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Reaction of P^+ (^3P) with Methylamine: A Detailed Study of the Potential Energy Surface and Reaction Mechanisms

Elso M. Cruz

Dpto. de Químimca, Universidad de Oriente, Av. Patricio Lumumba S/N, 90500, Santiago de Cuba, Cuba

Joseph E. Fowler, X. Lopez, and Jesus M. Ugalde*

Kimika Fakultatea, Euskal Herriko Unibertsitatea, P.K. 1072, 20080 Donostia, Euskadi, Spain

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In order to elucidate possible reaction paths to the formation of P−N bonds in interstellar space and to provide data for the interpretation of recent experiments, the reaction of P^+ (^3P) with methylamine has been investigated. In particular, the G2(MP2) methodology has been applied to the triplet potential energy surface of $[H_5, C, N, P]^+$. Numerous minima on this surface have been found, and transition state structures connecting those which lie along important reaction paths have been determined. The global minimum on the PES is the ion−molecule complex $P^+\ NH_2CH_3$, which lies 95.7 kcal/mol below the separated reactants. Barrier-free reaction paths leading to ($PNH_2^+ + CH_3$), ($PH + CH_2NH_2^+$), and atomic and molecular hydrogen abstraction have been found. In agreement with experimental results, these first two reactions appear to be favored.

I. Introduction

After many fruitless years of searches for phosphorus-containing compounds in interstellar space by various groups, the detection of PN was reported by Turner and Bally,[1] and Ziurys[2] in 1987. This exciting discovery and the later identification of PC in the envelope of a carbon star[3] sparked numerous additional studies, both experimental and theoretical. These studies have focused on the various possibilities and formation processes of phosphorus-containing compounds in space, a process expected to occur via ion−molecule reactions.[4]

The experimental studies established, among other things, two very important tendencies of phosphorus cations. First, PH_n^+ ions react endothermically with H_2, making PH_n, $n = 1-3$, compounds highly unlikely.[5] Second, the phosphorus atom of PH_n^+ ($n = 0-4$) molecules tends to insert itself into covalent bonds when reacting with various neutrals found in interstellar space.[6,7]

Theoretical work, *e.g.* refs 8−13, has explored the possible pathways of these insertions and what products are possible from them. Because the low temperature and density of space, these reactions must occur via barrier-free exothermic paths. Note, however, that due to the vast improbability of collisional cooling, barrier-free takes on the definition: free of any barrier with total energy greater than that of the separated reactants. Thus, if the reactants form a low-energy ion−molecule complex, as is frequently the case, there is much energy with which to overcome various rearrangement barriers and still the overall processes remain barrier-free by this definition.

The reactions of P^+ with numerous small molecules have been well described resulting in predictions of numerous barrier-free paths to molecules containing P−N, P−O, and P−C bonds, *e.g.*, refs 8−13. Recently the focus has turned to slightly larger molecules such as formaldehyde[14] and methanol.[15] Of special interest in these larger molecules has been the stabilizing effect of the methyl ligand. The binding energy of the P^+CH_3OH ion−molecule complex is 14.1 kcal/mol greater than that of the P^+OH_2 ion−molecule complex. A similar activation is seen for the corresponding Si^+ complexes.[16] In line with these works, we present the following study of the $[H_5, C, N, P]^+$ triplet potential energy surface.

As PN is to date the only phosphorus-containing molecule found in interstellar space,[1,2] the investigation of ion−molecule reactions which could lead to P−N bonds is very important indeed. Here, in line with works expanding our understanding of interstellar chemistry, we present the following study of the $[H_5, C, N, P]^+$ triplet potential energy surface and possible mechanisms for the reaction of P^+ with methylamine which could lead to the production of PN and/or other species of interstellar interest.

II. Methods

The G2(MP2)[17] procedure with the following minor changes has been utilized in carrying out this study. Because the positions and bonding of hydrogen atoms in the transition state structures located were very important, p polarization functions were added to the hydrogens. All geometry optimizations and frequency calculations were carried out at the MP2/6-31G(d,p) level of theory, rather than the suggested MP2/6-31G(d) level for geometries and the HF/6-31G(d) level for frequencies. The vibrational frequency scaling factor (0.94) was that suggested by DeFrees and McLean.[18] All of these calculations were carried out using the GAUSSIAN94[19] package.

The P−N, P−C, and N−C bond properties of the various isomers have been studied through the use of Bader[20] topological analysis of the MP2/6-31G(d,p) electron density as computed by the AIMPAC[21] suite of programs. NBO[22] analysis was carried out at the HF/6-31G(d,p)//MP2/6-31G(d,p) level of theory.

Atomic charges, spin densities, and dipole moments for each of the stationary points are reported in the Supporting Information.

III. Characteristics of the $[H_5, C, N, P]^+$ Triplet Minima

In Figures 1, 3, and 5 are depicted the local minima found on the triplet potential energy surface (PES) along with the stabilities (kcal/mol) relative to the reactants [P^+ (^3P) and CH_3NH_2 ($^1A'$)]. Due to the large number of stationary points, the structures have been classified into three groups depending on the connectivity of the three heavy atoms: C−N−P (Figure 1), C−P−N (Figure 3), and N−C−P (Figure 5).

