Calculated Properties and Ring-Chain Rearrangements of Triphosphirane (P_3H_3)

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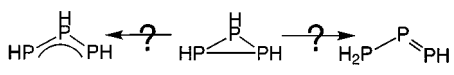
Keywords: Ab initio calculations / Ionization potentials / Phosphorus / Heterocycles / Small ring systems

Ab initio quantum chemical calculations have been used to explore the P_3H_3 potential energy surface focussing on the ring-chain rearrangements of the three-membered ring in $(PH)_3$ (**1**), the parent triphosphirane. Relative energies between stationary points were estimated using the QCISD(T)/6–311G(d,p) method based on MP2/6–31G(d,p) geometries and corrected for zero-point contributions. Ring strain, proton affinities, ionization and excitation energies and heats of formation have been evaluated using larger basis sets, e.g. 6–311++G(3df,2p). The cyclic *trans*-triphosphirane (**1a**) is the most stable P_3H_3 isomer and lies about 40 kJ/mol below the open-chain phosphanyldiphosphene (H_2P–P=PH). The decrease of ring strain in three-membered rings when CH_2 is replaced by PH is confirmed. Triphosphirane **1a** is a virtually strain-free ring and even gains some stabilization relative to three separate P–P single bonds. The reduced ring strain also helps diminish the phosphorus inversion barrier to 224 kJ/mol compared to the monocyclic isomers of $(CH_2)(PH)_2$ and $(CH_2)_2(PH)$. Compound **1a** follows a pure ring-opening or a 1,2-hydrogen shift rather than a combined motion pathway, in fundamental contrast with corresponding processes of diphosphirane and phosphirane. This is due to the existence of an open-chain P_3H_3 phosphorane intermediate stabilized by allylic conjugation. The pericyclic ring-opening of **1a** is the most favored process but the energy barrier in the gas phase is about 180 kJ/mol high. Electron density is largely delocalized within the three-membered P_3 ring not only in the C_{3v}-symmetric **1b** (all-*cis*) but also in **1a** (C_s). The proton affinity of **1a** is similar to that of PH_3. The proton affinities decrease with n in *cyclo*-$(CH_3)_{3-n}(PH)_n$ and their values were obtained: PA(**1a**) = 777 ±10, PA(diphosphirane) = 799 ±10 and PA(phosphirane) = 802 ±10 kJ/mol. Heats of formation are evaluated as follows ($\Delta H°_{f0}$ at 0 K in kJ/mol): **1a**, 70 ±10; *cyclo*-$(PH)_2(PH_2)^+$ (protonated **1a**), 821 ±10; diphosphirane, 85 ±10; *cyclo*-$(CH_2)(PH)(PH_2)^+$ (protonated diphosphirane), 814 ±10; phosphirane, 86 ±10; and protonated phosphirane, 812 ±10 kJ/mol. All P rings remain cyclic following ionization to the radical cations. Adiabatic ionization energies (IE_a) are estimated as: **1a** and diphosphirane, 9.3 ±0.3 eV and phosphirane 9.5 ±0.3 eV. The first UV absorption band shifts toward the longer wavelength region on going from phosphirane to **1a**. The GIAO/B3LYP computed magnetic shieldings for **1a** and related molecules reveal a clear relationship between the narrow bond angles in the rings and their unusually strong magnetic shielding. The similarity of the predicted ^{31}P-NMR signals in **1a** and its heteroanalog diphosphirane, $(CH_2)(PH)_2$, can be rationalized in terms of a compensation of the carbon-substituent effect (downfield shift) and the bond-bending effect imposed by the ring (upfield shift).

