Phosphonitrenium, Phosphonitrilium, and Aminophosphenium Cations. An *ab Initio* Study of the H_3PN^+ Isomers and the Decomposition of Azidophosphonium Salts†

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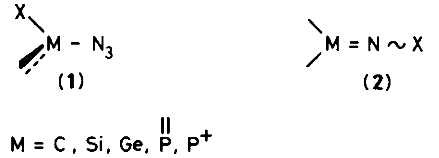
Portions of the singlet and triplet $[H_3PN^+]$ energy surfaces are investigated by *ab initio* calculations. Local minima corresponding to structures $H_3P{-}N^+$, $H_2P{-}NH^+$, and $HP{-}NH_2^+$, and transition structures connecting them *via* unimolecular 1,2-hydrogen shifts, were obtained at the HF/3-21G* level. Vibrational frequencies and thermochemical properties of the species considered are reported. The phosphonitrenium ion (H_3PN^+) has a triplet ground state ($^3A_2$) while its $^1A'$ singlet state corresponds to a saddle point. The singlet ground state H_2PNH^+ cation possesses a P–N triple-bond character and can thus be best regarded as a phosphonitrilium ion $H_2P{\equiv}N^+{-}H$. The singlet aminophosphenium ($HP{-}NH_2^+$) is the global minimum of the species considered. All the minima are separated from each other by large energy barriers. The intrinsic barriers ($\Delta G_0^\ddagger$, Marcus theory) are calculated to be 62 and 44 kcal mol^{-1} for the singlet and triplet $H_2PNH^+ \longrightarrow HPNH_2^+$ rearrangements, respectively. The triplet–singlet energy separations are compared with those of neutral and parent species. Calculated results appear *not* to support the proposition that the photolysis of azidophosphonium salts ($\geqslant P{-}N_3^+X^-$) involve nitrene ($\geqslant P{-}N^+$) as intermediate. They suggest rather a concerted migration–nitrogen loss mechanism or a nucleophile substitution depending upon the nature of the counteranion (X^-).

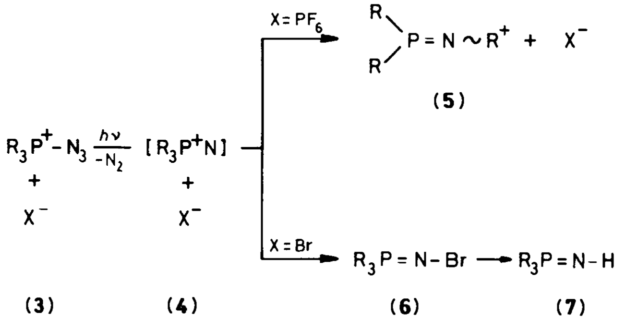
The Curtius-like rearrangement is now a well established route for the preparation of a wide variety of di-co-ordinated nitrogen derivatives (2) from the corresponding azides (1).[1] In the phosphorus series, several known examples involve species in which the azide group is bonded to a tetra-,[2] or to a penta-co-ordinated phosphorus atom.[1]

Recently Mulliez *et al.*[3] reported evidence for a Curtius-like rearrangement involving a phosphorus cation. When the azidophosphonium salt (3) was irradiated at room temperature, either an iminophosphonium salt (5) or an iminophosphorane (7) was obtained as the final product (with release of nitrogen) depending upon the nature of the counteranion. As a possible rationalization, these authors[3] postulated the existence of a phosphonitrenium ion (4) as a transient intermediate during the photolysis of (3). The poor nucleophile PF_6^- could facilitate migration of a phosphorus substituent onto the nitrogen atom whereas the active participation of the nucleophile Br^- could lead first to the formation of the bromine derivative (6) which is subsequently converted into the final product (7).

In connection with our continuing study on the mechanism of the Curtius rearrangement, we have carried out *ab initio* calculations on the energy surface of the model H_3PN^+ ion. Recent similar calculations on the H_2PN[4] and H_3CP[5] systems have contributed to the understanding of the decompositions of phosphinoazides ($>P{-}N_3$) and phosphinodiazomethane ($>P{-}CN_2$). Reported theoretical results[4,5] appear to support the proposition that the phosphinonitrene ($>P{=}N$) and phosphinocarbene ($>P{-}C{-}R$) species, respectively, are the intermediates in these reactions.

In this work, there was particular interest in determining the structure and relative stabilities of three possible isomers, namely the phosphonitrenium ($H_3P{=}N^+$), iminophosphonium ($H_2P{=}N{-}H^+$), and aminophosphenium ($HP{-}NH_2^+$) ions, and the transition structures linking them (*via* a unimolecular 1,2-hydrogen shift between the phosphorus and nitrogen atoms).





Scheme.

The rearrangement was considered in both the lowest singlet and triplet electronic states.