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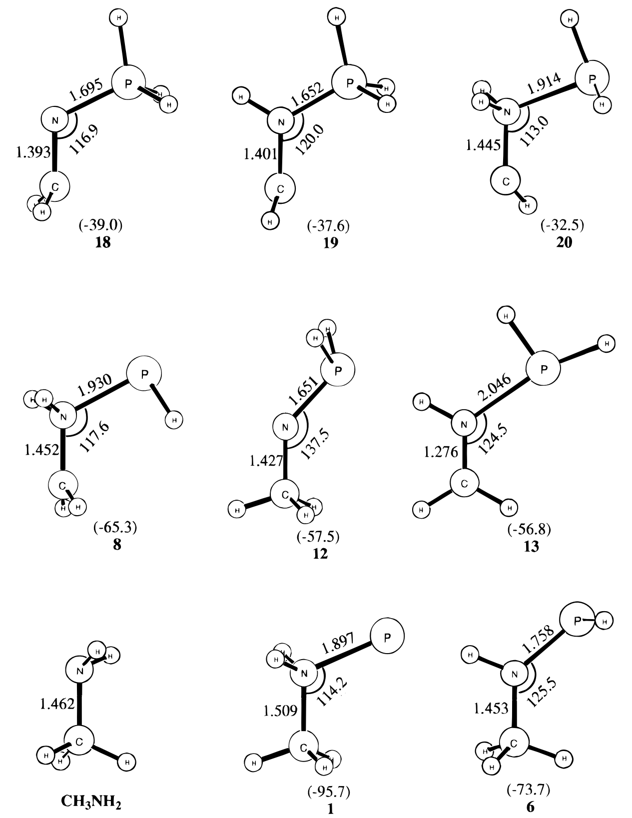

Figure 1. MP2/6-31G(d,p)-optimized geometries and G2(MP2) relative energies of the systems with a C−N−P heavy atom skeleton found on the $[H_5, C, N, P]^+$ triplet PES. Bond distances are in angstroms, angles in degrees, and relative energies in kilocalories per mole.

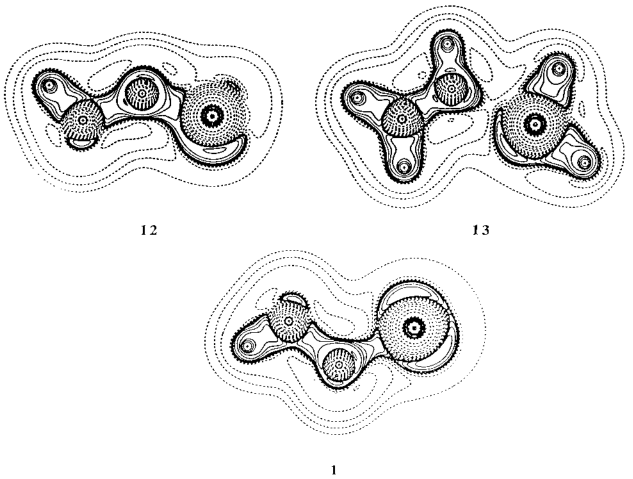

Figure 2. Contour maps of the Laplacian of isomers **1**, **13**, and **12**. Positive values of $\nabla^2\rho$ are represented by solid lines and negative values with dashed lines.

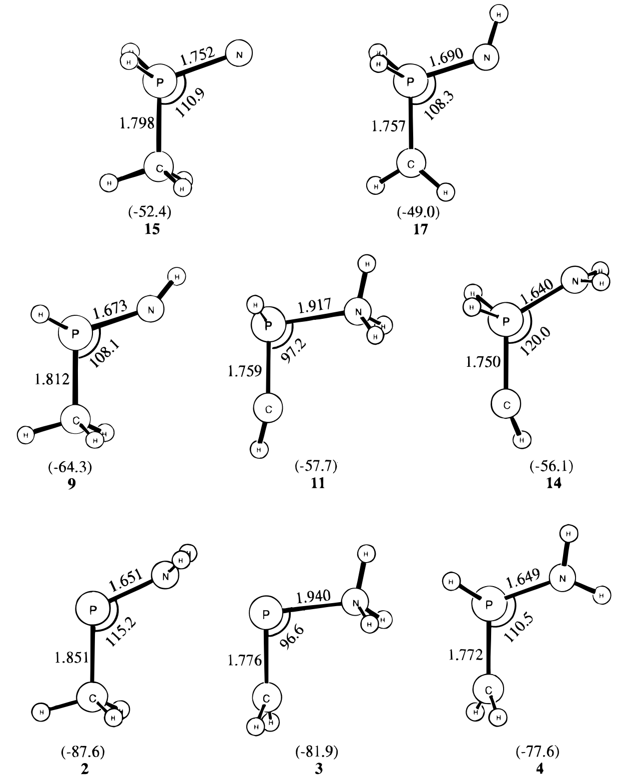

Figure 3. MP2/6-31G(d,p)-optimized geometries and G2(MP2) relative energies of the systems with a C−P−N heavy atom skeleton found on the $[H_5, C, N, P]^+$ triplet PES. Bond distances are in angstroms, angles in degrees, and relative energies in kilocalories per mole.

The C−N−P Skeleton. Isomer number **1** is the absolute minimum on the PES and can be considered as an ion-molecule complex, $P^+NH_2CH_3$. In this adduct, the charge and the spin density are centralized mainly on the phosphorus atom. The N−P bond is made stronger by the donation of electron density of the nitrogen lone pair into an empty 3p orbital of phosphorus. Consequently the length of the N−P bond is similar to that of a N−P single bond. The value of $\nabla^2\rho(r_c)$ (+0.0726) is indicative of electrostatic interactions, but the graphical depiction of the Laplacian (Figure 2) reveals the existence of areas of charge concentration between nitrogen and phosphorus, a characteristic of covalent bonds. The value of $H(r_c)$ for this bond (−0.0835) is also indicative of covalency,[23] lending a certain amount of certainty to this conclusion.