Introduction

Phosphorus, in a similar way to carbon, is able to form stable open-chain and cyclic compounds with homonuclear bonds.[1] While the five-membered nitrogen ring (pentazole) could only be postulated as an intermediate at −50 °C,[2][3] the corresponding phosphorus ring in pentaphosphaphosphol was identified[4] at room temperature. An impressive number of polyphosphorus compounds have thus been prepared by different groups.[5−11] A simple example illustrates the close similarity between the chemistries of phosphorus and carbon: The experimentally known monocyclic P_5^- ion[4] is analogous to the cyclopentadienyl anion.[12] In general, the existence of polyphosphorus compounds as rings or chains depends on the number of P atoms involved. The simplest polyphosphane, which may have a ring and a chain isomer, was detected in 1972.[13] While many substituent-stabilized three-membered phosphorus homocycles (called triphosphiranes or cyclotriphosphanes) have been synthesized since,[11,13,14] the corresponding open-chain isomers are rare. The triphosphorus hydride, P_3H_3, has been positively identified by mass-spectrometric techniques,[13] but no information on its molecular structure is available. The ^{31}P-NMR-chemical shifts of three-membered rings comprising tricoordinate phosphorus cannot be described with substituent increments.[15][16] The question arises as to whether there are relationships between the NMR-chemical



Scheme 1. Alternative ring-chain rearrangments of triphosphirane

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shifts and geometric or electronic parameters in the parent three-membered compounds with 1−3 endocyclic phosphorus atoms and the related acyclic molecules. The tendency of phosphorus to accommodate cyclic structures easily is well established;[17] the competition between ring and chain often turns in favor of the former. However, the rare observation of open-chain P_3R_3 compounds raises the question about their thermodynamic and kinetic stabilities.

Previous theoretical studies[18−23] on the P_3H_3 model system were mainly confined to the electronic structure, ring strain and inversion barriers of the cyclic triphosphirane. The ring-chain conversion of the simplest parent triphosphirane, *cyclo*-$(PH)_3$, has not been investigated before. As part of our theoretical study on the structure and reactivity of P-containing three-membered rings,[24−27] we examine here the P_3H_3 potential energy surface by means of ab initio molecular orbital methods. In particular, the molecules with open-chain structures and their thermodynamic stability were investigated. The computed molecular properties of triphosphirane are discussed in the context of its organic heteroanalogs (diphosphirane and phosphirane).

Computational Details

Ab initio molecular orbital calculations were performed with the Gaussian 94 series of programs.[28] To facilitate comparison with our previous studies on phosphirane and diphosphirane,[24][26] we provide data derived with the same theoretical method. Higher-level computational results are included in the discussion. Each stationary point was characterized by harmonic vibrational analysis. Furthermore, the identity of each transition structure was determined by intrinsic reaction coordinate (IRC) calculations. Transition structures are designated by the **X/Y** notation where **X** and **Y** are the equilibrium structures connected by the TS. Geometrical parameters of the relevant equilibrium and TS were optimized using second-order Møller-Plesset perturbation theory, MP2/6-31G(d,p), which partly incorporates electron correlation. Based on these MP2/6-31G(d,p) geometries, the relative energies of the points on the (P_3H_3) energy surface have been estimated by single-point electronic energy computations using the quadratic configuration interaction method, QCISD(T), and the 6-311G(d,p) basis set. Improved estimates for thermochemical quantities were obtained by calculations with the larger 6-311++G(d,p) and 6-311++G(3df,2p) basis sets. The GIAO approach[29] was used to calculate magnetic shieldings at B3LYP/6-311G(d) //MP2/6-31G(d,p) level. Electron distributions (Mulliken) and the Wiberg bond indices, WBI,[30] were evaluated at the same level. For the open-shell systems, correlated wavefunctions were constructed using unrestricted Hartree-Fock (UHF) references. Throughout this paper, bond lengths are given in Ångstrøms, bond angles in degrees, magnetic shieldings in ppm, total energies in hartrees, zero-point vibrational and relative energies, unless otherwise noted, in kJ/mol.

Results and Discussion

Before examining the various chemical properties of triphosphirane and the related three-membered rings, the P_3H_3 potential energy surface will be first presented in order to establish the thermochemical and kinetic stabilities of the possible isomers.

