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CHE 79-26479 (R.B.).

Registry No. Na$^+$HCr(CO)$_5^-$, 83399-32-0; Na$_2$Cr(CO)$_5$, 52154-81-1; PPN$^+$Cr(CO)$_5$I$^-$, 39048-35-6; PPN$^+$(μ-H)$_2$BH$_2$Cr(CO)$_4^-$, 83399-34-2; Ph$_4$P$^+$HCr(CO)$_5^-$, 83399-35-3; Cr(CO)$_5$(NC$_5$H$_{11}$), 15710-39-1; (μ-H)[Cr(CO)$_5$]$_2^-$, 19571-06-3.

Supplementary Material Available: Listings of the structure factor amplitudes for both structures as well as bond lengths and bond angles of the PPN$^+$ cation and ORTEP plots of the cations of both salts (28 pages). Ordering information is given on any current masthead page.

Phosphinonitrene, Phosphazene, and Aminophosphinidene. Structures and Stabilities

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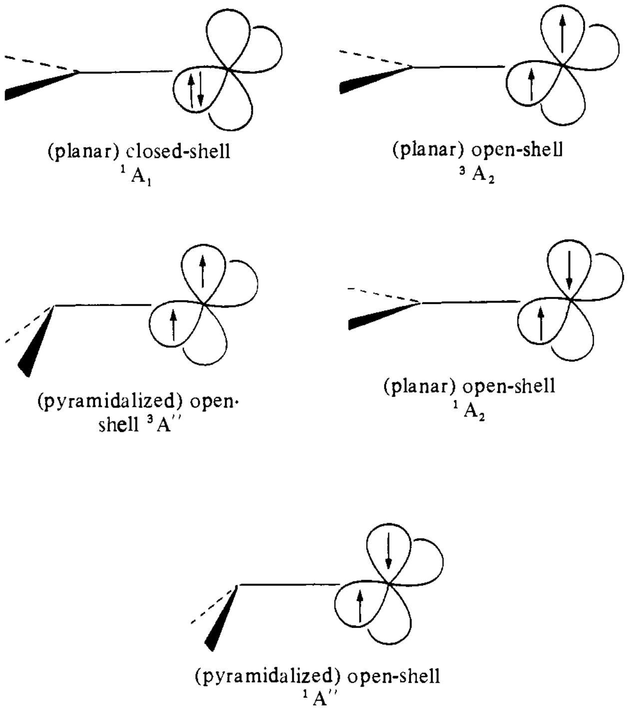
Abstract: Singlet and triplet H$_2$PN isomers are investigated through ab initio effective potential calculations using double-ζ + polarization basis sets; electron correlation is included. All singlet states are planar, indicating conjugation of the amino and phosphino π lone pairs in H$_2$N–P and H$_2$P–N, respectively. The corresponding triplet states show pyramidalized amino and phosphino groups. The calculated thermodynamic stability ordering for all isomers is HP=NH ^{1}A′ (trans) $\simeq$ H$_2$N—P ^{3}A″ $\simeq$ HP=NH ^{1}A′ (cis) < H$_2$N—P ^{1}A$_1$ $\ll$ HP—NH ^{3}A < H$_2$P—N ^{1}A$_1$ < H$_2$P—N ^{3}A″, corresponding to relative energies 0, 7, 28, 41, and 47 kcal/mol, respectively. The structure of singlet phosphinonitrene supports the phosphonitrile notation H$_2$P≡N, due to delocalization of the lone pairs $n_\pi(P) \rightarrow p_\pi(N)$ and $n_\pi(N) \rightarrow d_\pi(P)$. The structure of singlet aminophosphinidene shows less multiple character in the NP bond H$_2$N$\Rightarrow$P. The π contribution to the PN bond energy in HP=NH is estimated at about 40 kcal/mol. Cis/trans isomerization of HP=NH proceeds via a linear PNH configuration with an energy barrier of 15 kcal/mol.

Introduction

The number of compounds of dicoordinated phosphorus(III) involving a –P=N– double bond is fairly limited to date. However, they are becoming more and more numerous either in cyclic forms or noncyclic forms, the P=N bond being either conjugated or nonconjugated.[1-5] Some X-ray data[6-8] are now available. In a compound like R—P=N—R′, besides the P=N double bond the unsaturation can take a nitrene form, RR′P—N̈:, or a phosphinidene form, RR′N—P̈:. It is known that with only first-row atoms multiple bonding is always preferred over nitrene-like or carbene-like forms;[9] indeed the thermodynamic stability of aminonitrene, H$_2$N-N, is predicted to be 25 kcal/mol less than that of *trans*-diimide, HN=NH, according to the most refined calculations.[10] When a phosphorus atom is involved, the three forms >P—N, -P=N-, and P—N< compete; their thermodynamic stabilities are not a priori easily predictable. Moreover, a question arises concerning the spin multiplicity (singlet or triplet) of the ground state for the corresponding nitrene or phosphinidene forms.

Chart I



(planar) closed-shell ^{1}A$_1$

(planar) open-shell ^{3}A$_2$

(pyramidalized) open-shell ^{3}A″

(planar) open-shell ^{1}A$_2$

(pyramidalized) open-shell ^{1}A″

In this paper, we present an ab initio study of the structures and stabilities of all the H$_2$PN isomers in their low-lying singlet and triplet states. The three corresponding isomers are therefore (1) HP=NH (cis and trans), which we shall call phosphazene (phospha(III)azene); (2) H$_2$P—N̈:, which we shall call phosphinonitrene, without taking into account the hypervalency of phosphorus, but which can be designated as a model for phosphonitriles, H$_2$P≡N; (3) H$_2$N—P̈:, which we shall call aminophosphinidene. Emphasis will be put on HP=NH, which is a model for the -P=N- double bond. For our nitrene or phos-

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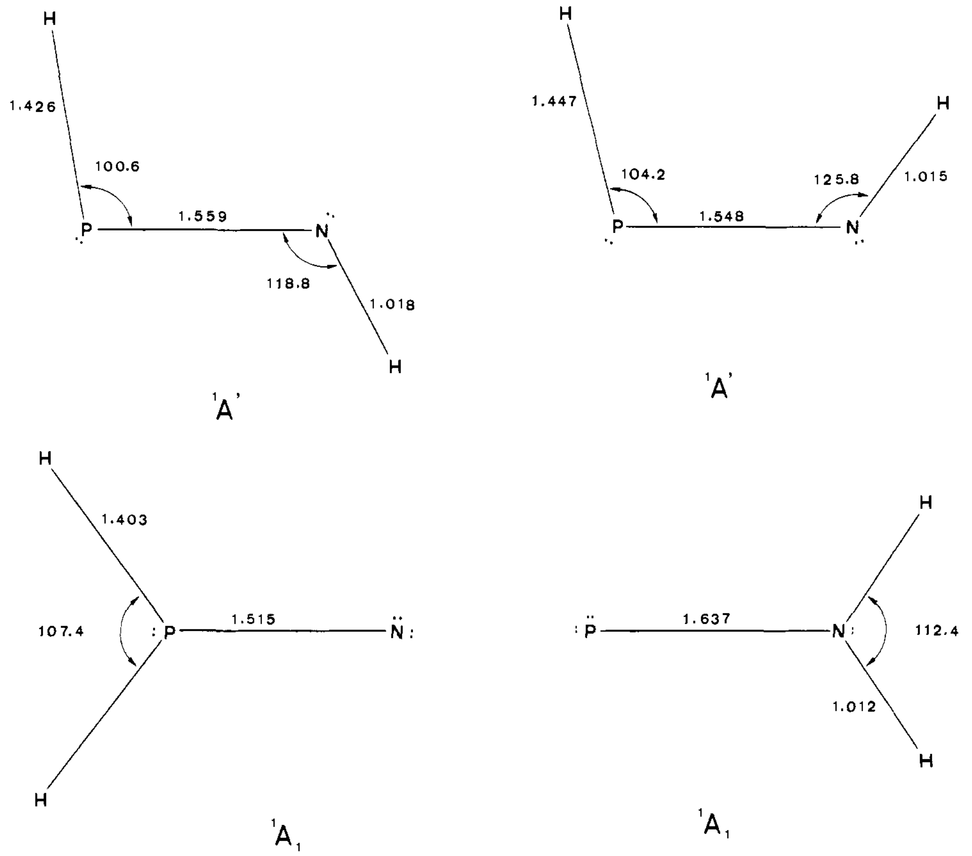