Calculations

Two basis sets have been employed in this work. The first consists of the 3-21G* set (split-valence plus *d*-functions on phosphorus only).[6] To form the second basis set, the 6-31G set was augmented with a set of polarization *d*-functions,[7] diffuse *s*- and *p*-functions[8] on phosphorus and nitrogen, and a set of *s*-diffuse functions on hydrogen. This basis is referred to as 6-31 + + G* in the text. Geometries of stationary points were optimized from analytically computed energy gradients at the single determinantal SCF level with the 3-21G* basis set. The triplet states were studied using the unrestricted Hartree–Fock (UHF) formalism. Corresponding harmonic vibrational frequencies

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† Non SI-units employed: 1 cal = 4.184 J.

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and some thermochemical parameters were determined at the HF/3-21G* level. The energies of the points along the rearrangement pathways were recomputed at the 3-21G*-optimized geometries by fourth-order Møller–Plesset perturbation theory (MP4SDQ including single, double, and quadruple electron excitations)[9] making use of the HF/6-31 + +G* wavefunctions as references for generating excited configurations. All calculations used the Gaussian 82 program.[10]

Results and Discussion

(1) *The Singlet State: Iminophosphonium* versus *Phosphonitrilium Cation.*—The geometries of the five stationary points on the singlet H_3PN^+ energy surface determined at the HF/3-21G* level are shown in Figure 1. They include three cations: phosphonitrenium (**8**), iminophosphonium (**10**), and aminophosphenium (**12**) and two transition states (**9**) and (**11**) for the 1,2-hydrogen shifts. Table 1 lists the corresponding calculated total and relative energies considered at three levels of accuracy, along with the zero-point vibrational energies (ZPE, 3-21G*), entropies (S), and specific heat capacities (C_p).

At the HF/3-21G* level, the closed shell singlet H_3PN (**8**) is a high-energy local minimum and converts into the more stable isomer (**10**) *via* the transition state (**9**) by an energy barrier of 13.3 kcal mol^{-1}. Extending the basis set reduces the latter to 7.4 kcal mol^{-1} (HF/6-31+ +G*). After correction for correlation and vibration, the transition state (**9**) finally becomes lower in energy than (**8**), indicating that the phosphonitrenium H_3PN^+ is, in fact, a saddle point in the singlet energy surface. Such a situation totally differs from that in the deprotonated species, H_2PN, which has been shown to be quite stable in its singlet ground state (with energy barrier of 33 kcal mol^{-1}).[4] In contrast, the non-existence of H_3PN^+ (**8**) classifies it with the closed-shell singlet methylnitrene (CH_3N,$^1A'$) for which no barrier for the conversion into singlet CH_2=NH was found.[11,12] For the latter, an open-shell singlet state ($^1A''$) has recently been shown to be a possible intermediate in the photodecomposition of methyl azide.[13]

It is noted in Figure 1 that (**10**) possesses a planar and (P–N–H) linear structure while isovalent molecules such as the phosphinocarbene H_2PCH[5] and phosphinosilylene H_2PSiH[14] have angular structures. The linearity of the P–N–H group no doubt arises from a strong interaction between the phosphorus lone pair and the empty *p* orbital on nitrogen as in (**13**). Nitrogen, which is more electronegative than phosphorus, should strongly attract the free electron pair on phosphorus thus allowing it to participate fully in the bonding. The calculated bond length in (**10**) (1.453 Å) is even shorter than those in phosphinonitrene (H_2PN, 1.511 Å), and iminophosphane (HP=NH, 1.553 Å, at HF/3-21G*).[4] Such a stabilization is no longer possible either in H_2P–CH or in H_2P–Si–H where the angular (H_2PCH) or non-planar (H_2PSiH) structure allows these systems to avoid a destabilizing repulsion between

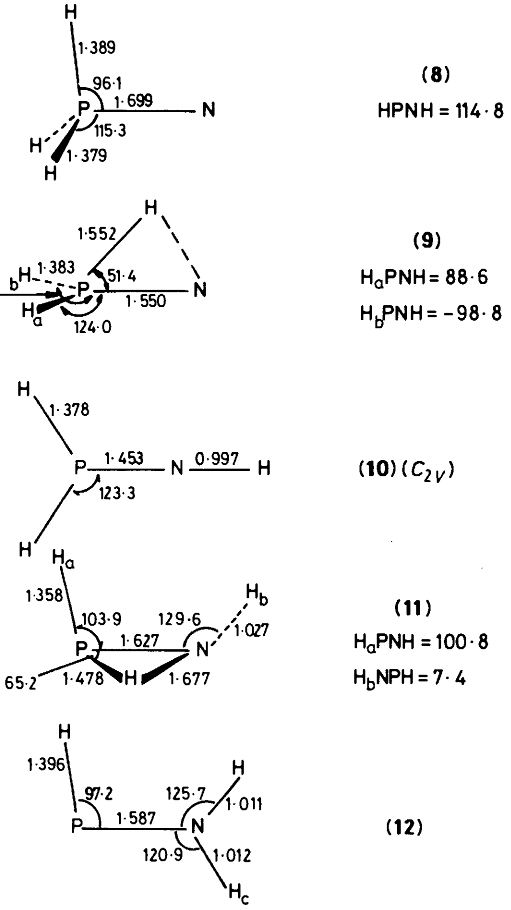
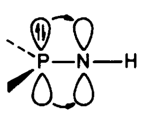