The P_3H_3 Potential Energy Surface

Selected optimized structural parameters of the relevant stationary points considered at the MP2/6−31G(d,p) level of accuracy are given in Figures 1 and 2. The calculated total and zero-point vibrational energies are recorded in Table 1 while the relative energies are summarized in Table 2. The potential energy profiles are illustrated schematically in Figures 3 and 4. In general, the same energy ordering between the P_3H_3 structures considered was found at all levels employed. The discussion in this section is based on QCISD(T)/6−311G(d,p) //MP2/6−31G(d,p) + scaled ZPE/HF/6−31G(d,p) //HF/6−31G(d,p) energies. Triphosphirane can exist in the *trans* (**1a**) and the *cis* (**1b**) form. The endocyclic P−P distances (2.210 to 2.225 Å, Figure 1) are slightly longer than in diphosphane (2.209 Å, H_2P-PH_2). As expected, **1a** is more stable than **1b** [E_{rel}(*cis*) = 17 kJ/mol]. In **1b** the P atom environments remain strongly pyramidal; the phosphorus inversion barrier of **1a** is 217 kJ/mol via the TS **1a/1a**. This is far larger than the inversion barrier in PH_3, which is only 148 kJ/mol at the same level of theory (a more accurate estimate is discussed below). As seen in Table 2, **1a** is the P_3H_3 global minimum lying well below the open-chain isomers **2**, **3** and **4**. The cyclic form **5**, with a formal P=P double bond and a tetracoordinate P atom, is a high energy isomer that lies 137 kJ/mol above **1a**. Of the three different types of open-chain species, phosphanyldiphosphenes **2** are the more stable, followed by phosphoranes **4** and then phosphanylphosphinidenes **3**. Each of these species exhibits several conformations and configurations; here we present only the most stable and representative structures. The symmetrical conformer **2b** (C_s) of phosphanyldiphosphene is marginally more stable, by 1 kJ/mol, than **2a** (C_1), which is 42 kJ/mol less stable than **1a**. The preference of the phosphanyl group for a symmetrical configuration is similar to that in analogous phosphapropenes[31] where an interaction between the P lone pair and π electrons is weak.[32] Among the phosphoranes with allyl conjugation of the π system on the phosphorus backbone structure, **4a** is most stable [E_{rel} (**4b**) = 9 kJ/mol relative to **4a**]. Nevertheless, **4a** is 115 and 73 kJ/mol less stable than **1a** and **2a**, respectively. Stabilization by allylic conjugation is more pronounced (P−P = 2.06 Å) in **4a** than in the corresponding acyclic $P(PH)_2^-$ anion[11] (P−P = 2.09 Å). In contrast to the formal Lewis description of the central phosphorus atom in these molecules as pentavalent, the sum of Wiberg bond indexes, ΣWBI, is only four (one single P−H and two allylic, 1.5 fold, bonds; ΣWBI is 3.8 for **4a**; in "CH_2=PH=PH" ΣWBI is 3.9). Therefore, σ^3,λ^4-P is the

best characterization[8] of the allyl-type phosphorus valence.