Figure 1. SCF calculated (DZ + d(P) basis set) equilibrium geometries for singlet *trans*- and *cis*-phosphazene, phosphinonitrene, and aminophosphinidene, in angstroms and degrees.

phinidene isomers, the basic electronic configurations corresponding to the three low-lying states can be depicted as in Chart I, with the open-shell singlet state being in any case the least stable of the three states.

When possible, comparisons with the H_2N_2 systems will be made with use of results obtained with comparable basis sets.

Computational Details

All SCF calculations were carried out with a modified version of the HONDO program package,[11] including pseudopotentials, the PSHONDO algorithm.[12] We used the pseudopotential method proposed by Durand and Barthelat.[13,14]

For each atom, the inner-shell core electrons are taken into account through a nonempirical pseudopotential determined from the double-ζ atomic Hartree–Fock calculations of Clementi and Roetti.[15] Valence atomic basis sets are optimized in a pseudopotential SCF calculation of the ground state of the atom by using a quadruple-ζ Gaussian basis set. These four Gaussian functions are contracted to the double-ζ level (DZ) by means of a 3 + 1 procedure. For phosphorus a 3d Gaussian function was added as a polarization function ($\eta_P = 0.57$). This basis set, which will be called DZ + d(P), is used to determine the equilibrium geometries.

At the equilibrium geometries, refined SCF and CI calculations were performed with use of a second basis set obtained from the former by adding a d function on nitrogen ($\eta_N = 0.95$) and a set of p functions on each hydrogen ($\eta_H = 0.8$). This second basis set therefore includes polarization orbitals on each atom and will be designated by DZ + pol.

The SCF valence energies for the open-shell singlet and triplet states were obtained by calculating the mean value of the H operator between the wave functions determined from a Nesbet type operator.[16] This procedure leads to optimized geometries that are quite comparable to the geometries optimized with use of Roothaan's RHF open-shell procedure.[17]

Valence-shell configuration interaction (CI) calculations were performed with use of an improved version[18] of the CIPSI algorithm.[19] A variational zero-order wave function was built from an iterative selection of the most important determinants, the other ones being taken into account through a second-order Möller–Plesset perturbation. At the final step we include in the zero-order wave functions all the determinants having a coefficient larger than 0.03 in the first-order wave function based on the reference determinants. With these conditions and with dependence on the isomer, the number of determinants included in the variational zero-order wave function range from 15 (singlet HP=NH) to 44 (triplet H_2P—N) while the number of determinants generated in the perturbation ranged from 3 × 10^5 (singlet HP=NH) to 10^6 (triplet HP-NH).

The geometrical parameters were optimized independently; in some instances two were optimized simultaneously because of their mutual dependence.

Equilibrium Geometries

A. Closed-Shell Singlet States. The geometries of the four closed-shell singlet isomers are displayed in Figure 1. All molecules are planar. The calculated P=N bond length in *trans*-phosphazene, 1.559 Å, compares favorably with trans P=N bond lengths determined from X-ray data in $Me_3Si(t\text{-}Bu)N$—P=N-*t*-Bu (1.544 Å)[6] and in $(Me_3Si)_2N$—P=N—$SiMe_3$ (1.545 Å).[6,7] In both these compounds the valence angles on phosphorus (105 and 108°, respectively) and nitrogen (124 and 130°, respectively) are less sharp than in our calculated trans isomer. This

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Table I. Harmonic Force Constants (in Symmetry Coordinates) and Vibrational Frequencies for Planar Singlet $^1A_1$ H_2P-N Calculated at the SCF Level (DZ + d(P) Basis Set)

	force const^a			vib freq^b	
A_1	F_{11}	PN str	7.66	ν_1	1148
	F_{12}		0.20		
	F_{13}		0.29		
	F_{22}	sym PH str	3.90	ν_2	2589
	F_{23}		−0.06		
	F_{33}	sym HPH bend	0.70	ν_3	1357
B_2	F_{44}	antisym PH str	4.10	ν_4	2682
	F_{45}		−0.01		
	F_{55}	HPH rock	0.58	ν_5	795
B_1	F_{66}	wag	0.12	ν_6	412

^{a} Units are in mdyn/Å, mdyn/rad, or mdyn Å/rad^2. ^{b} In cm^{-1}

is probably due to steric hindrance. Incidentally these experimental P=N geometries are closer to our calculated geometry for the cis isomer. The calculated P=N bond length in the cis isomer is 0.01 Å shorter than in the trans isomer. In the diimide, the N=N bond lengths were found to be equal in both cis and trans isomers by Ahlrichs and Staemmler,[20] Winter and Pitzer,[21] and Parsons and Dykstra.[10]

In both diimide and phosphazene, a 5–7° widening of the valence angle on nitrogen occurs from the trans isomer to the cis isomer. The lack of d polarization orbitals on nitrogen in our geometry optimization is certainly responsible for the somewhat large (in absolute terms) valence angles on nitrogen (trans, 119°; cis, 126°) in phosphazene with respect to diimide, which was optimized with d orbitals on nitrogen (trans, 108–110°; cis, 113–116°).[10,20,21] This is supported by the SCF- (DZ basis set without d orbitals) calculated CNH angle in methanimine (116,[22] 115°[23]) vs. its experimental value (110°).[24] On the other hand, the calculated valence angle on phosphorus in *trans*-phosphazene compares favorably with its theoretical[25] and experimental[26] values in phosphaethylene (98°), and its experimental value in (2,4,6-(t-Bu)$_3$Ph—P=)$_2$ (103°).[27]

A basic difference in HP=NH with respect to HN=NH is that the H^-–^+P and N^-–^+H dipoles favorably interact in the cis isomer; probably due to this effect, the trans isomer energy is only 0.6 kcal/mol below while the *trans*-diimide energy is 6 kcal/mol below that of *cis*-diimide.[10,20]

For singlet phosphinonitrene a complete force field was computed. The corresponding full sets of harmonic force constants and vibrational frequencies are reported in Table I. One must keep in mind that SCF force fields usually overestimate frequencies.

The short PN bond length in single phosphinonitrene should be pointed out, while in aminophosphinidene the PN bond length is close to that of a single σ PN bond. The NH_2 moiety in aminophosphinidene is comparable to the NH_2 moiety in singlet aminonitrene as calculated by Ahlrichs[20] (NH = 1.016 Å, ∠HNH = 114°). Although there are few data that we may compare with, our calculated nitrene and phosphinidene structures seem intuitively correct.