Figure 1. Optimized geometries (3-21G*) of five stationary points on the singlet [H_3PN^+] energy surface. Bond lengths in Å and bond angles in degrees



(**13**)

Table 1. Total (a.u.) and relative (kcal mol^{-1}, in parentheses) energies and some thermochemical parameters of five stationary point on the singlet [H_3PN^+] energy surface[a]

	(8) H_3PN^+	(9)	(10) H_2PNH^+	(11)	(12) $HPNH_2^+$
HF/3-21G*	−394.530 29	−394.509 80	−394.636 30	−394.555 90	−394.714 45
	(115.6)	(128.9)	(49.0)	(99.5)	(0.0)
HF/6-31+ +G*	−396.457 96	−396.446 18	−396.557 16	−396.485 67	−396.635 50
	(111.4)	(118.8)	(49.2)	(94.0)	(0.0)
MP4SDQ/6-31+ +G**	−396.712 71	−396.730 84	−396.843 85	−396.777 07	−395.922 43
	(131.6)	(120.2)	(49.3)	(91.2)	(0.0)
ZPE[b]	19.9	17.4	21.3	19.0	24.5
S_{298}[c]			58.8	58.0	57.6
$C_{p_{298}}$[d]			11.8	10.0	9.6

[a] Using HF/3-21G* geometries given in Figure 1. [b] Zero-point energies at HF/3-21G*, kcal mol^{-1}. [c] Entropy at 298 K, cal mol^{-1} K^{-1}. [d] Specific heat capacity at 298 K, cal mol^{-1} K^{-1}.

electron pairs. Moreover, the calculated P–N stretching frequency of 1 508 cm^{-1} (Figure 2) is markedly larger than those previously found in typical P=N double bonds (1 200—1 250 cm^{-1}). Also, the N–H stretching frequency (3 829 cm^{-1}) is larger (*ca.* 200 cm^{-1}) than those of a typical amino group (see Figure 2). These molecular features thus suggest a triple-bond character (or at least more than double-bond character) for the P–N bond in the singlet H_2PNH^+ (**10**). As a consequence, this species may be best regarded as a phosphonitrilium cation ($H_2P{\equiv}N{-}H^+$) rather than an iminophosphonium ion (or phosphinonitrenium cation, $H_2P{-}N{-}H^+$).

With regard to the aminophosphenium ion (**12**), the present 3-21G* geometry compares well with that determined in a previous *ab initio* pseudo-potential study (using a double-zeta plus *d*-functions on P)[15] which also investigated the rotational barrier around the P–N bond and proton affinities of the H_2PN species. The geometric aspects of (**12**) have been discussed in detail in ref. 15. It is noted that: (a) the ion (**12**) is planar with a bent HPN group; (b) its calculated P–N bond length of 1.587 Å (1.592 Å by SCF pseudopotentials[15]) is comparable to the *X*-ray value of 1.61—1.62 Å obtained for $[P(Pr^i_2N)_2{}^+, AlCl_4{}^-]$;[16] (c) the P–N stretching frequency of 1 162 cm^{-1} (Figure 2) is smaller but close to those of a typical P=N double bond (1 200—1 250 cm^{-1}).[4]

Finally, the transition state (**11**) connecting (**10**) to (**12**) possesses a non-planar structure. Like the $H_2PN \longrightarrow HPNH$ conversion,[4] the out-of-plane migration of the hydrogen-atom can be seen as a result of the predominance of the electronic factor over the steric one.

It is noted that there is an overall shift to lower stretching frequencies in the transition structure (**11**) with respect to those in both minima (**10**) and (**12**) (Figure 2). The imaginary frequency (1 198i cm^{-1}) is similar to that previously found (1 222i cm^{-1}) for the $H_2P{-}CH \longrightarrow HP{=}CH_2$ rearrangement.[5]

