

D. Conclusions

The treatment of cimetidine with NaNO_2 and aqueous HCl affords a *N*-nitroso derivative which can be readily isolated in good yield (~80%) as either the neutral form using pH 3.0 and 30 mol excess of NaNO_2 or as the nitrate salt using pH ≤ 1.0 and 4 mol excess of NaNO_2 . This nitrosation of cimetidine causes a shift in the guanidine π -electron distribution from predominantly conjugated cyanimino-type bonding to a more delocalized arrangement typically observed for unsubstituted guanidines. Nitrosocimetidine free base forms an intramolecular complex involving the imidazole and nitrosoguanidine moieties, with rapid initial hydrogen bonding leading to slow equilibration to a relatively stable complex. The final complex in neutral nitrosocimetidine exhibits increased absorption in the visible range, probably as a result of charge transfer involving promotion of an imidazole η electron to a π^* orbital of the nitrosoguanidine. The character of this CT transition is similar to that of the η - π^* transition normally found in nitrosoguanidines, suggesting that nearly equivalent orbital energies are occupied by the η electrons of the nitrosoguanidine and imidazole in the complex.

Although cimetidine is not mutagenic in the short term bacterial and mammalian mutagen assays, both the neutral nitrosocimetidine and its nitrate salt are mutagenic in these assays with the neutral compound having a much greater mutagenicity. The *N*-nitroso moiety is certainly a contributing factor to the mutagenicity, but the difference in mutagenicity between the neutral nitrosocimetidine and its nitrate salt may be the result of the

physical properties of the compounds and the biological systems in which they were tested. These would include pharmacological properties such as solubilities and membrane transport as well as inherent chemical reactivity. The significance of charge transfer to the mutagenicity of nitrosocimetidine is unknown. Neutral nitrosocimetidine exhibits mutagenic and nuclear fragmentation activity similar to that measured for the known animal carcinogen MNNG, and MNNG also forms an intramolecular complex with rapid proton exchange.²³ The nitrate salt does not form this intramolecular complex and does not appear to readily convert in aqueous solution at physiological pH to the charge-transfer complex.

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A Theoretical Study of the Phosphinonitrene ($\text{H}_2\text{P}=\text{N}$)-Iminophosphane ($\text{HP}=\text{NH}$) Rearrangement

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Abstract: The interconversion of phosphinonitrene, H_2PN , and iminophosphane, $\text{HP}=\text{NH}$, is studied in both the singlet and triplet electronic states using *ab initio* methods. At the MP4SDQ/6-31++G*/HF/3-21G* level plus zero-point energy contributions, the energy barrier for the rearrangement to iminophosphane in the singlet state is calculated to be 33.1 kcal/mol. In the triplet state, the barrier is 30.2 kcal/mol. The triplet-singlet energy separation in H_2PN is predicted to be small (7 kcal/mol). There is thus no intersystem crossing. In both states, the predicted energy barriers appear to be sufficient to guarantee the existence of the H_2PN species, if formed during the decomposition of iminophosphanes in an inert matrix at low temperature. The vibrational frequencies of the species studied are also calculated, and the P-N stretching frequency of H_2PN is predicted to lie in the region of 1250-1300 cm^{-1} . Finally, the *Z-E* isomerization in iminophosphane and the mechanism of the 1,2-hydrogen shift (from a LMO analysis) are considered.

The question of whether or not nitrenes (RN) exist as discrete intermediates during the thermolysis and photolysis of azides (RN_3) has long attracted the attention of both experimentalists and theoreticians.¹ It now appears that their existence strongly depends upon the nature of the substituents R. In the case of azidophosphines (R_2PN_3), evidence for the formation of phosphinonitrenes (R_2PN) has recently been reported by Bertrand, Majoral, and collaborators^{2,3}. These authors have shown that the products **1** obtained by photolysis of an azidophosphine at room temperature in the presence of various trapping agents AX can be considered as 1,2-adducts on the P-N bond of intermediate

phosphinonitrenes, and no insertion products of type **2** were observed in their experiments. In the absence of trapping agents, phosphinonitrenes undergo dimerization, yielding stable cyclo-diphosphazenes **3** in quantitative yield.³ Furthermore, in contrast to tetra- or pentacoordinated phosphorus azides,^{4,5} a Curtius-type rearrangement leading to iminophosphanes **4** (or phospho(III)-azenes) does not take place. Hence the reported experimental data^{2,3} clearly demonstrate the stabilization of nitrenes by phosphino (R_2P) groups.