The geometrical features already give important information concerning the electronic structures and bonding in these singlet molecules. The planar forms for the nitrene and phosphinidene molecules suggest good delocalization of the phosphino and amino π lone pairs, as in aminonitrene.[28] Table II provides a comparison of NN and PN bond lengths in various model molecules. This table is self-explanatory and makes clear (i) the double-bond character of the NN bond in singlet aminonitrene, (ii) the more-than-double-bond character of the PN bond in singlet phosphinonitrene, and (iii) the more-than-single-bond character of the PN bond in singlet aminophosphinidene. The multiplicity of these bonds results from the π delocalization of the amino or phosphino lone pair into the empty orbital of the terminal nitrogen

Table II. Comparison of Bond Lengths in Closed-Shell Singlet Systems

	NN bond lengths, Å		PN bond lengths, Å
H_2N-NH_2	1.45^a	H_2P-NH_2	1.66,^{e} 1.68^f
HN=NH	1.21,^{b} 1.22^c	HP=NH	1.56^g
N≡N	1.10^d	P≡N	1.47^g
H_2N-N	1.22^{b,c}	H_2P-N	1.52^g
		$P-NH_2$	1.64^g

^{a} Experimental.[29] ^{b} SCF calculated, DZ + pol basis set.[20] ^{c} SCF calculated, DZ + pol basis set.[10] ^{d} Experimental.[30] ^{e} SCF calculated, minimal basis set.[31] ^{f} SCF calculated, DZ + pol basis set, with geometry restrictions.[32] ^{g} SCF calculated, DZ + d(P) basis set, this work.

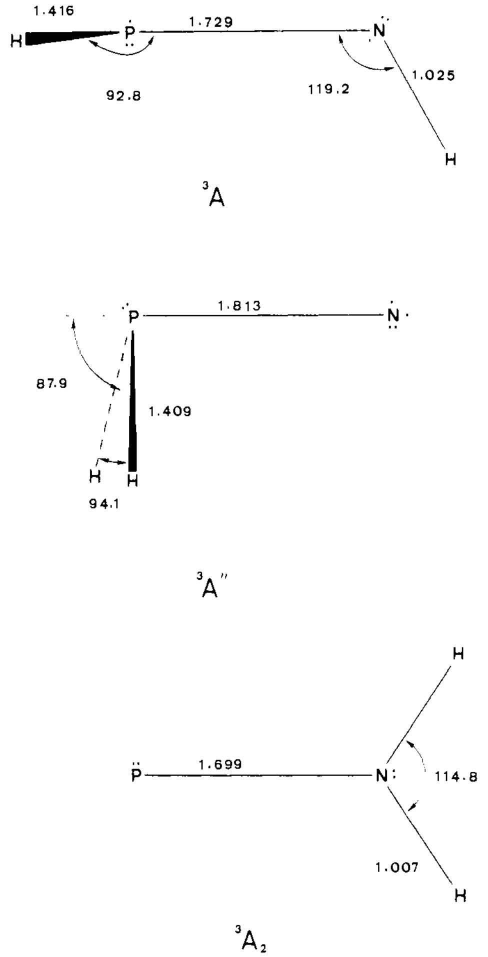

Figure 2. SCF calculated (DZ + d(P) basis set) equilibrium geometries for triplet phosphazene, phosphinonitrene, and aminophosphinidene, in angstroms and degrees.

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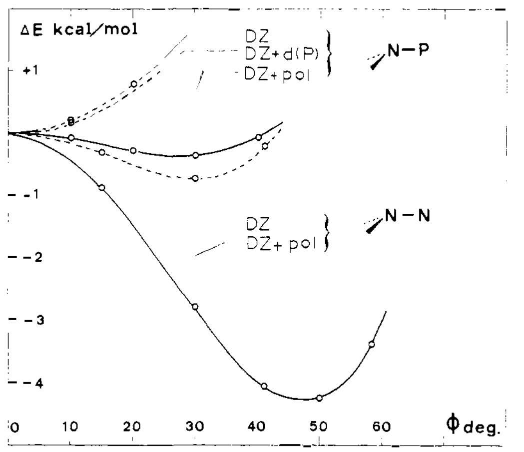


Figure 3. Basis set effects on pyramidalization of the amino group in triplet aminophosphinidene and triplet aminonitrene. Pyramidalization angle ϕ is defined as in Figure 4.

or phosphorus. The geometries suggest that such a π delocalization is stronger for $N \rightleftharpoons N$ than for $N \rightleftharpoons P$. Moreover, in phosphinonitrene an additional "back-delocalization" can occur from the terminal nitrogen π lone pair into a d orbital of phosphorus. These analyses will be detailed in the following sections, but they already suggest a certain amount of triple-bond character for singlet phosphinonitrene and tend to support its phosphonitrile $H_2P{\equiv}N$ notation.

B. Open-Shell Triplet States. The geometries for the open-shell triplet states, determined with use of the DZ + d (P) basis set, are reported in Figure 2. As expected, triplet phosphazene is twisted, with a PN bond length increased by 0.17 Å with respect to the trans singlet ground state. The valence angle on phosphorus is more acute (by 8°) than it is in the trans singlet state while the nitrogen valence angle remains unchanged. The same trends were observed from singlet ground-state methanimine to triplet methanimine[22] (CN bond length increased by 0.15 Å, valence angle on nitrogen practically unchanged).

Triplet phosphinonitrene is pyramidal with a strong pyramidalization angle on phosphorus (88°); the PN bond length is increased by a very large value, 0.30 Å, with respect to the planar singlet state, and is beyond a typical single PN bond length. In fact, variations in the pyramidalization angle ϕ and the PN bond length are strongly coupled and it was necessary to perform simultaneous optimization of these two interdependent parameters to obtain the minima corresponding to the strong phosphorus pyramidalization and to the long PN bond length. The valence angles on phosphorus are close to 90°, which is the natural bond angle for single bonds to phosphorus, e.g., as in PH_3. This shows the reluctance of phosphorus to hybridize in this system.

The geometry of triplet aminophosphinidene determined without nitrogen d functions in the basis set is planar (Figure 2). Since d orbitals are usually required to obtain correct pyramidalization on nitrogen atoms, we reoptimized the pyramidalization angle in triplet aminophosphinidene with the DZ + pol basis set. As a test of reliability for our Nesbet type procedure, the pyramidalization angle in triplet aminonitrene was also investigated in a similar way. The results are given in Figure 3. Starting from the other geometrical parameters determined by Ahlrichs and Staemmler,[20] the DZ + pol basis set gave, for triplet aminonitrene, a pyramidalization angle of 47° and an inversion barrier of <4.3 kcal/mol, in agreement with Ahlrichs and Staemmler's results (42°, 2.7 kcal/mol)[20] and Davis and Goddard's results (42°, 4.4 kcal/mol).[28] Without polarization orbitals (i.e., d AO's on nitrogen and p AO's on the hydrogens) the curve is much flatter; a 28° pyramidalized form is obtained, which is only 0.7 kcal/mol below the planar form.

Starting from our DZ + d(P) planar geometry, we optimized the pyramidalization angle for aminophosphinidene using the DZ + pol basis set. Pyramidalization of 27° was obtained; the curve is very flat and the energy gain is only 0.3 kcal/mol with respect to the planar form (Figure 3). The flatness of this curve is responsible for the planar geometry obtained without nitrogen d atomic orbitals. Finally the geometry of triplet aminophosphinidene was entirely optimized with the DZ + pol basis set and is reported in Figure 4. Apart from the pyramidalization on nitrogen, it is interesting to point out that the other geometrical parameters (mainly the PN bond length) are little modified with respect to their DZ + d(P) values.