The binding energy of this isomer ($D_e = 95.7$ kcal/mol) reveals that the interaction of P^+ with methylamine is quite strong, 23.7 kcal/mol stronger than the P^+−methanol interaction[15] and 9.9 kcal/mol more energetic than the P^+−ammonia[24] interaction. The large difference between the P^+−methanol and the P^+−methylamine bond energies is due to the strength of the N → P electron donation, as was seen to be the difference between the P^+−water[25] and P^+−ammonia[24] complexes. In comparison with the corresponding P^+−ammonia complex, here the electron density at the bond critical point is 0.0054 au greater and the $H(r_c)$ is more negative by 0.0027 au. This difference is due to methyl substitution on the nitrogen, and while it is significant, the effect is not as strong as in the water/methanol case, where methyl substitution on the oxygen increases the complexation energy by 14.1 kcal/mol.[15,25]

The forming of this P^+−N bond does weaken the C−N bond. This is seen most readily by comparing the C−N bond lengths of methylamine before (1.462 Å) and after (1.509 Å) complexation. Other bond properties also reflect this weakening. The $\rho(r_c)$ diminishes by 0.0419 au, and $H(r_c)$ is more negative by 0.0259 au (see Table 2).

The transfer of one hydrogen atom from nitrogen to phosphorus forms isomer **6** at −73.7 kcal/mol relative to the original reactants. While this transfer causes a destabilization of 22.0 kcal/mol to the system, it does strengthen the C−N−P skeleton. For this isomer, the positive charge density is centered primarily on the phosphorus atom and the spin is shared between the phosphorus and nitrogen.

A second hydrogen transfer from nitrogen to phosphorus yields aduct **12** at −57.5 kcal/mol relative to the reactants. Again, the system is destabilized (this time by 16.2 kcal/mol), and the C−N−P skeleton is strengthened. In particular, the P−N bond is the strongest in this group of isomers, as seen by

TABLE 1: G2(MP2) Total Energies (hartrees), Relative Energies (kcal/mol), and Estimated Values of $\langle S^2 \rangle$ for the Local Minima Found on the [H_5, C, N, P]$^+$ Triplet PES

system	G2(MP2)	$\Delta E_{G2(MP2)}$	$\langle S^2 \rangle$
$P^+ + CH_3NH_2$	−436.093 31	0.0	2.00
1	−436.245 90	−95.7	2.026
2	−436.232 86	−87.6	2.020
3	−436.223 89	−81.9	2.035
4	−436.216 91	−77.6	2.024
5	−436.214 99	−76.4	2.022
6	−436.210 81	−73.7	2.027
7	−436.197 98	−65.7	2.062
8	−436.197 36	−65.3	2.027
9	−436.195 82	−64.3	2.029
10	−436.190 11	−60.7	2.017
11	−436.185 21	−57.7	2.025
12	−436.184 96	−57.5	2.057
13	−436.183 77	−56.8	2.030
14	−436.182 64	−56.1	2.019
15	−436.176 75	−52.4	2.017
16	−436.174 25	−50.8	2.017
17	−436.171 36	−49.0	2.022
18	−436.155 53	−39.0	2.015
19	−436.153 21	−37.6	2.011
20	−436.145 17	−32.5	2.013

the bond lengths in Figure 1 and reflected in the values of $\rho(r_c)$ (0.1710) and $H(r_c)$ (−0.1298) (for comparisons see Table 2). Also, the plot of the Laplacian (Figure 2) shows an increase in the charge density between N and P if compared to isomer **1**. The results of the NBO analysis give more evidence of the strong bonding between N and P, reporting a π_{N-P} orbital with population 0.9770. In isomer **12**, the positive charge is centered on phosphorus and the spin density on nitrogen.

Returning to isomer **1** as a point of departure, successive migrations of hydrogens from carbon to phosphorus give isomers **8** and **20** (−65.3 and −32.5 kcal/mol, respectively). In these isomers, the effect on the C−N−P skeleton is to strengthen the C−N bond and weaken the P−N interaction (see Figure 1 and Table 2).

Isomer **13** (−56.8 kcal/mol) represents the extreme case of C−N bond strength and N−P bond weakness among this group of isomers—so much so that **13** can be considered as an ion-molecule complex between the cation CH_2NH^+ and PH2. The plot of the Laplacian (Figure 2) shows this quite well, depicting an electrostatic interaction between two closed systems. However, the value of $H(r_c)$ (−0.0430) indicates some covalency between the N and P and the NBO analysis gives a σ_{N-P} orbital with a population of 0.9862. The properties of the C−N bond of **13** demonstrate that it is the strongest among this group. The bond length is significantly shorter than in any other isomer, the value of $H(r_c)$ is more than double that of methylamine, and the NBO analysis detects the existence of a double bond.

Isomers **18** and **19** (−39.0 and −37.6 kcal/mol, respectively) are the only ones among this group in which the phosphorus atom is bonded to three hydrogens. These aducts are among the least favored energetically on the [H_5, C, N, P]$^+$ triplet PES, following the pattern that hydrogen migration to phosphorus destabilizes the system (though sometimes it does strengthen the heavy atom skeleton). The C−N and N−P bonds of isomers **18** and **19** are quite similar to those of isomer **12**, described above.

The C−P−N Skeleton. The most stable isomer with a heavy atom connectivity of C−P−N is isomer **2** (at −87.6 kcal/mol relative to the separated reactants). This isomer is formed by the insertion of the P^+ cation into the C−N bond of methylamine and is 8.1 kcal/mol less stable than the ion−molecule complex **1**. This energetic ordering is in direct contrast to that of the two corresponding isomers in the P^+−methanol system. There the insertion of P^+ into the C−O bond is favored over the ion−molecule complex by 7.5 kcal/mol.[15] In isomer **2**, the positive charge and the spin density are centered principly on the phosphorus atom. By observing Figure 4, one can observe the domination of covalent interactions in the C−P and P−N bonds. This is confirmed by the negative values of $H(r_c)$ for both bonds (see Table 3). The P−N bond is very strong. The short bond length (1.651 Å), comparable to that of isomers **12**, **18**, and **19** of the former group, is indicative of some double bonding character. Giving more support to the hypothesis of double bond character is the NBO analysis of the β electron density, which reports a π_{P-N} orbital with a population of 0.9865, similar to that found in the aforementioned isomers.