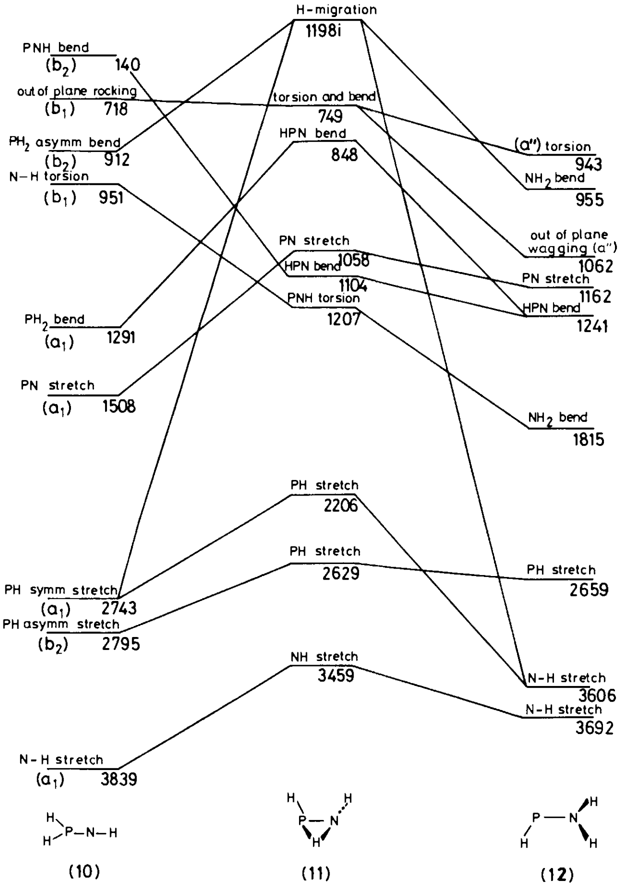


Figure 2. Vibrational frequency correlation diagram for three singlet species calculated at 3-21G*, values are given in cm^{-1} (scale is arbitrary)

Table 2 lists some thermochemical parameters relating to the singlet phosphonitrilium–aminophosphenium isomerization. As expected, the entropy variation is negligible. The transformation (**10**) $\longrightarrow$ (**12**) is mildly exothermic with a free energy of reaction ΔG (298 K) of -46.4 kcal mol^{-1} and has a substantial free energy of activation, $\Delta G^{\ddagger}$ (298 K) of 39.3 kcal mol^{-1}. Both the values ΔH (0 K) -46.1 and $\Delta H^{\ddagger}$ (0 K) 39.6 kcal mol^{-1} are larger than those of -39.6 and 33.1 kcal mol^{-1}, respectively, previously computed for the isomerization of neutral species.[4] In this context, the principal effect is that the nitrogen protonation stabilizes both protonated species.

Employing energy data from ref. 4, the N-site proton affinities (PAs) of the H_2PN species (at the MP4SDQ/6-31 + + G* level plus ZPE corrections) are:

$H_2P{=}N$: PA (N-site) 200.2 kcal mol^{-1}
trans-HP=NH: PA (N-site) 206.7 kcal mol^{-1}

The MP4 value, without ZPE corrections, for the PA of the *trans*-HP=NH of 216.1 kcal mol^{-1} compares favourably with the CIPSI-pseudopotential value of 220 kcal mol^{-1}[15] and lies in the range of expected values for sp^2 and sp^3 nitrogen compounds.[17]

It is also noted that the energy barrier [ΔH(0 K)] for the isoelectronic $H_2PCH \longrightarrow HPCH_2$ rearrangement amounts only to 18 kcal mol^{-1} at the same level of calculations.[5] This correlates well with the fact that the phosphonitrilium cation can actually be isolated in a salt[3] whereas the existence of the phosphinocarbene is hypothetical.[18]

Finally, Table 3 shows the net charges and dipole moments of three singlet species (**10**)—(**12**). In all cases, the nitrogen atom is negatively charged. Owing to the electronegativity difference, the N $\longrightarrow$ P back-donation of the nitrogen lone pair into the 3*p* empty orbital of phosphorus in (**12**) is small, thus leading to an appreciable negative charge on N in (**12**).

Table 2. Thermochemical properties of the singlet H_2PNH^+ (**10**) $\longrightarrow$ $HPNH_2{}^+$ (**12**) rearrangement

Property[a]		Estimated value
Heat of reaction (kcal mol^{-1})	ΔH (0 K)	-46.1
	ΔH (298 K)	-46.8
Entropy of reaction (cal mol^{-1} K^{-1})	ΔS (298 K)	-1.2
Free energy of reaction (kcal mol^{-1})	ΔG (298 K)	-46.4
Energy barrier (kcal mol^{-1})	$\Delta H^{\ddagger}$ (0 K)	39.6
	$\Delta H^{\ddagger}$ (298 K)	39.1
Activation entropy (cal mol^{-1} K^{-1})	$\Delta S^{\ddagger}$ (298 K)	-0.8
Free energy of activation (kcal mol^{-1})	$\Delta G^{\ddagger}$ (298 K)	39.3

[a] ΔK (0 H) = Δ(MP4) + ΔZPE, see Table 1; ΔH (298 K) = ΔH (0 K) + $\int \Delta C_p dT$; $\Delta S_{12} = S_2 - S_1$; $\Delta G = \Delta H - T\Delta S$.

Table 3. Atomic net charges and dipole moments of three singlet stationary points (HF/6-31 + + G*)

	(**10**)	(**11**)	(**12**)
Net charges			
P	0.81	0.60	0.86
N	-0.59	-0.31	-0.91
H[a]	0.12	0.18	0.50
Dipole moment (D)	1.69	3.96	1.29

[a] Migrating hydrogen.