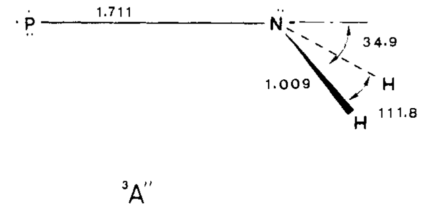
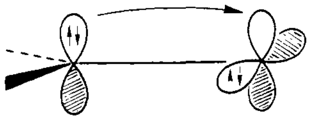


Figure 4. SCF calculated (DZ + pol basis set) equilibrium geometry for triplet aminophosphinidene, in angstroms and degrees.

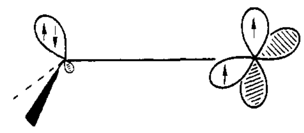
Calculated with the DZ + pol basis set, the SCF energy for triplet aminophosphinidene at its DZ + pol geometry is only 0.5 kcal/mol below its energy at its DZ + d(P) geometry. This difference is reduced to 0.01 kcal/mol at the CI level. For the sake of homogeneity all discussions about energies will involve the energies calculated at the DZ + d(P) geometries. For the triplet geometry discussions, the DZ + pol geometry of aminophosphinidene will be considered. This basis-set-effect study once more shows the importance of d orbitals in describing the pyramidalization of nitrogen atoms.

C. Factors Governing the Geometries. The main factor governing the geometry of $H_2N{-}P$ and $H_2P{-}N$ is the conjugation of the NH_2 or PH_2 lone pair with the orbitals of the neighboring phosphinidene or nitrene end. In the singlet states, a π orbital on terminal P or N is empty and allows a full delocalization of the NH_2 or PH_2 lone pair:



The purer the π character of the lone pair on NH_2 or PH_2, the stronger the dative bond formed of this two-electron interaction. This is why singlet $H_2N{-}P$, $H_2P{-}N$, and $H_2N{-}N$ (and probably $H_2P{-}P$) are found to be planar with bond lengths shorter than typical single-bond lengths.

In the triplet states, delocalization involves three electrons since the two π orbitals of the P or N end are singly occupied. The situation is close to that for vinylamine or aniline type molecules with pyramidal nitrogen:



In triplet aminonitrene the NN distance was calculated by Ahlrichs and Staemmler[20] to be 1.34 Å, which is a bond length intermediate between a single and a double NN bond length. As noted previously, the pyramidalization angle is 42° and the inversion barrier was calculated by these authors at 2.7 kcal/mol[20] and by Davis and Goddard at 4.4 kcal/mol.[28] In comparison the experimental inversion barrier for NH_3 is 5.8 kcal/mol.[33,34] In triplet aminophosphinidene the PN bond length is found to be ~0.02 Å longer than a PN single-bond length and the inversion barrier on nitrogen is very weak (<0.3 kcal/mol). In triplet phosphinonitrene the PN bond length is more than 0.1 Å longer than a PN single-bond length. This could be accounted for by

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Table III. Relative Energies (kcal/mol) for the Minima of the Low Lying Singlet Potential Surface[a]

		SCF		CI
	states	DZ + d(P)	DZ + pol	DZ + pol
$H_2P–N$	$^1A_1$	43.7	42.0	41.3
$P–NH_2$	$^1A_1$	0	1.4	7.2
HP=NH	$^1A'$ cis	3.0	0.7	0.6
HP=NH	$^1A'$ trans	3.3	0	0

[a] The zero energies correspond to total valence energies −17.136 733 (DZ + d(P)), −17.164 099 (DZ + pol), and −17.436 711 au (CI).

Table IV. Relative Energies (kcal/mol) for the Minima of the Low-Lying Triplet Potential Surface[a]

	states	DZ + d(P)	DZ + pol	CI
$H_2P–N$	$^3A''$	48.3	50.3	47.3
HP–NH	^3A	39.5	36.1	28.0
$P–NH_2$	$^3A''$	0	0	0

[a] The zero energies correspond to total valence energies −17.152 302 (DZ + d(P)), −17.171 113 (DZ + pol), and −17.436 624 au (CI).

Table V. CI Calculated Relative Energies (kcal/mol) of the Low-Lying States for Each Isomer

isomers	states	rel energies	isomers	states	rel energies
$H_2P–N$	$^1A''$	42.6	HP=NH	^1A	39.8
	$^3A''$	6.0		^3A	28.0
	$^1A_1$	0		$^1A'$ cis	0.6
$H_2N–P$	$^1A''$	22.7		$^1A'$ trans	0
	$^1A_1$	7.1			
	$^3A''$	0			

Table VI. Singlet–Triplet Adiabatic Separations in Some Nitrenes and Phosphinidenes (kcal/mol)[a]

nitrenes		phosphinidenes	
H–N	36[b]	H–P	22[h]
$CH_3–N$	39[c]		
CHO–N	31[d]	CHO–P	20[d]
$NH_2–N$	2–3[e] −15[f]	$NH_2–P$	7[g]
$PH_2–N$	−6[g]		

[a] A negative sign indicates a singlet ground state. [b] Experimental.[30] [c] DZ + pol + CI.[22] [d] DZ + pol + estimated CI effects.[35] [e] Extended basis set + IEPA–PNO CI.[20] [f] GVB calculations; DZ + d basis set + extended CI.[28] [g] DZ + pol + CIPSI–CI, this work. [h] Extended basis set + CI.[37]

the very bent PH_2 group (pyramidalization angle 88°) and could be responsible for the poor relative stability of this isomer.

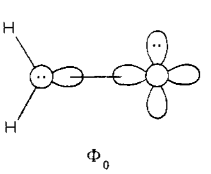
As is often the case, the geometries for open-shell singlet states were assumed to be identical with the triplet geometries.[35,36]

Energies

Because of our Nesbet type procedure, the energies of singlet and triplet isomers cannot be directly compared at the SCF level. However, for each potential surface, singlet closed-shell or triplet open-shell, one may compare the SCF energies obtained from the two different basis sets and the CI energies (obtained from the DZ + pol basis set) for all four isomers.

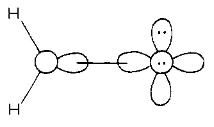
A. Singlet Surface. The relative energies for the singlet isomers are displayed in Table III. At the SCF level aminophosphinidene and *cis*- and *trans*-phosphazene are close in energy while phosphinonitrene is much higher in energy. The inclusion of the nitrogen d orbitals in the basis set gives a relative stabilization of phosphazene; *cis*-phosphazene is only 0.7 kcal/mol above *trans*-phosphazene (in diimide, N_2H_2, the cis isomer was calculated to be 6–7 kcal/mol above the trans isomer at the SCF level).[10,20] Its relative stabilization could be due to a favorable electrostatic interaction between the $H^-–^+P$ and $N^-–^+H$ dipoles. The valence correlation energies were calculated as the following: H_2PN, 171.7 kcal/mol; H_2NP, 165.2 kcal/mol; *cis*-HPNH, 171.1 kcal/mol; *trans*-HPNH, 171.0 kcal/mol. They leave unchanged the cis/trans energy difference as in diimide[10,20] and relatively stabilize (by 5.9 kcal/mol) the covalent π-bonded molecule HP=NH with respect to the "dative π" molecule $H_2N\rightleftharpoons P$. Comparable correlation effects were found to stabilize (by 7 kcal/mol) *trans*-diimide with respect to aminonitrene.[10,20] The valence correlation energy is greater (by 0.7 kcal/mol) for phosphinonitrene than for phosphazene. This is consistent with the high multiplicity (>2) of the PN bond in H_2PN.