The present theoretical study aims to quantitatively assess this stabilization by *ab initio* calculations on the interconversion pathway between two model species: phosphinonitrene (H_2PN) and iminophosphane ($\text{HP}=\text{NH}$) via a 1,2-hydrogen shift. This

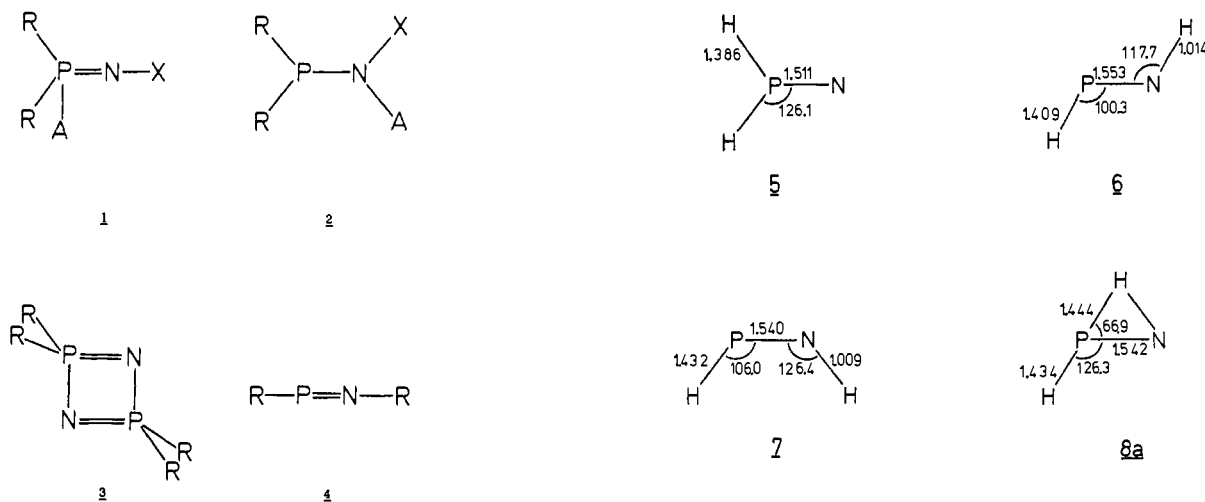
(1) For leading references, see: Wentrup, C. "Reactive Molecules"; Wiley: New York, 1982; Chapter 4, pp 162.

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rearrangement is considered in both the lowest lying singlet and triplet electronic states.

Calculations

The geometries of stationary points were optimized using the analytical gradient procedure and the 3-21G*^{6,7} basis set (including d functions on the phosphorus atoms only). Improved relative energies were determined from single-point calculations with 3-21G* geometries at the SCF and Møller-Plesset perturbation theory (second through fourth order)⁸ levels employing the 6-31++G* basis set⁹ (a 6-31G basis plus a set of diffuse s and p functions on P and N, a set of diffuse s functions on H, and a set of polarization d functions also on N and P). Harmonic vibrational frequencies (except for *trans*-HP=NH) and Boys localized molecular orbitals¹⁰ were computed with the 3-21G* basis set while some molecular properties were obtained from the HF/6-31++G* wave functions. The unrestricted Hartree-Fock (UHF) method was used for the triplet states. Calculations were carried out using the MONSTERGAUSS¹¹ and GAUSSIAN 80¹² programs on an AMDAHL 470 computer.