Isomers **3** and **11** (−81.9 and −57.7 kcal/mol respectively) can be considered as ion−molecule complexes of the ions PCH_2^+ and $HPCH^+$ with NH_3. The fact that **3** is one of the lowest energy isomers on the PES is not especially surprising considering the fact that all the hydrogens are still bonded to nitrogen and carbon. These adducts, formed by the donation of nitrogen lone pair electron density into an empty 3p orbital of phosphorus, have a P−N bond distance greater than that of a normal single bond between these two atoms. Note that although these isomers can be thought of as ion−molecule complexes, the N → P donation gives some covalent character to the bond. The plot of the Laplacian for isomer **3** reveals the existence of considerable charge concentration between P and N (Figure 4). Also the $H(r_c)$ values for this bond (−0.0718 and −0.0773 for **3** and **11**, respectively) ratify the existence of some covalent character.

Successive sigmatropic transpositions [1,2], with hydrogen migration from carbon to phosphorus, produce isomers **4** and **14** (−77.6 and −56.1 kcal/mol, respectively). These migrations destabilize the system without greatly changing the C−P−N skeleton. The largest change comes in the C−P bond length which is shorter by 0.079 Å in **4** and 0.101 Å in **14**. The values of $\rho(r_c)$ and $H(r_c)$ also reflect this strengthening (see Table 3). This C−P bond strengthening is due to π type interaction between the 2p semioccupied orbital of carbon and the σ^*_{P-N} orbital. The positive charge for both of these isomers is centered on phosphorus, while the density of spin is shared between carbon and phosphorus in **4** and is mostly isolated to carbon in isomer **14**.

Starting again with isomer **2**, migrations of hydrogen from nitrogen to phosphorus to form isomers **9** and **15** (−64.3 and −52.4 kcal/mol, respectively) destabilize the system even more than migrations from the carbon. These isomers are 23.3 and 35.2 kcal/mol higher in energy than isomer **2**. Note that in contrast the first H transfer from C to P costs the system only 10.0 kcal/mol. The effects on the C−P−N skeleton due to these migrations are minimal. For both isomers the charge remains centered on the phosphorus, although the spin is shared between phosphorus and nitrogen in **9** and mostly on nitrogen in **15**.

The N−C−P Skeleton. Only four minima with a N−C−P skeleton were found on the potential energy surface. Of those four, two are in a region of the PES which is *very* flat. At the G2(MP2)//MP2/6-31G(d,p) level of theory, isomer number **5** is 76.4 kcal/mol lower in energy than the separated reactants, only 3.8 kcal/mol below the products $CH_2NH_2^+$ + PH. The other minimum found in this level region of the surface is isomer number **7** (−65.7 kcal/mol). These two isomers have very long P−C bonds. The bond length in isomer **5** is a whopping 3.312 Å! In isomer **7** the P−C bond is 1.222 Å shorter, but at 2.090 Å is still longer than any of the other P−X bonds found on this triplet PES. The P−C bond in **7** is formed through an interaction of the semioccupied orbitals of phosphorus and the

TABLE 2: MP2/6-31G(d,p) Bond Properties (in au) of Methylamine and Systems with the C−N−P Skeleton Found on the [H_5, C, N, P]$^+$ Triplet PES[a]

	C−N				N−P			
system	distance	ρ	$\nabla^2\rho$	H	distance	ρ	$\nabla^2\rho$	H
CH_3NH_2	1.462	0.2682	−0.7834	−0.3105				
1	1.509	0.2263	−0.5365	−0.2846	1.897	0.1127	0.0726	−0.0835
6	1.453	0.2507	−0.4925	−0.3707	1.758	0.1368	0.3939	−0.0960
8	1.452	0.2556	−0.5672	−0.3767	1.930	0.1069	0.0019	−0.0789
12	1.427	0.2583	−0.4078	−0.3943	1.651	0.1710	0.6234	−0.1289
13	1.276	0.3727	−0.5026	−0.6526	2.046	0.0886	0.0047	−0.0430
18	1.393	0.2871	−0.4944	−0.4582	1.695	0.1743	0.3736	−0.1496
19	1.401	0.2762	−0.4758	−0.4306	1.652	0.1791	0.5977	−0.1413
20	1.445	0.2616	−0.6079	−0.3873	1.914	−0.1071	0.0399	−0.0793

[a] Bond distances in angstroms.

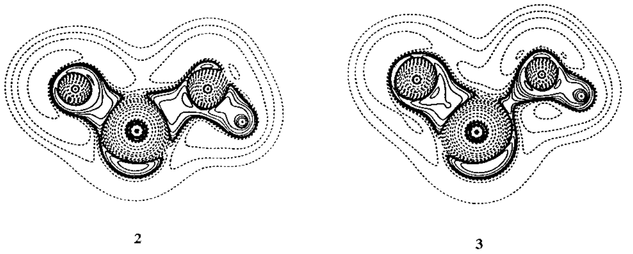

Figure 4. Contour maps of the Laplacian of isomers **2** and **3**. Positive values of $\nabla^2\rho$ are represented by solid lines and negative values with dashed lines.