It is interesting to analyze the contributions of the main configurations to the multideterminantal wave functions of the singlet nitrene and phosphinidene isomers. Besides the reference Φ_0, the

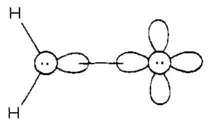


Φ_0

two configurations of importance are Φ_1 and Φ_2. The repulsion



Φ_1



Φ_2

between the π lone pairs makes the energy of Φ_2 high at short distances. For this reason, Φ_2 makes little contribution in $H_2P–N$ (as in $H_2N–N$):

$$\Phi_{H_2P–N} = 0.98\Phi_0 - 0.16\Phi_1 - 0.03\ \Phi_2 + ...$$

The longer NP bond length in $H_2N–P$ permits a stronger interaction between Φ_0 and Φ_2, which becomes predominant:

$$\Phi_{H_2N–P} = 0.97\Phi_0 - 0.09\Phi_1 - 0.14\Phi_2 + ...$$

Despite its multiple PN bonding, H_2PN is found to be the least stable of all singlet isomers. After CI, phosphazene is the most stable isomer (the cis and trans isomers being nearly degenerate) while phosphinonitrene is only 7 kcal/mol higher in energy. As a comparison, aminonitrene was found to be 26 kcal/mol above diimide (at the CI level).[10,20] One may also notice that the energy difference between $H_2N–P$ and $H_2P–N$ (ΔE_{1C} = 34 kcal/mol) corresponds approximately to twice the energy difference between a NH bond and a PH bond ($\Delta E \approx$ 17–18 kcal/mol).

B. Triplet Surface. The relative energies for the open-shell triplet isomers are given in Table IV. The three levels of theory give the same stability ordering, aminophosphinidene < phosphazene < phosphinonitrene. As for the singlet isomers, aminophosphinidene is much more stable than phosphinonitrene.

C. Low-Lying States. Table V displays the three low-lying states for each isomer, corresponding to one closed-shell singlet state and two open-shell states. The open-shell singlet state for HP=NH formally belongs to the singlet ground-state surface and only constitutes the transition state for the rotation around the PN double bond. The open-shell $^1A''$ states are always the highest in energy.

Phosphinonitrene has a singlet ground state with a singlet–triplet separation calculated at the CI level at 6.0 kcal/mol. Aminophosphinidene has a triplet ground state with a triplet–singlet separation of 7.1 kcal/mol. Little is known about singlet–triplet separations in nitrenes or phosphinidenes. Table VI compares

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(35) Mavridis, A.; Harrison, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7651.

(36) Trinquier, G.; Barthelat, J. C.; Satgé, J. *J. Am. Chem. Soc.* **1982**, *104*, 5931.

(37) Cade, P. E. *Can. J.* Phys. **1968**, *46*, 1989.

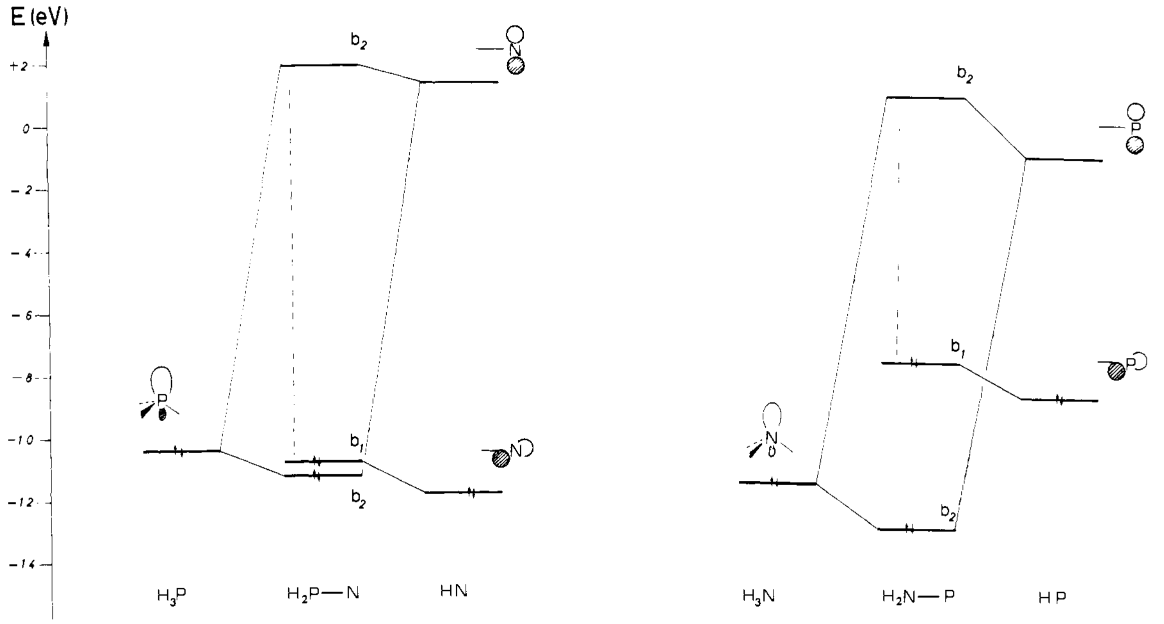

Figure 5. Relevant MO energy levels in singlet phosphinonitrene and aminophosphinidene.

our results with related available data. Most nitrenes have a triplet ground state. Davis and Goddard's discussion[28] shows that a π lone pair, owing to its possible delocalization into the vacant π orbital of the terminal N, must stabilize the closed-shell singlet state. Indeed, they calculated a singlet ground state for aminonitrene with the triplet state 15 kcal/mol higher in energy. However, Ahlrichs and Staemmler[20] found for this molecule a triplet ground state with the singlet state 3 kcal/mol above. In fact both works agree for the SCF results (triplet ground state, S–T separation of 5 kcal/mol), and the approximate electron-correlation calculations (IEPA–PNO) performed in ref 20 may not provide the correct differential lowering of the singlet state with respect to the triplet state. In view of our calculated singlet ground state for phosphinonitrene, aminonitrene should also have a singlet ground state. The delocalization of the π lone pair of the planar phosphino group is therefore sufficient to stabilize the singlet state to the point where it becomes the ground state. However, the delocalization of the π lone pair of the planar amino group in aminophosphinidene does not seem sufficient to give a singlet ground state.

The molecular orbital energy levels indicate that both phosphino and amino lone pairs are conjugated since their energy levels are lowered with respect to PH_3 (by 0.7 eV) and NH_3 (by 1.4 eV), showing a better conjugation of the amino lone pair (see Figure 5). However, the main factor governing the ground-state multiplicity is the separation, in the singlet state, between the b_1 (in-plane) HOMO level and the b_2 (out of plane) LUMO level. A large gap can be related to a singlet ground state, and a small gap can be related to a triplet state, as in the a_1–b_1 separation in carbene-like molecules. Figure 5 shows that this separation remains small in aminophosphinidene despite the nitrogen lone-pair level lowering.