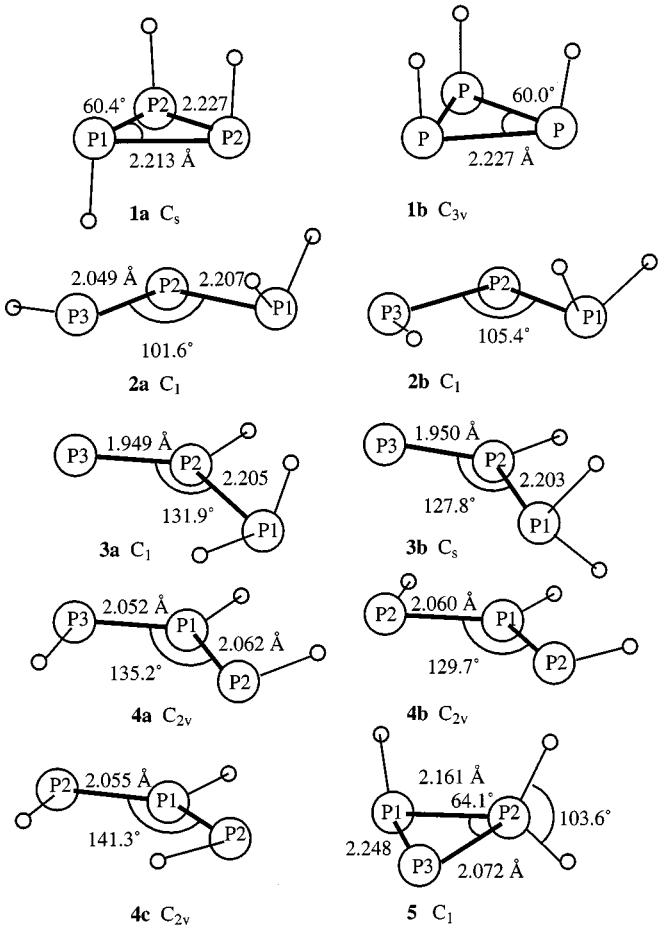

Figure 1. Minimum structures of P_3H_3 optimized at RMP2(fc) /6−31G(d,p)

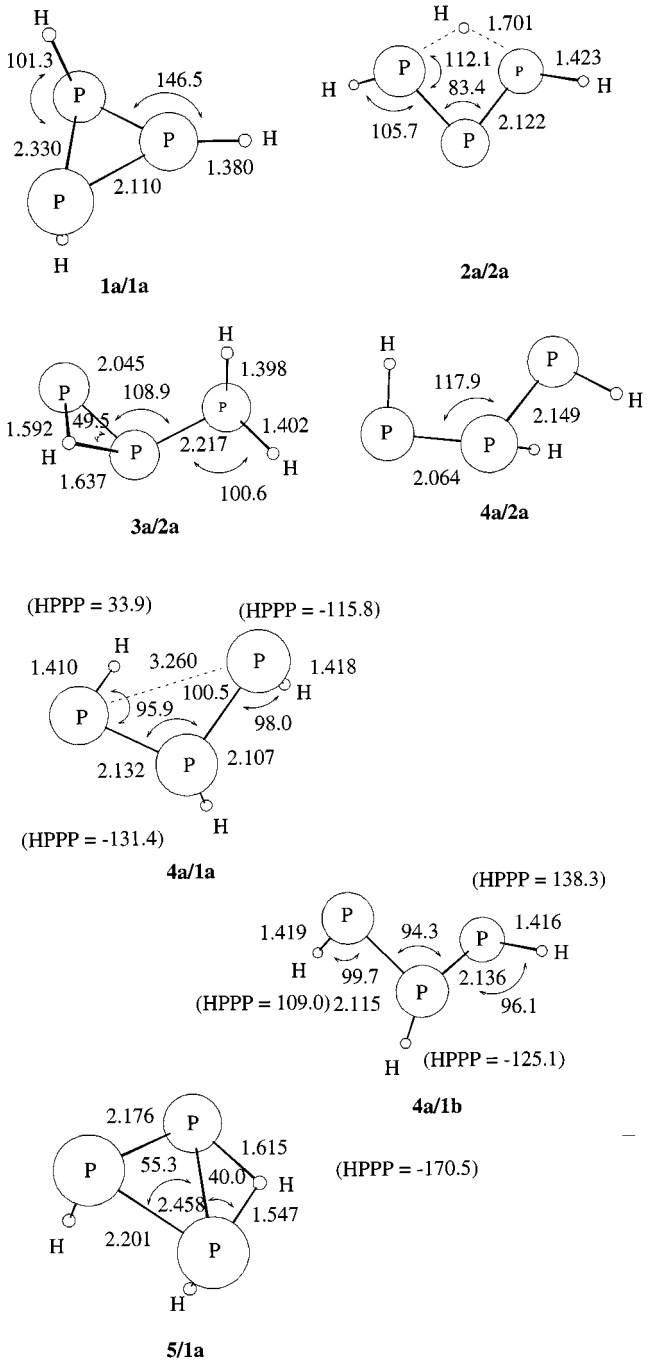

Figure 2. Transition structures of P_3H_3 optimized at RMP2(fc) /6−31G(d,p)