Results and Discussion

(a) Singlet States. We examined six stationary points on the closed-shell singlet surface. Besides the three structures of primary interest, [namely, phosphinonitrene (H_2PN , **5**, 1A_1); the *trans* iminophosphane (HP=NH, **6**, $^1A'$); and the transition state **8** (1A) for the 1,2-hydrogen shift connecting them], the *cis*-iminophosphane (HP=NH, **7**, $^1A'$) and the transition structure **9** ($^1A'$) for the *Z-E* isomerization between **6** and **7** were investigated. In addition, for a better understanding of the electronic reorganization during the 1,2-hydrogen shift, the planar maximum structure **8a** was also included. The relevant 3-21G*-optimized geometrical parameters are displayed in Figure 1. Table I lists the total and relative energies calculated at each level of theory, the zero-point vibrational energies (ZPE, 3-21G*), and our best estimates of the relative energies separating the stationary points (obtained from the MP4SDQ/6-31++G* calculations plus ZPE contributions).

Several *ab initio* studies of the structures and stabilities of $[H_2PN]$ species¹³⁻¹⁵ have been reported. In particular, Trinquier¹³ investigated the singlet energy surface at both SCF and CI levels (by the CIPSI procedure) employing a nonempirical pseudopotential for inner-shell core electrons (designated hereafter as "PsP")

Figure 1. Optimized geometries (3-21G*) of six stationary points on the singlet $[H_2PN]$ energy surface. Bond lengths are in Åströms and bond angles in degrees. All structures are planar, except for **8**.

and "PsP-CIPSI"), and calculated the energy differences between the four species **5**, **6**, **7**, and **9**.

The 3-21G*-optimized geometries for structures **5**, **6**, and **7** are quite close to those obtained from the PsP calculations¹³ using a DZ+d(P) basis set. The experimental literature dealing with the geometry of P=N compounds has been discussed by Trinquier.¹³ Note that, whereas the PNH bond angle of the transition state **9** was constrained in the PsP study to be linear, our fully optimized data indicate that a slight *trans* configuration is adopted with the PNH angle equal to 172°. The 1,2-hydrogen shift transition state **8** is found to be nonplanar with both the PN and the migrating PH bonds significantly stretched (>0.1 Å) with respect to those of **5**. The HPN bond angle of 53.6° is much smaller than the HNN angle of 65.7° (6-31G*) previously found in the transition state connecting aminonitrene (H_2NN) to *trans*-diazene ($HN=NH$).¹⁶ The planar structure **8a** corresponds to a minimax of order two in the energy surface, having two imaginary frequencies (see Table III).

As seen from Table I, inclusion of correlation energies markedly reduces the energy difference between **5** and **8**, while the relative energies of potential minima are quite accurately estimated at the SCF level. It is well established that the inversion barrier for *Z-E* isomerization is not affected by the correlation effects,¹⁵ and Table II shows that the previously reported PsP-CIPSI data¹³ are in remarkably good agreement with the present results. Phosphinonitrene **5** is calculated to lie about 40 kcal/mol above *trans*-iminophosphane **6** which is the global minimum of the singlet $[H_2PN]$ energy surface. The *cis* form **7** is about 1–1.5 kcal/mol less stable than the *trans* **6**, while the inversion barrier for the interconversion of the two amounts to 15 kcal/mol. Our calculations also predict an energy barrier of 33.1 kcal/mol for the singlet H_2PN (**5**) – HP=NH (**6**) rearrangement, much smaller than that of 47 kcal/mol previously calculated for the conversion of H_2NN to *trans*-HN=NH (at MP4SDTQ/6-31G** + ZPE level¹⁶).