Lastly, the singlet–triplet separation calculated in HP=NH (28.0 kcal/mol) is much less than the singlet–triplet separation calculated in methanimine (64.5 kcal/mol).[22]

D. Relative Energies. The relative energies of all first singlet and triplet H_2PN isomers are recorded in Table VII together with possible dissociation products, namely, PN, H_2, PH, NH, and 2H in their ground states. These diatomic molecules were optimized at the SCF DZ + d(P) level; their geometries are given in Table VIII.

Table VII. Summary of Relative Energies Calculated at the CI Level

isomers	ΔE, kcal/mol	isomers	ΔE, kcal/mol
H_2P–N $^3A''$	47.3	H_2N–P $^3A''$	0.1
HP=NH $^1A_1$	41.3	HP=NH $^1A'$ trans	0
HP–NH ^3A	28.0	P≡N + H–H	−0.6
H_2N–P $^1A_1$	7.2	P≡N + 2H	102.5
HP=NH $^1A'$ cis	0.6	P–H ($^3\Sigma^-$) + N–H ($^3\Sigma^-$)	84.6

Table VIII. SCF Geometries for Ground-State Diatomic Molecules (DZ + d(P) Basis Set)

	state	ref	r_e, Å	ω_e, cm^{-1}
PN	$^1\Sigma^+$	this work	1.467	1554
		exptl[a]	1.491	1337
H_2	$^1\Sigma^+$	this work	0.747	4639
		exptl[a]	0.741	4401
PH	$^3\Sigma^-$	this work	1.426	2656
		exptl[a]	1.422	2365
NH	$^3\Sigma^-$	this work	1.042	3416
		exptl[a]	1.036	3282

[a] Reference 30.

First, let us comment on the relative stability of the H_2PN isomers. A striking result is the near-degeneracy of singlet phosphazene and triplet aminophosphinidene, which are the most stable isomers. Above them we find singlet aminophosphinidene at 7 kcal/mol, next triplet phosphazene at 28 kcal/mol, and last singlet and triplet phosphinonitrene more than 41 kcal/mol above. Therefore the covalent π-bonded compound does not depart from the other isomers as far as its thermodynamic stability is concerned. The unsaturation equally prefers to be borne by the only phosphorus, in a triplet state, rather than shared in a π bond. Once more, this supports the reluctance of second-row atoms to form stable double bonds, unlike the case for first-row atoms. Indeed the calculated stability for N_2H_2 was HN=NH (^1A_g, trans) < H_2N—N ($^1A_1$) by 26 kcal/mol[10,20].

The two main conclusions of these calculated energies are (i) the stability of triplet aminophosphinidene and (ii) the instability of both singlet and triplet phosphinonitrene, despite its multiple bonding in the singlet state.

The three most stable isomers compete with the ground-state dissociation products PN + H_2 (note that a direct dissociation from the singlet isomers is symmetry forbidden as for diimide[38]). This is due to the relatively poor stability of PN (D_0 = 147 kcal/mol).[30] In contrast, N_2 + H_2 were computed to be 46

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[38] Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Toronto, 1977; p 375.

Table IX. Valence Energy Levels for Closed-Shell Singlet States (eV, DZ + pol Basis Set)

	HP=NH $^1A'$		H_2P-N $^1A_1$		H_2N-P $^1A_1$	
	trans	cis				
2a'' (π^*)	+1.33	+1.31	$2b_2$ (p_π(N))	+1.92	$2b_2$ (p_π(P))	+1.00
5a' (n_σ)	−10.02	−10.55	$2b_1$ (n_p(N))	−10.84	$2b_1$ (n_p(P))	−7.53
1a'' (π)	−11.58	−11.68	$1b_2$ (n_p(P))	−11.20	$1b_2$ (n_p(N))	−12.81
4a'	−14.50	−12.87	$3a_1$	−13.56	$3a_1$	−13.65
3a'	−16.03	−17.39	$1b_1$	−16.64	$1b_1$	−19.18
2a'	−21.61	−21.53	$2a_1$	−21.99	$2a_1$	−21.43
1a'	−31.56	−31.60	$1a_1$	−30.54	$1a_1$	−32.67

Table X. Estimated Ionization Potentials (eV)

N≡N			P≡P			P≡N			HP=NH $^1A'$				H_2P-N $^1A_1$		$P-NH_2$ $^1A_1$	
	est	exptl[a]		est	exptl[b]		est	exptl[c]	trans		cis					
$3\sigma_g$	16.3	15.6	$2\pi_u$	10.3	10.6	7σ	11.7	11.9	5a'	9.6	5a'	10.3	$2b_1$ (n_p(N))	8.5	$2b_1$ (n_p(P))	7.2
$1\pi_u$	16.8	17.0	$5\sigma_g$	10.8	10.8	2π	12.3	12.3	1a'' (π)	11.6	4a'	11.2	$3a_1$	10.6	$1b_2$ (n_p(N))	10.8
$2\sigma_u$	20.4	18.8	$4\sigma_u$	16.4	15.5	6σ	17.6	15.7	4a'	13.2	1a'' (π)	11.7	$1b_2$ (n_p(P))	10.9	$3a_1$	13.0

[a] Reference 42. [b] Reference 43. [c] Reference 44.

Table XI. Results from Mulliken Population Analyses (DZ + pol Basis Set)

molecule	state	net atomic charges P	N	H(P)	H(N)	π charges in singlet states P	N	resulting dipole moment, D	pop of d orbitals on P atom, e
HP=NH	$^1A'$ trans	0.25+	0.37−	0.04−	0.16+	0.17+	0.17−	1.23	0.17
	$^1A'$ cis	0.31+	0.37−	0.10−	0.16+	0.18+	0.18−	2.25	0.17
	^3A	0.18+	0.39−	0.03+	0.18+			1.96	0.12
H_2P-N	$^1A_1$	0.27+	0.30−	0.02+		0.70+	0.70−	4.45	0.23
	$^3A''$	0.28+	0.32−	0.02+				2.89	0.14
H_2N-P	$^1A_1$	0.01−	0.34−		0.17+	0.32+	0.32−	2.72	0.09
	$^3A''$	0.06+	0.41−		0.17+			2.43	0.08

kcal/mol below *trans*-diimide[20] due to the great stability of N_2 (D_0 = 225 kcal/mol).[30] This difference of stability between N_2 and PN together with the difference of the strength of the ($\sigma + \pi$) −N=N− and −P=N− bonds is responsible for the different exothermicities of the reactions

$$\mathrm{HP{=}NH(trans)} \rightarrow \mathrm{PN} + 2\mathrm{H} \qquad (\Delta E = +103\ \mathrm{kcal/mol})$$

$$\mathrm{HN{=}NH(trans)} \rightarrow \mathrm{N_2} + 2\mathrm{H} \qquad (\Delta E = +60\ \mathrm{kcal/mol})$$

The direct, allowed dissociation energy of *trans*-HP=NH into ground-state fragments HP and NH was computed at 85 kcal/mol, without taking into account zero-point vibration energies. This can be considered as a measurement of the ($\sigma + \pi$) PN bond energy. With the basis set we use, one can expect to underestimate such an energy difference; thereby an estimate for the ($\sigma + \pi$) PN double-bond energy should be about 90–95 kcal/mol.