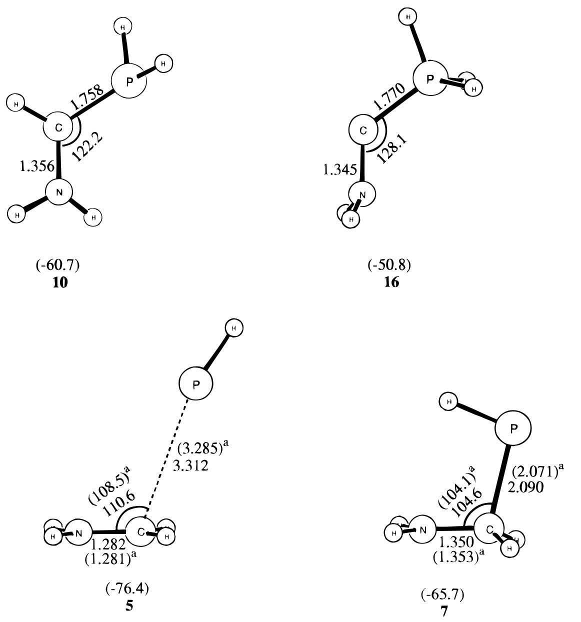

Figure 5. MP2/6-31G(d,p)-optimized geometries and G2(MP2) relative energies of the systems with a N−C−P heavy atom skeleton found on the [H_5, C, N, P]$^+$ triplet PES. Bond distances are in angstroms, angles in degrees, and relative energies in kilocalories per mole. (a) Geometrical parameters optimized at the MP2/6-311G(d,p) level of theory.

π_{C-N} orbital. The NBO analysis assigns this interaction a value of 50.8 kcal/mol and also detects an interaction between a phosphorus lone pair and the π^*_{C-N} orbital worth 25.1 kcal/mol.

The flatness of this region of the PES places some doubt on whether these minima are true features of the system, or only artifacts of the methods used. When the transition structure between **5** and **7** was characterized, it was found to have an energy 0.2 kcal/mol lower than that of **7** (remember that the G2(MP2) method includes zero-point vibrational energy corrections). Due to this, a larger basis set was used to better characterize this region. At the G2(MP2)//MP2/6-311G(d,p) level of theory, **7** has an energy of −73.7 kcal/mol relative to the reactants, isomer **5**, −75.0 kcal/mol, the transition state between the two, −71.2 kcal/mol, and the separated products, −74.3 kcal/mol. Here, although the transition state is now higher in energy than both **7** and **5**, we find that all of the points in this region are within 2 kcal/mol of −73 kcal/mol. As the margin of error for the G2(MP2) method is 2 kcal/mol, the only definite thing that can be said about this region of the PES is that it is very flat and any reaction mechanisms involving these structures should proceed quite easily.

Also within the group with the skeleton N−C−P are isomers **10** and **16** (−60.7 and −50.8 kcal/mol, respectively). These structures have P−C bonds of length similar to many of those with the C−P−N skeleton. In both isomers, the NBO analysis of the β electron density detects a π_{C-N} orbital, giving a description of partial double bond character to the C−N bond. The NBO analysis of the α electron density notes interactions between the semioccupied orbitals of carbon and the σ^*_{P-H} orbitals (one for isomer **10** with an interaction energy of 12.4 kcal/mol and two for isomer **16**, each with an interaction energy of 7.4 kcal/mol).

IV. Reaction Mechanisms

The experimental studies carried out by Smith and colleagues[6,7] utilizing the SIFT technique reported the following products of the $P^+ + CH_3NH_2$ reaction:

$$P^+ + CH_3NH_2 \rightarrow CH_2NH_2^{\ +} + PH \qquad (I)$$

$$P^+ + CH_3NH_2 \rightarrow {}^{\bullet}CH_3 + PNH_2^{\ +} \qquad (II)$$

with a distribution of 68% reaction I and 32% reaction II. In Table 5 are shown the total and relative energies (G2(MP2)) for these species. In addition, the energies of (atomic and molecular) hydrogen liberation are given. These energies are reported because hydrogen liberation is quite exothermic and also often involved in processes including the phosphorus cation. In Table 6 are collected the total and relative energies and the $\langle S^2\rangle$ expectation values of the transition state structures involved in the various reaction mechanisms proposed. These transition structures are depicted in Figure 6 and the proposed reaction mechanisms presented schematically in Figure 7. In all mechanisms, the starting point is the ion−molecule complex **1** which is formed without barrier from the reactants, as was the case for the reactions of P^+ with NH_3 and CH_3OH. The formation of **1** provides the system with an energy excess of 95.7 kcal/mol with which to overcome the barriers on the PES.

Formation of $CH_2NH_2^+$ and PH. The formation of $CH_2NH_2^+ + PH$ can occur through mechanism I depicted in Figure 7a. Starting with the ion−molecule complex **1**, migration of

TABLE 3: MP2/6-31G(d,p) Bond Properties (in au) of the Systems with the C−P−N Skeleton Found on the [H$_5$, C, N, P]$^+$ Triplet PES[a]

	C−P				P−N			
system	distance	ρ	$\nabla^2\rho$	H	distance	ρ	$\nabla^2\rho$	H
2	1.851	0.1551	−0.3402	−0.1417	1.651	0.1688	0.6985	−0.1198
3	1.776	0.1681	0.1143	−0.1596	1.940	0.1019	0.0235	−0.0718
4	1.772	0.1735	0.0192	−0.1811	1.649	0.1724	0.6917	−0.1251
9	1.812	0.1701	−0.2154	−0.1760	1.673	0.1683	0.5553	−0.1290
11	1.759	0.1678	0.1494	−0.1576	1.917	0.1057	0.0434	−0.0773
14	1.750	0.1747	0.1559	−0.1673	1.640	0.1804	0.6753	−0.1380
15	1.798	0.1755	−0.1708	−0.1830	1.752	0.1684	0.1779	−0.1535
17	1.757	0.1806	0.0475	−0.1808	1.690	0.1745	0.4384	−0.1453

[a] Bond distances in angstroms.