Proceeding in the opposite direction, from **6** to **5**, the transition state **8** lies 72.7 kcal/mol above *trans*-iminophosphane **6**. Since the NH bond dissociation energy in *trans*-diazene was recently

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Table I. Total (au) and Relative (values in parentheses, kcal/mol) Energies of Six Stationary Points on the Singlet [H₂PN] Energy Surface^a

species ^b	5	6	7	8	8a	9
HF/3-21G*	-394.281 32 (0.0)	-394.346 01 (-40.6)	-394.346 56 (-40.9)	-394.232 38 (30.7)	-394.163 43 (74.0)	-394.332 82 (-32.3)
HF/6-31++G*	-396.213 62 (0.0)	-396.283 33 (-43.7)	-396.281 48 (-42.6)	-396.169 09 (27.9)	-396.102 10 (70.0)	-396.260 87 (-29.6)
MP2/3-21G*	-394.517 32 (0.0)	-394.577 18 (-37.6)	-394.576 27 (-37.0)	-394.444 76 (45.5)	-394.436 61 (50.6)	-394.556 98 (-24.9)
MP2/6-31++G*	-396.490 89 (0.0)	-396.556 73 (-41.3)	-396.553 58 (-39.3)	-396.425 91 (40.8)	-396.418 39 (45.5)	-396.530 39 (-24.9)
MP3/6-31++G*	-396.500 24 (0.0)	-396.570 25 (-43.9)	-396.567 56 (-42.2)	-396.446 07 (34.0)	-396.412 93 (54.8)	-396.544 34 (-27.7)
MP4SDQ/6-31++G*	-396.511 96 (0.0)	-396.578 05 (-41.5)	-396.575 28 (-39.7)	-396.455 23 (35.6)	-396.432 41 (49.9)	-396.551 69 (24.9)
ZPE estimated ^c	13.2 (0.0)	15.1 (-39.6)	14.8 (-38.1)	10.7 (33.1)	9.8 (46.5)	13.8 (-24.3)

^a Zero-Point energies (ZPEs) are given in kcal/mol. ^b Using 3-21G* geometries given in Figure 1. ^c Including MP4SDQ/6-31++G* relative energies and ZPE contributions.

Table II. Energy Differences between Singlet [H₂PN] Stationary Points (kcal/mol)

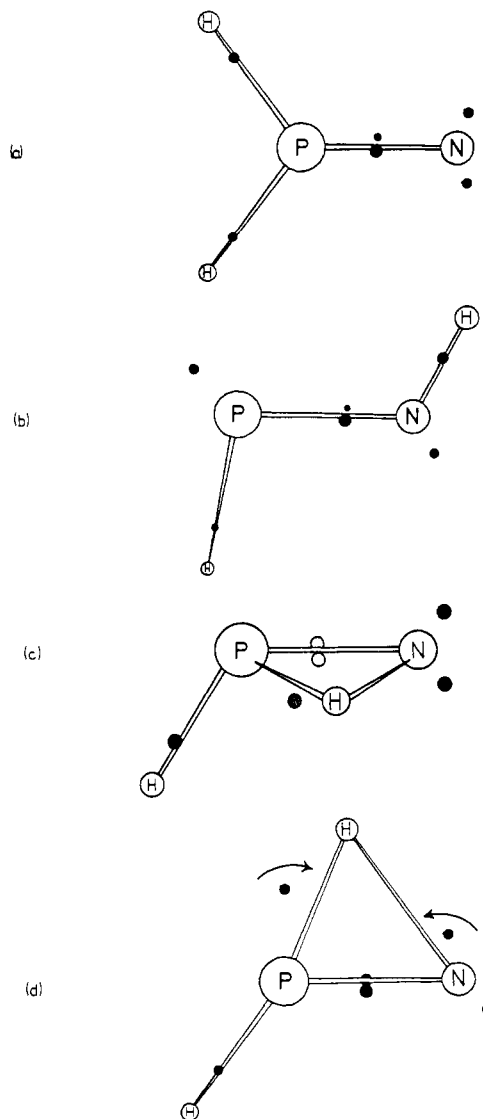
	MP4 ^a	MP4 + ZPE	PsP-CIPSI ^b
<i>E</i> (5 - 6)	41.5	39.6	41.3
<i>E</i> (7 - 6)	1.8	1.5	0.6
<i>E</i> [*] (6 - 9 - 7)	16.6	15.3	15.2
<i>E</i> [*] (5 - 8 - 6)	35.6	33.1	

^a MP4 denotes MP4SDQ/6-31++G* level (Table I). ^b CI calculations with pseudopotential, taken from ref 13.

estimated by GVB-CI methods¹⁷ to be only 71 kcal/mol, the above value suggests that the conversion of 6 and 5 via a unimolecular 1,2-hydrogen shift, and the processes occurring via a dissociation-recombination mechanism are quite competitive.