Electronic Structures and Discussion

A. Valence Energy Levels for Singlet States. The valence energy levels for the closed-shell singlet states are reported in Table IX. The HOMO of phosphazene is a σ level (this MO combines the two lone pairs, mainly that of phosphorus, but is rather delocalized all over the molecule); the π level is the second level ($\pi_{P=N}$ = 11.58 eV) as in methanimine ($\pi_{C=N}$ = 12.24 eV)[23] and *trans*-diimide ($\pi_{N=N}$ = 14.21 eV).[39] In contrast, the π level is the HOMO level in phosphaethylene,[25] germanimine ($\pi_{Ge=N}$ = 9.69 eV),[36] and germanephosphimine ($\pi_{Ge=P}$ = 8.48 eV).[40]

The molecular energy levels for the nitrene and phosphinidene isomers shed light on the conjugation of the phosphino and amino lone pairs in the two respective isomers. As shown in Figure 5 and Table IX, the lone pairs take a component on the b_2 p_π orbital of their neighboring atom, resulting in a significant lowering of their levels with respect to PH_3 or NH_3.

These monoelectronic levels are related to ionization potentials (IP's) according to Koopmans' theorem (KT). However, KT IP's do not take into account polarization and correlation effects, which should affect differently the lone pairs and π levels in our molecules. Polarization effects generally lower the IP's (which are positive values) and are larger for lone pairs. Correlation effects strongly raise the IP's of bonds, especially π bonds. The following procedure[41] has been used to estimate the corrections (to KT values) required to reach more realistic IP's or at least a correct ordering for molecules containing π levels and lone pairs.

Polarization of the positive ion is approximated by first-order perturbation theory, as

$$\Delta\epsilon_k(\mathrm{pol}) = \sum_{ij^*} \frac{\langle i|F_k{}^+|j^*\rangle^2}{\epsilon_i - \epsilon_{j^*}}$$

where $F_k{}^+$ is the Fock operator obtained after removal of one electron from orbital k; i and j^* are the SCF molecular orbitals of the neutral molecule. The main part of correlation decrease in the positive ion is due to the lack of double excitations from orbital k and can be approximated by

$$\Delta\epsilon_k(\mathrm{cor}) = \sum_{j^*l^*} \frac{\langle kj^*|kl^*\rangle^2}{2\epsilon_k - \epsilon_{j^*} - \epsilon_{l^*}}$$

Both contributions are easy to evaluate and only need a computing effort equivalent to one SCF iteration.

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[39] Snyder, L. C.; Basch, H. "Molecular Wave Functions and Properties"; Wiley: New York, 1972; p T-64.

[40] Barthelat, J. C., private communication.

[41] Daudey, J. P.; Malrieu, J. P. Trinquier, G., unpublished work.

[42] Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970.

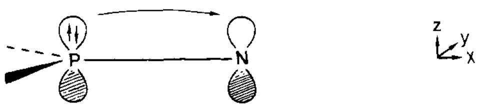
[43] Bulgin, D. K.; Dyke, J. M.; Morris, A. *J. Chem. Soc., Faraday Trans. 2*, 1976, *72*, 2225.

[44] Bulgin, D. K.; Dyke, J. M.; Morris, A. *J. Chem. Soc., Faraday Trans. 2*, 1977, *73*, 983.

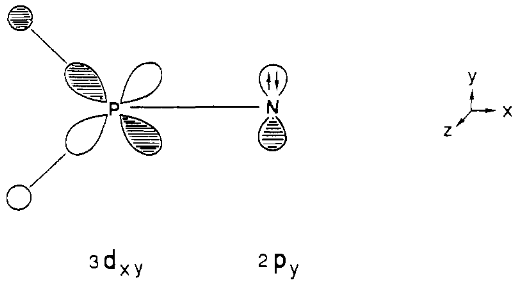
Our evaluation of the loss of correlation energy in the ion is underestimated for π ionizations, and in most cases the π levels are well described by Koopmans' approximation. Therefore, we retain the KT IP's for the π levels in our final results, which are reported in Table X. They concern the three lowest IP's for singlet H_2PN isomers together with those for N_2, P_2, and PN, for which experimental data are available. Note here the correct ordering for the diatomic molecules whereas KT gives a wrong ordering. These estimated IP's for the H_2PN isomers could be of interest for assignments of the photoelectron spectra of related structures.

B. Charge Distributions and Bonding. Some results of the Mulliken population analyses are displayed in Table XI. There are no surprises concerning the polarity in phosphazene. The net atomic charges clearly show how the polarizability of the PH bond allows maximization of the stabilizing electrostatic interaction in the cis isomer.

The strong polarity in singlet $H_2P–N$ is due to the delocalization of the phosphorus π lone pair into the nitrogen vacant $2p_zAO$:



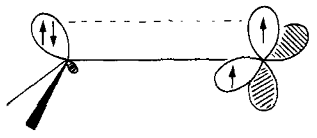
The π charges indicate a migration of up to 0.7 e. On the other hand, the analysis of the $2b_1$ HOMO shows a fair "back-bonding" of the nitrogen π lone pair into the phoshorus $3d_{xy}$ orbital, together with hyperconjugation with hydrogen atoms:



This phosphorus $3d_{xy}$ orbital appears filled by 0.16 e; this results in an overall phosphorus d population of 0.23 e, which is larger than that of the other isomers (see Table XI).[45] These two delocalizations are responsible for the short PN bond length and its somewhat "triple" bond character; however, since the former effect prevails, the electronic structure is better depicted by $H_2P\rightleftharpoons N$ rather than by $H_2P\equiv N$.

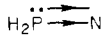
Formally, the bonding in singlet $H_2N–P$ proceeds from similar effects but with different intensities. The delocalization of the nitrogen π lone pair toward phosphorus is in contradiction to the electronegativities; therefore only 0.32 e migrates and there is less difference in the charge distribution (see Table XI). As expected from the high position (in energy) of the nitrogen 3d orbitals, $3d(N)\leftarrow p_\pi(P)$ back-bonding is nearly nonexistent in singlet $H_2N–P$.

In the triplet states, a two-center–three-electron interaction also occurs



which is less important than the two-electron interactions occurring in closed-shell singlet states.

It seems reasonable to ascribe the poor stability of $H_2P–N$ to its high polarity, which is induced by both σ and π polarities:



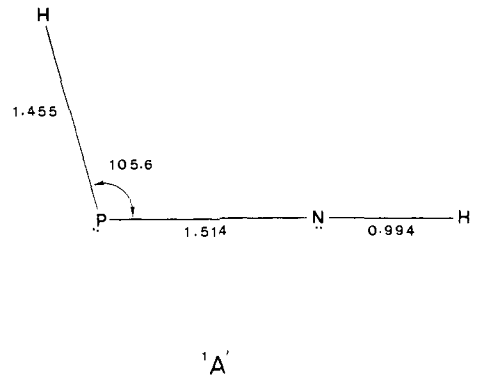
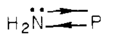


Figure 6. SCF (DZ + d(P) basis set) predicted transition state for cis/trans isomerization of phosphazene, HP=NH, in angstroms and degrees.

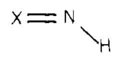
On the other hand, the stability of the $H_2N–P$ could be due to antagonistic σ and π polarities



which result in weakly polarized PN bonds.

C. Further Results on the –P=N– Double Bond. 1. Cis/Trans Isomerization in Phosphazene. Starting from the equilibrium geometry of *trans*-phosphazene, linearization of the hydrogen atom on the phosphorus atom requires 111 kcal/mol while the corresponding linearization on the nitrogen atom requires 10 kcal/mol (SCF DZ + d(P) level). Since the rotational barrier around the PN bond was calculated at 40 kcal/mol (CI level), the cis/trans isomerization in phosphazene proceeds via a linear nitrogen, as in diimide.