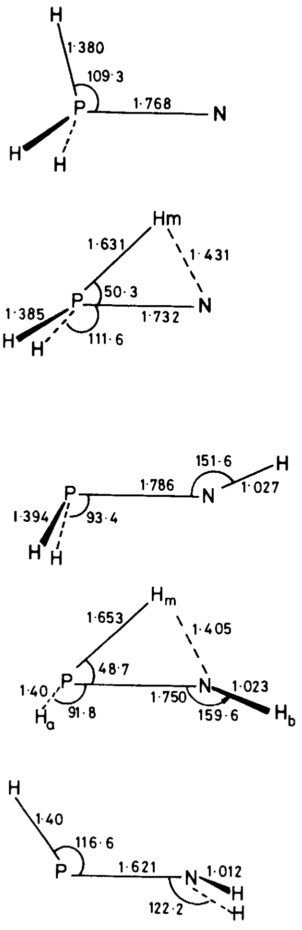
The transition structure (**11**) is the most polar species having a large dipole moment (3.96 D). A polar solvent would thus stabilize it most. Under this condition, the activation barrier would be lowered making the interconversion (**10**) $\rightleftharpoons$ (**12**) energetically more favourable and consequently destabilizes the phosphonitrilium ion (**10**).

(2) *The Triplet State*.—The HF/3-21G*-optimized geometries of five stationary points (**14**)—(**18**) on the lowest triplet H_3PN^+ energy surface are displayed in Figure 3. Corresponding total and relative energies are recorded in Table 4 along with some thermochemical parameters. Harmonic vibrational frequencies are given as a correlation diagram in Figure 4.

As expected, H_3PN^+ (**14**) has C_{3v} symmetry ($^3A_2$) and both the H_2PNH^+ (**16**) and $HP\text{-}NH_2^+$ (**18**) exhibit pyramidalized and *trans*-bent configurations.

In comparison with the 3-21G*-geometries of the triplet H_2P–N and H_3C–P species previously reported, in refs. 4 and 5, the following points are noted.

(a) Both the P–N bond lengths of 1.768 Å in (**14**) and 1.786 Å



(**14**)

(C_{3v})

(**15**) (C_s)

$HPNH_m = \pm 116{\cdot}3$

(**16**)

$HPNH = \pm 130{\cdot}8$

(**17**)

$H_aPNH_m = 92{\cdot}3$

$H_bNPH_m = 146{\cdot}6$

(**18**)

$HNPH = \pm 95{\cdot}9$

Figure 3. Optimized geometries (3-21G*) of five stationary points on the triplet [H_3PN^+] energy surfaces. Bond lengths in Å and bond angles in degrees

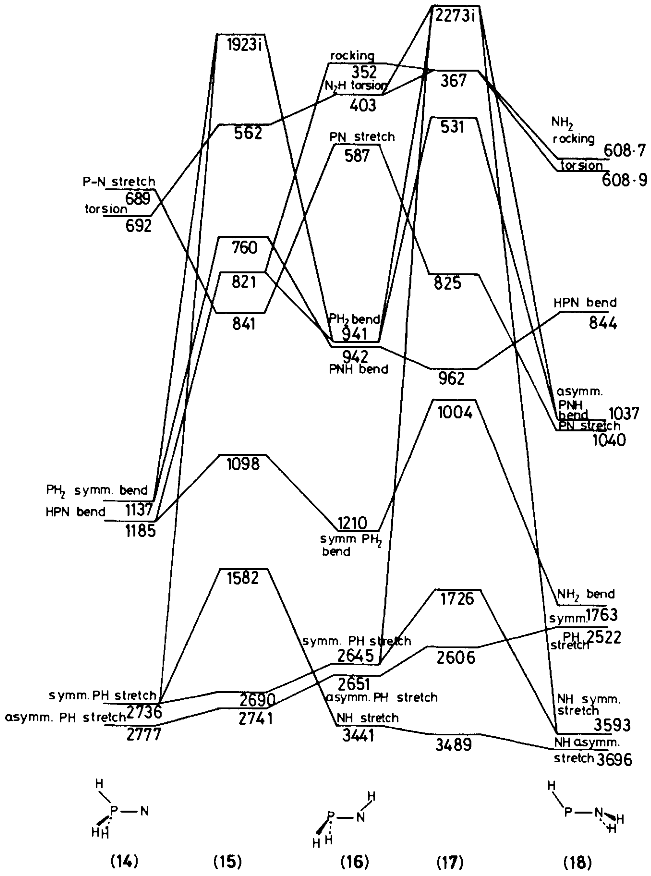


Figure 4. Vibrational frequency correlation diagram for the five triplet species calculated at 3-21G*. Values are given in cm^{-1} (scale arbitrary)

Table 4. Total (a.u.) and relative (kcal mol^{-1}, in parentheses) energies and some thermochemical parameters for five stationary point on the singlet [H_3PN^+] energy surface[a]

	(14) $H_3P\text{-}N^+$	(15)	(16) $H_2P\text{-}NH^+$	(17)	(18) $HP\text{-}NH_2^+$
HF/3-21G*	−394.627 30	−394.524 51	−394.631 89	−394.556 76	−394.638 10
	(0.0)	(64.5)	(−2.9)	(44.3)	(−6.8)
HF/6-31 + +G*	−396.556 94	−396.457 17	−396.553 27	−396.478 85	−396.581 47
	(0.0)	(62.6)	(2.3)	(49.0)	(−15.4)
MP4SDQ/6-31 + +G**	−396.786 81	−396.708 62	−396.792 41	−396.738 99	−396.819 66
	(0.0)	(49.1)	(−3.5)	(30.0)	(−34.5)
ZPE[b]	19.8	15.9	18.8	16.5	22.5
S_{298}[c]	58.9	61.1	62.8	61.8	60.6
$C_{p_{298}}$[d]	11.2	11.3	13.1	12.1	11.3

[a] Using HF/3-21G* geometries given in Figure 3. [b] Zero-point energies at HF/3-21G*, kcal mol^{-1}. [c] Entropy at 298 K, cal mol^{-1} K^{-1}. [d] Specific heat capacity, cal mol^{-1} K^{-1}.