The harmonic vibrational frequencies of three minima 5, 6, and 7 and two maxima 8 and 8a are collected in Table III. For comparison, 4-31G* data for both structures 6 and 7 are also reported. Note that the change in the frequencies between either 3-21G* and 4-31G* or HF/3-21G* and PsP(DZ+d(P)) calculations are quite small. The values relevant to the P-N stretching modes are of particular interest. Firstly, the frequencies of 1250–1260 cm⁻¹ calculated for both the *trans*-6 and *cis*-7 iminophosphanes are comparable to those of 1240–1250 cm⁻¹ recently measured for a number of amino-*tert*-butyliminophosphanes (R₂NP=C(CH₃)₃).¹⁸ The P=N frequency is thus about twice as large as the 610 cm⁻¹ associated with the P=P stretching mode in diphosphenes.¹⁹ Secondly, the P-N stretching frequency in phosphinonitrene 5 (1269 cm⁻¹ at 3-21G*) is negligibly larger than those of 6 and 7 suggesting that the strengths of the P-N bonds in both constitutional isomers are similar. An analogous situation has been observed for the aminonitrene-*trans*-diazene system. The experimental N=N stretching frequency of 1574 cm⁻¹ in H₂NN is in fact slightly larger than that of 1529 cm⁻¹ in *trans*-HN=NH.²⁰ It is thus confidently predicted that the P-N stretching frequencies of R₂PN species should lie in the region of 1250–1300 cm⁻¹. It is noted that the imaginary frequency of 634*i* (cm⁻¹) carrying the migration of the hydrogen atom in the nonplanar transition state 8 is markedly smaller than the corresponding value of 2653*i* in the planar structure 8a, where the lower of the two imaginary frequencies, 1264*i*, describes the out-of-plane mode of the migrating hydrogen. Such a rotation stabilizes the transition state 8 by 13.4 kcal/mol.

The foregoing discussion raises questions concerning the precise nature of the P-N bond in phosphinonitrenes R₂PN. A comparison of bond lengths in related systems and the charge distribution in the singlet H₂PN led Trinquier¹³ to state that, although

**Figure 2.** Localized orbital (LMO) charge centroids in structures 5 (a), 6 (b), 8 (c), and 8a (d).

the P-N bond contains a certain amount of triple-bond character (ref 13, p 6972), its electronic structure is better depicted as H₂P=N rather than as H₂P≡N (ref 13, p 6976). The similarity mentioned above between the calculated vibrational frequencies of H₂PN and those of the H₂NN system also suggests a double-bond character. On the other hand, Bertrand, Majoral, and coworkers^{2,3} preferred to employ the term "phosphonitrile" involving a P-N triple bond in their recent experimental work. These

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Table III. Harmonic Vibrational Frequencies of Phosphinonitrene (H_2PN , **5**), *trans*-Iminophosphane (**6**), *cis*-Iminophosphane (**7**), and Planar **8a** and Nonplanar **8** Transition States for 1,2-Hydrogen Shift (in cm^{-1})

5		6		7		8	8a
3-21G*	(PsP) ^a	3-21G*	4-31G*	3-21G*	4-31G*	3-21G*	3-21G*
2693	2589 (a_1 , PH symm)	3613	3729	3673	3783 (a' , NH)	2386 (PH)	2415
1306	1357 (a_1 , symm bend)	2533	2404	2380	2281 (a' , PH)	2122 (PH)	2267
1270	1148 (a_1 , PN)	1254	1251	1268	1260 (a' , PN)	1107 (HPN)	1122
2704	2682 (b_2 , PH asym)	1123	1178	1150	1182 (a' , HPN bend)	1051 (PN)	952
852	795 (b_2 , HPH rock)	958	996	829	919 (a' , HNP bend)	817 (torsion)	1264i (a'' , torsion)
420	412 (b_1 , out-of-plane)	1097	1096	1042	1041 (a'' , out-of-plane)	634i (H-migrn)	2653i (H-migrn)

^aPseudopotential calculations PsP(DZ+d(P)), taken from ref 13.