TABLE 4: MP2/6-31G(d,p) Bond Properties (in au) of the Systems with the N−C−P Skeleton Found on the [H$_5$, C, N, P]$^+$ Triplet PES[a]

	N−C				C−P			
system	distance	ρ	$\nabla^2\rho$	H	distance	ρ	$\nabla^2\rho$	H
5	1.282	0.3647	−0.4059	−0.6317	3.312	0.078	0.0236	+0.0011
7	1.350	0.3238	−0.8128	−0.5401	2.090	0.0947	−0.0677	−0.0441
10	1.356	0.3145	−0.7110	−0.5135	1.758	0.1746	0.0051	−0.1735
16	1.345	0.3241	−0.7589	−0.5370	1.770	0.1723	−0.0360	−0.1732

[a] Bond distances in angstroms.

TABLE 5: G2(MP2) Total Energies (in hartrees) and Relative Energies ($\Delta E_{G2(MP2)}$ in kcal/mol) of the Reactants and Possible Products of the Reaction P$^+$ (^{3}P) + CH$_3$NH$_2$ (^{1}A′)

system	G2(MP2)	$\Delta E_{G2(MP2)}$
P$^+$ (^{3}P) + CH$_3$NH$_2$ (^{1}A′)	−436.093 31	0.0
CH$_2$NH$_2$$^+$ (^{1}A′) + PH ($^3\Sigma^-$)	−436.209 00	−72.6
CH$_2$NHP$^+$ (^{3}A″) + H$_2$ ($^1\Sigma_g{}^+$)	−436.204 56	−69.8
PNH$_2$$^+$ (^{2}A′) + CH$_3$ (^{2}A′)	−436.179 58	−54.1
CH$_3$NHP$^+$ (^{2}A′) + H (^{2}S)	−436.165 01	−45.0

TABLE 6: G2(MP2) Total Energies (in hartrees), Relative Energies (in kcal/mol), and Estimated Values of $\langle S^2\rangle$ for the Transition States Involved in the Proposed Mechanisms for the P$^+$ (^{3}P) + CH$_3$NH$_2$ (^{1}A′) Reaction

system	G2(MP2)	$\Delta E_{G2(MP2)}$	$\langle S^2\rangle$
TS 5/7	−436.196 16	−64.5	2.073
TS 1/8	−436.177 33	−52.7	2.074
TS 7/8	−436.144 21	−31.9	2.112
TS 1/H$_2$	−436.121 31	−17.6	2.026

one hydrogen atom from carbon to phosphorus through **TS 1/8** leads to isomer **8**. The PH group then migrates from the nitrogen to the carbon to form isomer **7**. From that point, the separation into CH$_2$NH$_2$$^+$ and PH is quite facile, proceeding through **TS 5/7** and **5**.

As discussed previously, the surface in the region of isomers **7** and **5** is so flat that a higher level of theory [G2(MP2)//MP2/6-311G(d,p)] was applied. For the sake of consistency, this method was applied to all of the stationary points along this reaction path. The relative energies according to this higher level of theory appear in parentheses in Figure 7a. For this reaction path, there are two major barriers and in energy both are well below the level of the separated reactants. The largest single step barrier is the first one, where **TS 1/8** lies 43.1 kcal/mol above the minimum **1**. There is a drop in energy from that point of 12.4 kcal/mol to form **8** and then a rise of 23.9 kcal/mol to reach the highest point energetically on this path, **TS 8/7**. This transition state structure is still 39.8 kcal/mol *below* the energy of the original reactants. Following this peak is a drop of approximately 33 kcal/mol into the region of **7**, **TS 7/5**, **5**, and the separated products. The high exothermicity of this reaction and the accessibility of all transition states involved in the mechanism make this process one of the most probable in the reaction of the triplet phosphorus cation with methylamine. This is in accord with the experimental results.[6,7]

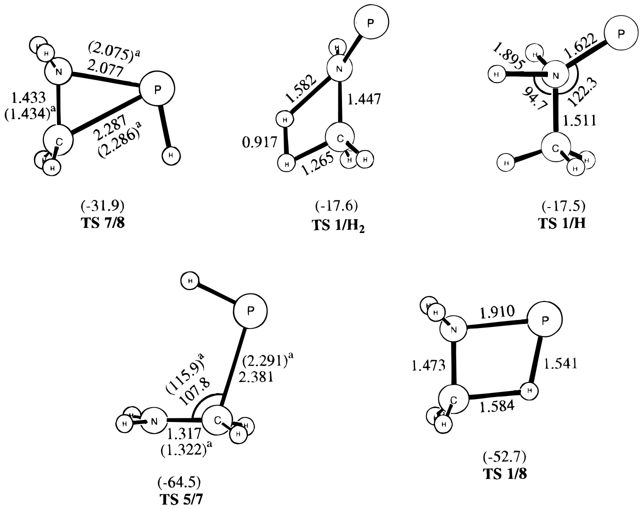

Figure 6. MP2/6-31G(d,p)-optimized geometries and G2(MP2) relative energies of the various transition states found on the [H$_5$, C, N, P]$^+$ triplet PES. Bond distances are in angstroms, angles in degrees, and relative energies in kilocalories per mole. (a) Geometrical parameters optimized at the MP2/6-311G(d,p) level of theory.

Formation of PNH$_2$$^+$ and CH$_3$. The liberation of CH$_3$ (^{2}A′) can occur through mechanism II of Figure 7a. After the formation of the ion−molecule complex **1**, the C−N bond is broken to permit the formation of the PNH$_2$ (^{2}A′) cation and the methyl radical. The MP2/6-31G(d,p) level of theory predicts that this bond-breaking step occurs without barrier, the only obstruction being the increase in energy from **1** to the products. This energy difference of 41.6 kcal/mol is nearly equal to the greatest single step barrier found in mechanism I (43.0 kcal/mol at the G2(MP2)//MP2/6-31G(d,p) level of theory). This similarity, along with the fact that reaction II is less exothermic than reaction I by 18.5 kcal/mol, is an indication that the two processes may be competitive. Smith and co-workers[6,7] found experimentally that the product distribution of the reaction of P$^+$ with CH$_3$NH$_2$ is 68% (CH$_2$NH$_2$$^+$ + PH) and 32% (PNH$_2$$^+$ + CH$_3$).