Table 5. Thermochemical properties of the triplet **(14)** ⟶ **(16)** and **(16)** ⟶ **(18)** rearrangements

		Estimated value	
Property[a]		**(14)** ⟶ **(16)**	**(16)** ⟶ **(18)**
Heat of reaction (kcal mol^{-1})	ΔH (0 K)	−4.5	−27.3
	ΔH (298 K)	−4.0	−27.8
Entropy of reaction (cal mol^{-1} K^{-1})	ΔS (298 K)	3.9	−2.2
Free energy of reaction (kcal mol^{-1})	ΔG (298 K)	−5.2	−27.1
Energy barrier (kcal mol^{-1})	$\Delta H^{\ddagger}$ (0 K)	45.2	31.2
	$\Delta H^{\ddagger}$ (298 K)	42.2	30.9
Activation entropy (cal mol^{-1} K^{-1})	$\Delta S^{\ddagger}$ (298 K)	2.2	−1.0
Free energy of activation (kcal mol^{-1})	$\Delta G^{\ddagger}$ (298 K)	41.5	31.2

in **(16)** are comparable to that of 1.776 Å in H_2P–N ($^3A''$) (the C–P bond in H_2P–CH is 1.782 Å) while the distance of 1.621 Å in **(18)** is shorter than that of 1.705 Å in HP–NH (the C–P bond in HP–CH_2 being 1.801 Å).

(b) The degree of pyramidalization of the P atom in **(16)** (H$\hat{\mathrm{P}}$N 93.4°) is slightly stronger than those in H_2P–N (H$\hat{\mathrm{P}}$N 96.9°) and in H_2P–CH (H$\hat{\mathrm{P}}$C 99.1°). In contrast the N atom in **(18)** is marginally pyramidal.

(c) The PNH bond angle of 151.6° in **(16)** is much larger than that of 120.4° in HP–NH and the PCH angle in H_2PCH (134°). Likewise, the HPN angle of 116.6° in **(18)** is larger than that of 96° in PH–NH. Structure **(16)** resembles a strong complex between $PH_2{}^+$ and NH species. Hence, one can say that geometric parameters of the triplet phosphinonitrene are less affected by both the P- and N-site protonations than its isomer iminophosphane.

As would be expected, the hydrogen-shift in the transition state **(15)** occurs in the C_s-plane (as in CH_3P and CH_3N) whereas that in **(17)** adopts a lateral pathway (similar to H_2PCH and H_2PN).

Consistent with its shorter bond lengths (see above) the P–N stretching frequency of 1 040 cm^{-1} in **(18)** is markedly larger than those in other triplet states (Figure 4). This suggests a certain P–N double-bond character for the triplet aminophosphenium ion **(18)**. The P–N stretching frequencies in two potential minima **(14)** and **(16)** lie in the region 600—700 cm^{-1}. We note that the PN bond in both transition structures **(15)** and **(17)** possesses larger stretching frequencies than the minima **(14)** and **(16)**.

The positions of the migrating-hydrogen atoms are similar in both triplet transition states. For instance, the ratio of P–H_m and N–H_m distances are rather close: 1.139 in **(15)** and 1.176 in **(17)**. They differ, however, from that of 0.881 in the singlet transition state **(11)**.

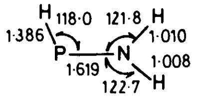
Table 5 shows some thermochemical parameters relevant to both triplet unimolecular rearrangements. In contrast to what would be suggested by the imaginary frequencies in associated transition states, the isomerization **(14)** ⟶ **(16)** *via* **(15)** (ν_i 1 923i cm^{-1}) has a larger free activation of energy [$\Delta G^{\ddagger}$ (298 K) 41.5 kcal mol^{-1}] than **(16)** ⟶ **(18)** *via* **(17)** [ν_i 2 273i cm^{-1} and $\Delta G^{\ddagger}$ (0 K) 31.2 kcal mol^{-1}].

The entropy variation in the process **(14)** ⟶ **(16)** is small but positive while that in the **(16)** ⟶ **(18)** becomes negative. Both interconversions are moderately exothermic having free energy of reaction, ΔG (298 K), of −5.2 kcal mol^{-1} for the former and −27.1 kcal mol^{-1} for the latter.

In the opposite direction, the conversions **(18)** ⟶ **(16)** and **(16)** ⟶ **(14)** are more difficult to perform, with free energies of activation of 46.7 and 58.3 kcal mol^{-1}, respectively.