Table IV. Total (au) and Relative (values in parentheses, kcal/mol) Energies of Four Triplet H_2PN Stationary Points^a

species ^b	10	11	12	13
HF/3-21G*	-394.334 30 (0.0)	-394.329 27 (3.2)	-394.256 09 (49.1)	-394.318 09 (10.2)
HF/6-31++G*	-396.261 23 (0.0)	-396.263 92 (-1.7)	-396.187 00 (46.6)	-396.246 59 (9.2)
MP2/3-21G*	-394.500 86 (0.0)	-394.511 43 (-6.6)	-394.440 73 (37.7)	-394.502 83 (-1.2)
MP2/6-31++G*	-396.463 50 (0.0)	-396.486 18 (-14.2)	-396.412 16 (32.2)	-396.473 90 (-6.5)
MP3/6-31++G*	-396.493 30 (0.0)	-396.510 81 (-11.0)	-396.438 74 (34.2)	-396.496 91 (-2.3)
MP4SDQ/6-31++G*	-396.499 89 (0.0)	-396.517 62 (-11.1)	-396.447 18 (33.1)	-396.504 14 (-2.7)
ZPE estimated ^c	12.6 (0.0)	13.3 (-10.4)	9.7 (30.2)	12.7 (-2.6)

^aZero-point energies (ZPEs) are given in kcal/mol. ^bEmploying the 3-21G* geometries given in Figure 3. ^cIncluding MP4SDQ/6-31++G* relative energies and ZPE contributions.

authors have also quoted ref 13 in order to support their preference. Although there is an incorrect statement in ref 2 (see ref 24), the situation appears to be somewhat confusing.

In an attempt to clarify this, we have calculated localized molecular orbitals (LMOs) using the Boys procedure.¹⁰ It is well known that the Boys LMO description can often specify the number and hence the nature of the chemical bonds in a molecular system.²¹ Parts a and b of Figure 2 show that there are only two LMO charge centroids between the phosphorus and nitrogen atoms in both **5** and **6**. In **5**, the second electron pair arises from the migration of the phosphorus lone pair. A similar localization has been observed for the H_2NN species²² involving two charge centroids around the terminal nitrogen atom of the aminonitrene $H_2N=N$. The LMO analysis thus shows that we are dealing with a dative double bond in **5** as shown previously in ref 13.

The distribution of LMO charge centroids in the transition state **8** (Figure 2c) suggests that the electronic reorganization along the interconversion pathway from **5** to **6** adopts the same mechanism as that occurring in the H_2NN to $HN=NH$ rearrangement.²² Accordingly, the hydrogen atom migrates as a hydride in the early stages of the rearrangement and as a proton in the later stages. The redistribution of the electron pairs occurs as follows:

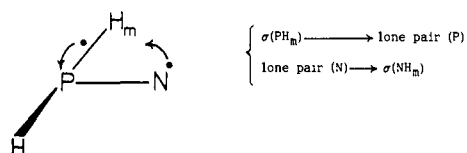


Figure 2d clearly shows that, during the shift of the hydrogen atom in the molecular plane (structure **8a**), migrating electron

