4** *trans* ($C_s$) | −431.91485 | (60.6) | −433.55789 | (63.0) |
| **5** ($C_1$) | −431.92148 | (56.4) | −433.57073 | (54.9) |
| **6** ($C_1$) | −431.88206 | (81.1) | −433.53781 | (75.6) |

The phosphinidene **4** undergoes a cyclization to a more stable product **5** with a small endothermic effect ($\Delta E = -8.1$ (*trans* **4**) and $-4.9$ kcal/mol (*cis* **4**), 4-31G (d(P)). The azaphosphirene may form a carbene **6** through a N—C bond cleavage. The isomer **6** has the highest relative energy (Table 1). The structures that are analogous to **4**–**6** have been suggested previously to explain the respective product formation [11–13]. The MNDO relative energetic positions of isomers **1–6** qualitatively agree with *ab initio* data, the exceptions being the cyclic species **3** and **5**. The intermediate resulting from [1,3] hydrogen shift in aminophosphaethyne is more stable than the ones from [1,2]-hydrogen shift (Table 1). Nevertheless, taking into account steric and electronic influence of the substituent on the relative energies of the isomers, we assumed that 1-aza-2,4-diphospholes may be formed by reaction of **1** with **3**–**5**:



The first way represents a [3 + 2] cycloaddition, as previously suggested [2]. The second path is a [2 + 2] cycloaddition reaction with a subsequent endocyclic P-C cleavage. And the latter includes interaction of **1** with the carbene structure **3** followed by P-C cleavage and a migration of hydrogen. It is difficult to choose the way without supplementary experimental and theoretical study.

## ACKNOWLEDGMENTS

We are grateful to Academician B. Arbuzov for his valuable comments and suggestions.

## REFERENCES

[1] M. Regitz, *Chem. Rev.*, *90* (1990), 191. M. Regitz in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (M. Regitz, O. J. Scherer eds.), Thieme, Stuttgart, 1990, p. 58.
[2] R. Appel, M. Poppe, *Angew. Chem. 101*, 1989, 70; *Angew. Chem. Int. Ed. Engl. 18*, 1989, 53.
[3] A. S. Ionkin, S. N. Ignat'eva, I. A. Litvinov, V. A.

Naumov, B. A. Arbuzov, *Heteroatom Chem.*, *2*, 1991, 577.

[4] Heating of aminophosphaethyne ($R_1$ = cy-Hex, $R_2$ = $SiMe_3$) leads to the corresponding 1-aza-2,4-diphosphole (b.p. = 121°C/$10^{-3}$, $\delta^{31}P$ = 93.6; 210.8). Unpublished results.

[5] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.*, *107*, 1985, 3902; M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, AMPAC (IBM), version 3.0, QCPE No. 527 (1987).

[6] The activation barrier is 4.3 kcal/mol for the [1,2] shift of hydrogen to phosphorus atom in cis-phosphinidene. An activation barrier for cyclization of *cis* **4** is 1.5 kcal/mol.

[7] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Amer. Chem. Soc.*, *104*, 1982, 2797.

[8] W. J. Hehre, W. A. Lathan, *J. Chem. Phys.*, *56*, 1972, 5255.

[9] S. M. Cowell, The Cambridge Hartree-Fock Program. 1987.

[10] M. Yoshifuji, T. Niitsu, K. Toyota, N. Inamoto, K. Hirotsu, Y. Odagaki, T. Higuchi, S. Nagase, *Polyhedron*, *7*, 1988, 2213.

[11] W. Rösch, T. Facklam, M. Regitz, *Tetrahedron*, *43*, 1987, 3247.

[12] M. Hermesdorf, M. Birkel, H. Heydt, M. Regitz, *Phosphorus, Sulfur, and Silicon*, *46*, 1989, 3.

[13] H. Bock, *Phosphorus, Sulfur, and Silicon*, *49 / 50*, 1990, 3.