Previously, the barrier to rotation around the P–N bond in the singlet aminophosphenium **(12)** has been calculated at 55 kcal mol^{-1}, using a pseudopotential-CI method.[15] For purposes of comparison, the transition structure **(19)** for the internal rotation in the triplet species **(18)** has been located (UHF/3-21G*).

At the MP4SDQ/6-31++G* level, with ZPE corrections,



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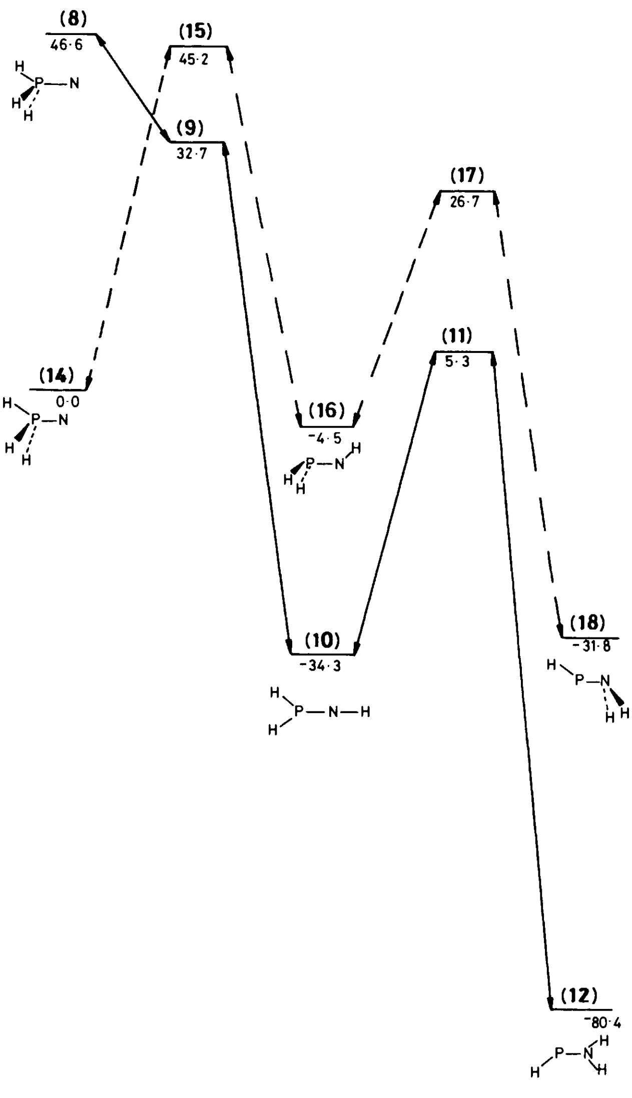


Figure 5. Relative energies [ΔH (0 K) in kcal mol^{-1}] of the pathways for isomerization of the singlet and triplet [H_3PN^+] species

the energy difference between (**18**) and (**19**) amounts only to 13 kcal mol^{-1}. Accordingly, the multiple-bond character of the N–P bond is rather strong in the singlet electronic state.

(3) *Comparison with Previous Studies.*—To facilitate comparison with previous studies,[4,5] we summarize in Figure 5 the energy differences between stationary points considered at the MP4 level, corrected by ZPE contributions [ΔH and $\Delta H^{\ddagger}$ (0 K) values given are in Tables 2 and 5].

The singlet aminophosphenium ion (**12**) is the globally most stable species. The phosphonitrilium ion has a singlet ground state (**10**) while the phosphonitrenium ion exhibits a triplet ground state (**14**).

The latter lies at 80.4 and 34.3 kcal mol^{-1} above the singlets (**12**) and (**10**), respectively.

The triplet–singlet separation energies can be compared with those in relevant neutral and parent species as follows:

$H_2P\text{–}NH^+$: 29.8 kcal mol^{-1} (this work)
$H_2P\text{–}N$: 7 kcal mol^{-1} (ref. 4)
$H_2P\text{–}CH$: 3 kcal mol^{-1} (ref. 5)
$H\text{–}NH^+$: -29 kcal mol^{-1} (ref. 19)
$HP{=}NH_2{}^+$: 48.6 kcal mol^{-1} (this work)
$HP{=}NH$: 36.2 kcal mol^{-1} (ref. 4)
$HP{=}CH_2$: 39.0 kcal mol^{-1} (ref. 5)
$H\text{–}P\text{–}H^+$: 22.0 kcal mol^{-1} (ref. 20)

Hence, the singlet states of cationic species seem to have gained stability relative to the triplets. In addition, both the phosphino- and amino-substituents exert a strong π-donor effect by stabilizing the singlet electronic state at the expense of the relevant triplets.

As stated above, the energy barrier for the isomerization (**14**) $\longrightarrow$ (**15**) $\longrightarrow$ (**16**) is high, the $\Delta H^{\ddagger}$ (0 K) being 45.2 kcal mol^{-1}. Likewise, the barrier necessary to convert (**16**) into (**18**) is substantial, $\Delta H^{\ddagger}$ (0 K) 32.2 kcal mol^{-1}.