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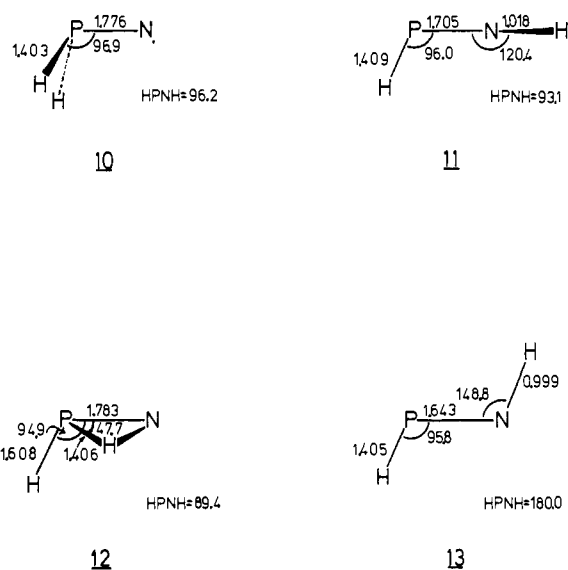


Figure 3. Optimized geometries (3-21G*) of four stationary points on the triplet $[H_2PN]$ energy surface. Bond lengths are in Ångströms and bond angles in degrees.

pairs move in opposite senses. Such a movement naturally creates a strong electronic repulsion and the in-plane pathway is disfavored. The out-of-plane pathway via the true transition structure **8**, although apparently uncomfortable from a geometrical point of view, allows the system to minimize the destabilization arising from the electronic reorganization. The tendency of electron pairs to move in the same sense during the course of a chemical reaction is well documented.²⁶

(23) Ha, T. K.; Nguyen, M. T.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1982**, *92*, 459.

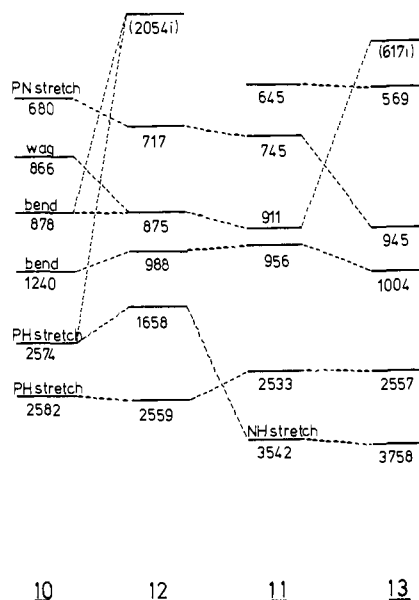


Figure 4. Vibrational frequency correlation diagram for four triplet species calculated at 3-21G* level. Values are given in cm⁻¹ and the scale is arbitrary.

(b) Triplet States. We considered four stationary points: phosphinonitrene **10** (³A''), iminophosphane **11** (³A), the 1,2-hydrogen shift transition structure **12** (³A), and the transition state **13** (³A'') for the autoisomerization of **11**. Structures **10** and **11** have been examined in detail by Trinquier.¹³ It is also known that the iminophosphinidene (H₂NP) represents the global minimum of the triplet [H₂PN] energy surface.¹³

The optimized geometries of each species determined at the HF/3-21G* level are shown in Figure 3, and the corresponding total and relative energies calculated at different levels are collected in Table IV.

The calculated P–N bond lengths are appreciably shorter (0.03–0.04 Å) in both minima **10** and **11** than the corresponding PsP values.¹³ This difference is no doubt due to the fact that in ref 13 the wave functions describing the triplet states at the SCF level have been determined from a Nesbet-type hamiltonian.²⁵ As would be expected, the 1,2-hydrogen shift saddle point **12** is found to be almost perpendicular with a dihedral angle of approximately 90°, and the rotation transition structure **13** is planar. The PN bond length in **12** is almost unchanged from those of **10** and **11**, while that in **13** is significantly shorter (by 0.06 Å). Iminophosphane **11** is the more stable of the two triplet local minima and is favored by the inclusion of both polarization functions and correlation effects. Our best estimates of the energy separation between **10** and **11** (Table IV), 10.4 kcal/mol, is much smaller than that of 19.3 kcal/mol obtained from PsP + CIPSI calculations.¹³ As stated above, the disagreement may arise from the difference in the use of references for calculating correlation energies of triplet states. In contrast to the situation in the singlet case, the UHF + MP4SDQ procedure employed in this work and the Nesbet–CIPSI in ref 13 do not always lead to similar results. Nevertheless, it can be pointed out from these data (agreement for singlet states, disagreement for triplet states) that the use of pseudopotentials is not responsible for the disparity. The energy barrier for the 1,2-hydrogen shift converting **10** to **11** is predicted