The singlet phosphanylphosphinidenes **3** represent the least stable open-chain isomers. As in $P-PH_2$, i.e. the unsubstituted case,[33−35] the central P atom has a planar configuration (**3b**; approximately planar in **3a**). The staggered conformer **3a** is slightly more stable than the C_s-symmetrical conformer **3b** with the phosphorus lone pair in the plane of the phosphinidine π bond. Conformer **3a** is 141 kJ/mol above **1a** and 99 kJ/mol above **2a**. Compared with the parent tautomers,[35] RHP=P/RP=PH with R=H, the phosphanyl group in **3a** ($R = PH_2$) has little effect on the relative energy of the tautomers. Accordingly, the P−P distances in **2**, as well as in **3**, remain almost unaffected upon replacing H in the parent by PH_2. It is well known that phosphinidenes usually have a triplet electronic ground state.[36][37] For the simplest phosphanylphosphinidene (H_2P-P), the triplet state with C_s symmetry was shown to lie about 28 kJ/mol below the corresponding closed-shell singlet state (see our previous study at the same level of accuracy).[35] In contrast, for **3a** calculations indicate that the triplet state is not clearly preferred (lowest-lying singlet is only 6.6 kJ/mol higher in energy than the triplet). While the π-donor effect of the PH_2 group is negligable for the P2−P3 bond in **2** and triplet **3**, it shifts electron density into the phosphinidine bond (P2−P3 is polarized towards δ^1-P in singlet **3**). As a result the energy of the singlet **3a** relative to the triplet is distinctly reduced.

Overall, successive replacement of the CH_2 in cyclopropane by PH tends to reinforce the thermodynamic stability of the cyclic isomer. In the all-phosphorus case considered here, the ring is by and large the most stable form. Whether it is also the kinetically most stable isomer will be examined in the following section.

Table 1. Total energies at different levels of MP2 and QCI theory,[a−c] of P_3H_3 structures and zero-point vibrational energies[d]

Structure[a]	MP2[b]	MP2[c]	QCISD[c]	QCISD(T)[c]	ZPE[d]
1a, C_s	−1024.26821	−1024.30886	−1024.35494	−1024.37143	77
1b, C_{3v}	−1024.26027	−1024.30136	−1024.34817	−1024.36465	76
1a/1a, C_2	−1024.18281	−1024.22414	−1024.26967	−1024.28685	72
2a, C_1	−1024.24884	−1024.28917	−1024.33633	−1024.35407	73
2b, C_s	−1024.24816	−1024.28879	−1024.33647	−1024.35413	72
2a/2a, C_2	−1024.19355	−1024.23750	−1024.27358	−1024.29682	64
3a, C_1	−1024.20946	−1024.25100	−1024.29843	−1024.31578	72
3b, C_s	−1024.20750	−1024.24946	−1024.29777	−1024.31475	72
3a/2a, C_1	−1024.17300	−1024.21460	−1024.26427	−1024.28124	65
4a, C_s	−1024.22371	−1024.26337	−1024.30515	−1024.32579	72
4b, C_s	−1024.22051	−1024.26010	−1024.30197	−1024.32253	72
4a/1a, C_1	−1024.18705	−1024.22751	−1024.27167	−1024.29618	69
4b/1b, C_1	−1024.18974	−1024.23020	−1024.27573	−1024.30001	69
4a/2a, C_1	−1024.17114	−1024.21451	−1024.25809	−1024.28250	65
5, C_1	−1024.21969	−1024.25872	−1024.30229	−1024.31939	77
5/1a, C_1	−1024.18216	−1024.22813	−1024.27379	−1024.29121	68

[a] Based on MP2/6−31G(d,p)-geometries. Core orbitals are frozen. Point groups of the geometries (see Figures 1 and 2) obtained without symmetry constraint. − [b] Using full sets of MOs for the 6−31G(d,p) basis set. − [c] Using the 6−311G(d,p) basis set. − [d] Zero point vibration energy, ZPE, in kJ/mol obtained at HF/6−31G(d,p) and scaled by 0.9 to account for systematic overestimation.