With the assumption of the PNH angle to be equal to 180°, the geometry of the closed-shell molecule was fully optimized at the SCF DZ + d(P) level. The transition-state structure is given in Figure 6. The energy barrier for the trans-cis isomerization is calculated at 7.3 kcal/mol (SCF DZ + d(P)), 14.1 kcal/mol (SCF DZ + pol), and 15.2 kcal/mol (CI). As is the case for diimide,[10,20] correlation effects do not alter the barrier. We note that the trans/cis isomerization barrier is much weaker in HP=NH (15 kcal/mol) than in HN=NH (55 kcal/mol).[10,20] Since the nitrogen inversion for methanimine is 28–30 kcal/mol[46–48] it seems that the nitrogen inversion barrier in a system



increases with increasing polarity of the $X^+–^-N$ bond.

2. PN Bond Energy. The rotational barrier, calculated as the open-shell ^1A state relative energy (see Table V), is a possible estimate for the π contribution to the bond energy. This method predicts an ≃40 kcal/mol PN π bond energy. From the literature one can indirectly estimate the π contribution to a –N=N– bond energy at about 62 kcal/mol.[49,50] On the other hand, the enthalpy of the dissociation reaction

$$HP{=}NH \rightarrow HP + NH$$

can be taken as a measurement of the –P=N– ($\sigma + \pi$) bond energy. Under the conditions defined in part D of the Energies section, the estimated energy for the PN ($\sigma + \pi$) double bond should be about 90–95 kcal/mol. One can find in the literature the average P–N single bond energy to be estimated at ≃50

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[45] A similar back-bonding from a π lone pair into a vacant d orbital was also pointed out in $H_2Ge{=}O$.[36]

[46] Jennings, W. B.; Al-Showiman, S.; Boyd, D. R.; Campbell, R. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1501.

[47] Lehn, J. M.; Munsch, B. *Theor. Chim. Acta* **1968**, *12*, 91.

[48] For reviews on inversion barriers at nitrogen, see: Jennings, W. B.; Worley, S. D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1512. Leroy, G.; Nguyen, M. T.; Sana, M.; Villaveces, J. L. *Bull. Soc. Chim. Belg.* **1980**, *89*, 1023.

[49] Pauling, L. "College Chemistry", 3rd ed.; W. H. Freeman: San Francisco, 1964; p 316.

[50] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972.

kcal/mol,[50] which confers a certain consistency to our results.

D. Concluding Remarks. The unimolecular reactivities for each H_2PN isomer involve 1,2-hydrogen shifts.[51] We did not study the corresponding barrier heights, but theoretical results on 1,2-hydrogen shifts with breaking of a NH bond are available, for instance

$$\mathrm{H_2C{=}NH \rightarrow H_3C{-}N{:}}$$

singlet, $\Delta E = +85$ kcal/mol; no barrier[22]

$$\mathrm{H_2C{=}NH \rightarrow H_3C{-}N{:}}$$

triplet, $\Delta E = -18$ kcal/mol; $\Delta E^{\ddagger} = 35$ kcal/mol[22]

$$\mathrm{HN{=}NH \rightarrow H_2N{-}N{:}}$$

singlet, $\Delta E = +26$ kcal/mol; $\Delta E^{\ddagger} = 83$ kcal/mol[10]

These results together with others concerning breaking of CH bonds such as

$$\mathrm{HC{\equiv}CH \rightarrow H_2C{=}C{:}}$$

singlet, $\Delta E = +40$ kcal/mol; $\Delta E^{\ddagger} = 48$ kcal/mol[52]

$$\mathrm{HC{\equiv}CH \rightarrow H_2C{=}C{:}}$$

triplet, $\Delta E = +1$ kcal/mol; $\Delta E^{\ddagger} = 70$ kcal/mol[53]

$$\mathrm{H_3C{-}CH \rightarrow H_2C{-}CH_2}$$

triplet, $\Delta E = -2$ kcal/mol; $\Delta E^{\ddagger} = 53$ kcal/mol[54]

tend to suggest significant energy barriers for all the 1,2-hydrogen shifts that are possible in our singlet and triplet H_2PN isomers. However, one must bear in mind that bimolecular hydrogen exchanges may require lower barriers, for instance, only 4 kcal/mol for the aminonitrene → *trans*-diimide reaction according to STO-3G calculations by Kemper and Buck.[55] On the other hand, it is obvious that a singlet >P–N framework prefers polymolecular reactivity and should give, for instance, stable cyclotriphosphazene.

This work, which deals only with the static description of the singlet and triplet H_2PN potential energy surfaces, led to the following main results: (1) $H_2P{-}N$ has a singlet ground state but is the least stable structure despite the high multiplicity of its PN bond; (2) $H_2N{-}P$ has a triplet ground state; (3) cis and trans singlet $HP{=}NH$ and triplet $H_2N{-}P$ are the most stable isomers and are nearly degenerate in energy.

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Registry No. *cis*-**1**, 58734-29-5; *trans*-**1**, 58734-30-8; **2**, 83486-79-7; **3**, 83486-80-0.

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Crystal Structure of Dehydrated Sr-Exchanged Zeolite A. Absence of Near-Zero-Coordinate Sr^{2+}. Presence of Al Complex

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Abstract: Single crystals of Linde zeolite 4A were ion exchanged with a mixed solution of $Sr(ClO_4)_2$ and $Sr(OH)_2$ at room temperature to take advantage of stability under basic conditions and clean exchange in chlorate solution. Electron microprobe analyses revealed only insignificant amounts of Na and K. X-ray diffraction data for a crystal dehydrated at 350 °C, and another at 500 °C, were refined with space group $Fm\bar{3}c$ ($a = 24.68$ Å). Only the (111) diffraction violated the space-group extinctions. The mean T–O distances (1.599 and 1.730 Å) correspond to alternation of tetrahedra populated by Si and $\sim Al_{0.9}Si_{0.1}$, in conformity with earlier structural analyses and in complete disagreement with recent speculations of a 3:1 ordering model. All Sr atoms lie near the center of 6-rings, in disagreement with an earlier structure determination of an unanalyzed crystal for which one Sr was placed in an 8-ring; perhaps this latter position actually corresponds to K scavenged during ion exchange. Approximately four-fifths of the Sr atoms (Sr(1), 4.5 atoms per pseudocell) project into the large cage, and one-fifth (Sr(2), 1.2 atoms) project into the sodalite unit. Both types are bonded to three O(3), respectively at about 2.4 and 2.5 Å. Electron density at the center of the sodalite unit and on the triad axes is attributed to Al in a tetrahedron of oxygen species, disordered in two orientations. Such electron density is found in most varieties ion exchanged with divalent cations.

The concept of zero-coordination[1] for monovalent cations was disproven by accurate structural determination of dehydrated zeolite A[2] and the dehydrated K-exchanged variety.[3] The present structure determination of the dehydrated Sr-exchanged variety provides a test of the claim for near-zero-coordination of divalent cations that is apparently supported by structure determinations[4,5] of crystals of zeolite A dehydrated after exchange with solutions containing Cd^{2+}, Eu^{2+}, Ca^{2+}, and Sr^{2+}. In the present study, electron microprobe analysis of exchanged crystals demonstrates problems caused by scavenging of trace impurities during ion exchange, but such problems were not considered in ref 4 and 5. Weak electron density in the sodalite unit of the present structure is ascribed to a spatially disordered, occluded tetrahedral complex produced during ion exchange, and not occluded during initial crystallization.[6]

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