It can thus be predicted that all triplet species could be detectable in inert matrices at low temperatures. The phosphonitrenium (**14**) can be seen as a quite stable species.

As mentioned above, in its singlet ground state, the phosphonitrilium ion (**10**) does not isomerize, *via* a direct 1,2-hydrogen shift, to the more stable isomer aminophosphenium (**12**). This is even more likely whenever the hydrogen atoms are replaced by poorer migrating groups (such as fluorine or bulky alkyl substituents).

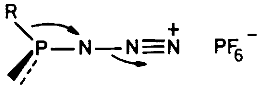
Within the framework of the Marcus theory,[21] the 'intrinsic barrier' ($\Delta G_0{}^{\ddagger}$, when $\Delta G = 0$) can be related to the free energy of reaction (ΔG) by relationship (1)[22,23] where α is the Brønsted exponent.

$$\alpha \equiv \frac{1}{2}\left(1 + \frac{\Delta G}{2\Delta G_0{}^{\ddagger}}\right) \qquad (1)$$

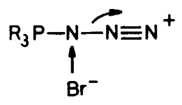
Employing energy data given in Tables 2 and 5, the parameters α and $\Delta G_0{}^{\ddagger}$ for each rearrangement can be derived and are listed in Table 6 (for details of calculations, see ref. 23). The calculated intrinsic barrier is almost the same for each triplet isomerization and amounts to $\Delta G_0{}^{\ddagger}$ *ca.* 44 kcal mol^{-1}. The intrinsic barrier for the singlet process is much larger, $\Delta G_0{}^{\ddagger}$ *ca.* 62 kcal mol^{-1}. It is however closer to the values of 64 ± 2 kcal mol^{-1} obtained for three unimolecular rearrangements $H_3P\text{–}X \rightleftharpoons H_2P\text{–}XH$ (X = O, NH and CH_2 at MP4SDQ/6-31G** with 3-21G*-geometries),[23] in their singlet ground states. Accordingly, the 1,2-hydrogen migrations occurring in the triplet and singlet electronic states belong rather to different homogenous series of reactions rather than only one.

Table 6. Bond order at transition state (n_{TS}), Brønsted exponent (α), and intrinsic barrier ($\Delta G_0{}^{\ddagger}$) of the three unimolecular rearrangements (**10**) $\longrightarrow$ (**12**), (**14**) $\longrightarrow$ (**16**), and (**16**) $\longrightarrow$ (**18**)

Rearrangement	[$\alpha = n_{TS}$]	$\Delta G_0{}^{\ddagger}$/kcal mol^{-1}
Singlet $H_2P\text{–}NH^+$ (**10**) $\longrightarrow$ $HP\text{–}NH_2{}^+$ (**12**)	0.314	62.6
Triplet H_3PN^+ (**14**) $\longrightarrow$ H_2PNH^+ (**16**)	0.471	44.0
Triplet H_2PNH^+ (**16**) $\longrightarrow$ $HPNH_2{}^+$ (**18**)	0.349	44.8



(**20**)



(**21**)

(4) *Concluding Remarks.*—Figure 5 provides some information on the possible role of phosphonitrenium ions (**4**) in azide photolysis (Scheme). (a) The phosphonitrilium ion (**5**) ($>P{=}N\text{–}{}^+$) seems to be formed *via* another mechanism, such as a concerted substituent migration–nitrogen loss process [from the singlet ground-state azide, see (**20**)] rather than *via* a (singlet or triplet) nitrene intermediate. The poor nucleophile $PF_6{}^-$ may not be involved at all in the rearrangement.

(b) If the bromo-compound (**6**) also exists as a further intermediate,[3] its formation could solely arise either from a fixation of the strong nucleophile Br^- onto the stable cation (**4**) in its triplet ground state or from a substitution of N_2 by Br^- in the starting azide (**3**) [see (**21**)]. Thus the direct photolysis of the bromo-azide may occur in both the triplet excited (fixation) and singlet ground (substitution) states. The participation of the counteranion is crucial.

(c) Since both azides have been irradiated under the same conditions but for the counteranion ($PF_6{}^-$ or Br^-),[3] their photodecompositions are likely to occur in the singlet electronic state. In this context, the nitrene (**4**) does not involve in the photochemical process.

In summary, the present theoretical study does not support the proposition that both transformations (**3**) $\longrightarrow$ (**5**) and (**3**) $\longrightarrow$ (**7**) (Scheme) take place *via* a nitrene intermediate (**4**).[3] It suggests rather a concerted migration–nitrogen loss mechanism for the former and a nucleophile substitution at nitrogen for the latter.

Acknowledgements

M.T.N. is indebted to the Department of Education (Irish Government) for financial support. We thank the U.C.D. Computer Centre for computer facilities. Professor J. Elguero, Madrid, and Dr. G. Bertrand, Toulouse, are gratefully acknowledged for helpful suggestions.

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Received 28th February 1986; *Paper* 6/414