Liberation of H and H$_2$. Because hydrogen liberation frequently occurs in reactions involving P$^+$, the energies of the

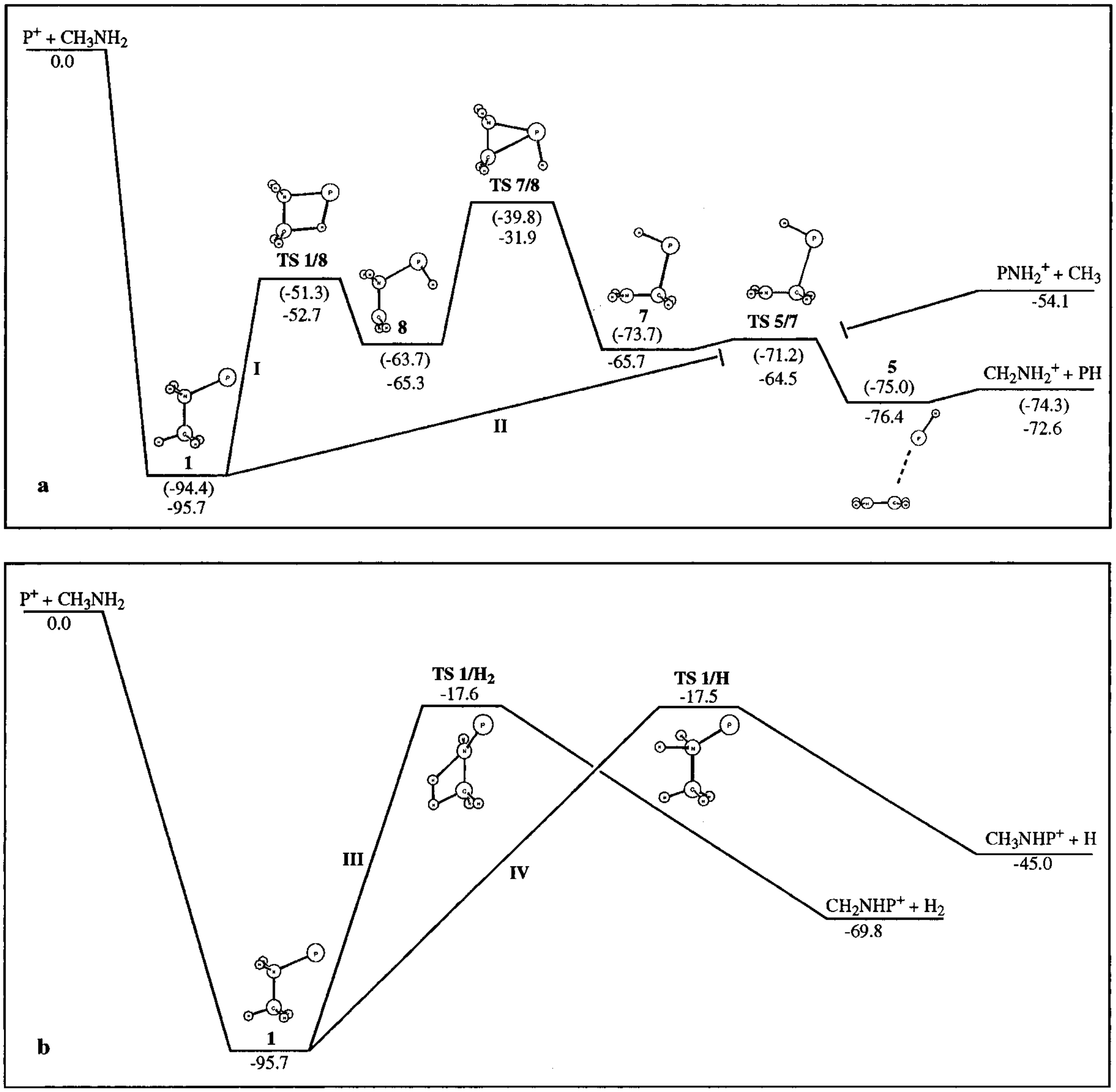

Figure 7. Schematic representation of the reaction mechanisms proposed. The energies given are the relative energies (in kcal/mol) calculated at the G2(MP2) level of theory. For mechanism I, the energies reported in parentheses are those given by the G2(MP2)//MP2/6-311G(d,p) level of theory.

following two reactions were determined:

$$P^+ ({}^3P) + CH_3NH_2 ({}^1A') \rightarrow CH_3NHP^+ ({}^2A') + H ({}^2S) \quad \text{(III)}$$

$$\Delta E_{G2(MP2)} = -45.0 \text{ kcal/mol}$$

$$P^+ ({}^3P) + CH_3NH_2 ({}^1A') \rightarrow CH_2NHP^+ ({}^3A'') + H_2 ({}^1\Sigma_g^{\ +}) \quad \text{(IV)}$$

$$\Delta E_{G2(MP2)} = -69.8 \text{ kcal/mol}$$

Both of these reactions are quite exothermic, but these products did not appear in the experiments of Smith *et al.*[6,7] In order to determine why this is true, the transition state structures for hydrogen elimination have been determined and are found to have energies a good bit higher than the transition states involved in either reaction I or II.