(24) In ref 2 (p 459, line 8), the authors stated by quoting ref 13 that: "Recently, ab initio effective potential calculations indicated that the structure of singlet λ³-phosphinonitrene H₂PN is better formulated as a nitrilo-λ⁵-phosphane H₂P=N due to delocalization of the lone pairs nπ(P)→pπ(N) and nπ(N)→dπ(P)", which would appear to be incorrect. Trinquier did not state this in ref 13.

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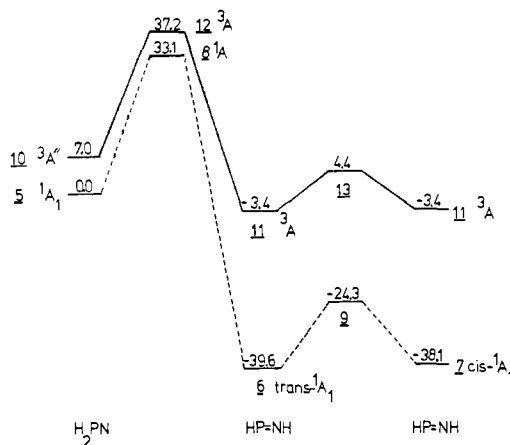


Figure 5. Relative energies, in kcal/mol, of the pathways for isomerization of the singlet and triplet [H₂PN] species.

to be 30.2 kcal/mol, and although smaller than the 33.1 kcal/mol estimated for the corresponding singlet state conversion, it is nevertheless appreciable. This reduction in endothermicity from the singlet state also decreases the energy barrier for the reverse reaction **11** to **10** to only 40.6 kcal/mol, rendering rearrangement via a direct 1,2-hydrogen shift more likely. The rotation barrier for the autoisomerization of **11** via the transition structure **13** is only 7.8 kcal/mol, suggesting the triplet iminophosphanes are quite unstable configurationally. Figure 4 summarizes the vibrational frequency correlation for the four structures considered at HF/3-21G* level. The calculated frequencies relevant to the PN stretching modes are considerably smaller than those of the singlet species, emphasizing the P–N single-bond character in both triplet minima.

(c) Summary. The final energy profile for both singlet and triplet electronic states is shown schematically in Figure 5 (values at MP4SDQ/6-31++G* + ZPE level).

Our calculations predict triplet–singlet separations of 7 and 36.1 kcal/mol for phosphinonitrene and *trans*-iminophosphane, respectively. The former is close to the value of 6 kcal/mol reported by Trinquier from PsP–CIPSI calculations,¹³ but the latter is larger than his estimation of 28 kcal/mol.

Two further points may be made. Firstly, the singlet and triplet energy surfaces do not cross during the phosphinonitrene–iminophosphane rearrangement. However, because the energy separation between the singlet ground state and the triplet excited state of H₂PN is so small (7 kcal/mol), this species could exist in both multiplicities if molecular collisions occur.²³ During decomposition of phosphinoazide, either the singlet or triplet H₂PN, if formed, could isomerize to the corresponding iminophosphane with an energy barrier of at least 30 kcal/mol, which is rather small in the gas phase, but appears to be large enough to guarantee the existence of a detectable H₂PN species, for example, in an inert matrix at low temperature. Secondly, in cases where the hydrogen atoms are replaced by poorer migrating groups,²⁻³ the existence of phosphinonitrenes as discrete intermediates is even more likely.

In summary, the present theoretical study of the 1,2-hydrogen shift in the model H₂PN–HPNH system supports the experimental findings that phosphinonitrenes R₂PN, once formed during the photolysis of corresponding azides, do not rearrange to iminophosphanes, but instead undergo addition or dimerization. For a full picture of the nature and reactivity of these intermediate species, calculations on 1,1-additions and 1,2-additions to AX reagents as well as cycloadditions may be desirable.

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