The liberation of H_2 can occur through mechanism III depicted in Figure 7b. The transition state structure **TS 1/H₂** shows that the process is a [1,2] elimination. This transition state lies only 17.6 kcal/mol below the reactants (78.1 kcal/mol above **1**). In terms of energetics, the liberation of atomic hydrogen is not very different from that of H_2. Mechanism IV in Figure 7b depicts this elimination. Here the **TS 1/H** transition state lies at −17.5 kcal/mol relative to the reactants, only 0.1 kcal/mol above **TS 1/H₂**. The process of atomic hydrogen liberation is, however, 24.8 kcal/mol less exothermic than that of molecular hydrogen.

Although both of these reactions are exothermic and the transition states lie below the original reactants in energy, the liberation of H and H_2 are disfavored with respect to reactions I and II. The elevated barriers of these reactions make them much less probable. Additionally, the transition structures involve long-distance hydrogen movement in potential wells which are much steeper than the wells involved in reactions I and II.

V. Conclusions

In this study of the $[H_5, C, N, P]^+$ triplet potential energy surface, many stationary points well below the energy level of the reactants, $P^+ ({}^3P) + CH_3NH_2$, have been found. The most stable adduct is the ion−molecule complex **1** (at −95.7 kcal/mol relative to the separated reactants) where $P^+ ({}^3P)$ is bound to the nitrogen of methylamine. The insertion of the phosphorus cation into the C−N bond is also a process which is energetically favorable, forming isomer **2** (−87.6 kcal/mol). Isomers **6** (−73.7 kcal/mol) and **7** (−65.7 kcal/mol), formed by the insertion of P^+ (^3P) into the N−H and C−H bonds, respectively, are higher in energy than the other isomers resulting from phosphorus insertion, but still well below the reactants. In general, the migrations of hydrogens from carbon or nitrogen to phosphorus destabilize the system although they frequently strengthen the heavy atom framework. This behavior was also found for the $[H_4, C, O, P]^+$ triplet PES.[15] The ion−molecule complex **1** has a N−C bond weaker than does methylamine; all other isomers found have stronger N−C bonds (if they have such a bond).

The formation of the ion−molecule complex **1** provides the system with a great amount of energy which is not easily dispersed in the conditions of interstellar media. Reaction mechanisms for the formation of ($CH_3NH_2^+ + PH$) and ($PNH_2^+ + CH_3$) have been found to have barriers which are easily surpassed with this excess energy. Mechanisms for hydrogen liberation have also been investigated, but the transition states for these processes lie only 18 kcal/mol below the reactants and involve long-distance hydrogen movement within steep potential wells. Thus, these processes are much less favored than the aforementioned reactions which have much smaller barriers. These results, along with the prediction that mechanisms I and II are energetically competitive along their paths, are in accordance with the experimental findings of Smith and co-workers.[6,7]

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Supporting Information Available: Table of atomic charges, spin densities, and dipole moments for the stationary points of the $[H_5, C, N, P]^+$ triplet PES (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Tuner, B. E.; Bally, J. *Astrophys. J.* **1987**, *321*, L75.

(2) Ziurys, L. M. *Astrophys. J.* **1987**, *321*, L81.

(3) Guelin, M.; Cernicharo, J.; Paubert, G.; Turner, B. E. *Astron. Astrophys.* **1990**, *230*, L9.

(4) Duley, W. W.; Williams, D. A. *Interstellar Chemistry;* Academic Press: New York, 1984.

(5) Thorne, L. R.; Anicich, V. G.; Huntress, W. T. *Chem. Phys. Lett.* **1984**, *280*, 139.

(6) Smith, D.; McIntosh, B. J.; Adams, N. G. *J. Chem. Phys.* **1989**, *90*, 6213.

(7) Adams, N. G.; McIntosh, B. J.; Smith, D. *Astron. Astrophys.* **1990**, *232*, 443.

(8) Nguyen, M. T.; Ha, T. K. *Chem. Phys.* **1989**, *131*, 245 and references therein.

(9) Maclagan, R. G. A. R. *J. Phys. Chem.* **1990**, *94*, 3373 and references therein.

(10) Glaser, R.; Horan, C. J.; Haney, P. E. *J. Phys. Chem.* **1993**, *97*, 6607 and references therein.

(11) Essefar, M.; Luna, A.; Mó, O.; Yáñez, M. *Chem. Phys. Lett.* **1994**, *223*, 240 and references therein.

(12) Largo, A.; Barrientos, C.; Lopez, X.; Coss'io, F. P.; Ugalde, J. M. *J. Phys. Chem.* **1995**, *99*, 6432 and references therein.

(13) Lopez, X.; Ayerbe, M.; Ugalde, J. M.; Coss'io, F. P. *J. Phys. Chem.* **1995**, *99*, 6812 and references therein.

(14) Esseffar, M.; Luna, A.; Mó, O.; Yáñez, M. *J. Phys. Chem.* **1994**, *98*, 8679.

(15) Cruz, E. M.; Lopez, X.; Ugalde, J. M.; Coss'io, F. P. *J. Phys. Chem.* **1995**, *99*, 12170.

(16) Luna, A.; Yáñez, M. *J. Phys. Chem.* **1993**, *97*, 10659.

(17) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(18) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

(19) Gaussian94 b.2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(20) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory;* Clarendon Press: Oxford, 1990.

(21) Biegler-König, F. W.; Bader, R. F. W.; Tang, T. *J. Comput. Chem.* **1982**, *3*, 317.

(22) NBO version 3.1. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.

(23) Biegler-König, F. W.; Bader, R. F. W.; Tang, T. *J. Comput. Chem.* **1980**, *27*, 1924.

(24) Largo, A.; Flores, J. R.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1991**, *95*, 170.

(25) Largo, A.; Redondo, P.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1991**, *95*, 5443.