Table 2. Relative energies in kJ/mol of P_3H_3 structures[a] at different levels of theory[a−c]

Structure[a]	MP2[b]	MP2[c]	QCISD[c]	QCISD(T)[c]	CI+ZPE[d]
1a	0.0	0.0	0.0	0.0	0.0
1b	20.9	19.7	17.8	17.8	16.8
1a/1a	224.4	222.6	224.0	222.2	217.2
2a	50.9	51.7	48.9	45.6	41.6
2b	52.7	52.7	48.5	45.5	40.5
2a/2a	196.2	187.5	213.8	196.0	183.0
3a	154.4	152.0	148.5	146.2	141.2
3b	159.5	156.1	150.2	148.9	143.9
3a/2a	250.0	247.6	238.2	237.0	225.0
4a	116.9	119.5	130.8	119.9	114.9
4b	125.2	128.0	139.2	128.5	123.5
4a/1a	213.2	213.7	218.8	197.7	189.7
4b/1b	206.2	206.7	208.1	187.6	179.6
4a/2a	255.0	247.9	254.5	233.6	221.6
5	127.5	131.7	138.3	136.7	136.7
5/1a	226.1	212.1	213.2	210.8	201.8

[a] Transition structures, are designated by the **X/Y** notation where **X** and **Y** are the equilibrium structures connected by the TS (see Figures 1 and 2). −[b] Using the 6−31G(d,p) basis set. − [c] Using the 6−311G(d,p) basis set. − [d] QCISD(T)/6−311G(d,p) + ZPE/HF/6−31G(d,p).

Interconversions Between the P_3H_3 Isomers

As shown in Figures 3 and 4, **1a** can undergo a ring-opening simply by breaking an endocyclic P−P bond to give phosphorane **4**. This opening, via **4a/1a**, is not accompanied at all by a hydrogen shift from one P center to another. Despite extensive searches, a single-step pathway connecting **1a** either to diphosphene **2a** or to phosphinidene **3a** could not be located. The behavior of **1a** thus differs basically from that of its homologous phosphirane and diphosphirane.[24] The pure ring openings in the latter molecules require activation energies that are much larger than those for pathways where hydrogen transfer is involved. This is presumably due to the fact that the TS **4a/1a** profits from the allyl delocalization, which stabilizes triphosphorane **4a**. The ring opening of the *cis*-triphosphirane (**1b**) through **4b/1b** is an even more facile process. This implies that a *cis*-triphosphirane might be formed kinetically upon ring-closure of a triphosphorane like **4b**. A 1,2-shift of the hydrogen between two ring atoms via **5/1a** is also possible, without ring opening, to yield the cyclic compound **5**. The energy barrier for transformation of **1a** to **5** is somewhat larger than that for ring-opening but slightly smaller than that for inversion. The energy diagram in Figure 3 demonstrates the peculiar feature of **1a**, which prefers either a pure ring opening or a 1,2-shift but does not undergo combined motions.

Chain-chain rearrangements are summarized in Figure 4. The isomers **2**, **3** and **4** are related to each other by a single 1,2- or 1,3-hydrogen shift. Structure **2a/2a** is the TS for an antarafacial 1,3-hydrogen shift between the two terminal P atoms of the diphosphene **2a**. The energy barrier of 141 kJ/mol relative to **2a** is rather low for this type of process.[31] The corresponding barrier for 1,3-H shift in diphosphapropene ($H_2P-CH=PH \rightarrow HP=CH-PH_2$) has been calculated to be 163 kJ/mol at the same level of accuracy. Again the reduced ring strain in **2a/2a** facilitates this isomerization. Two observations are worth noting: (i) a TS for a suprafacial migration could not be located, in contrast to the situation in phosphapropenes,[31] and the high stability of **4** renders this migrating mode inoperative; (ii) experimental results have shown that 1,3-shifts in P compounds are thermally accessible unimolecular processes.[38] The rearrangement via **2a/2a** is therefore quite a realistic connection. Both 1,2-H shift TSs **4a/2a** and **3a/2a** have similar energies but lie above the TS **2a/2a** for 1,3-H shift and **4a/1a** for ring opening. Ring-closure of phosphorane **4a** is favored over isomerization to another acyclic isomer. The connection between **1a** and the most stable open-chain phosphanyldiphosphene, **2a**, takes place in two steps through the intermediate **4a**. The most energy-demanding step is the 1,2-H shift (**4a/2a**). While the reaction barriers in the triphosphorus system differ fundamentally from those con-

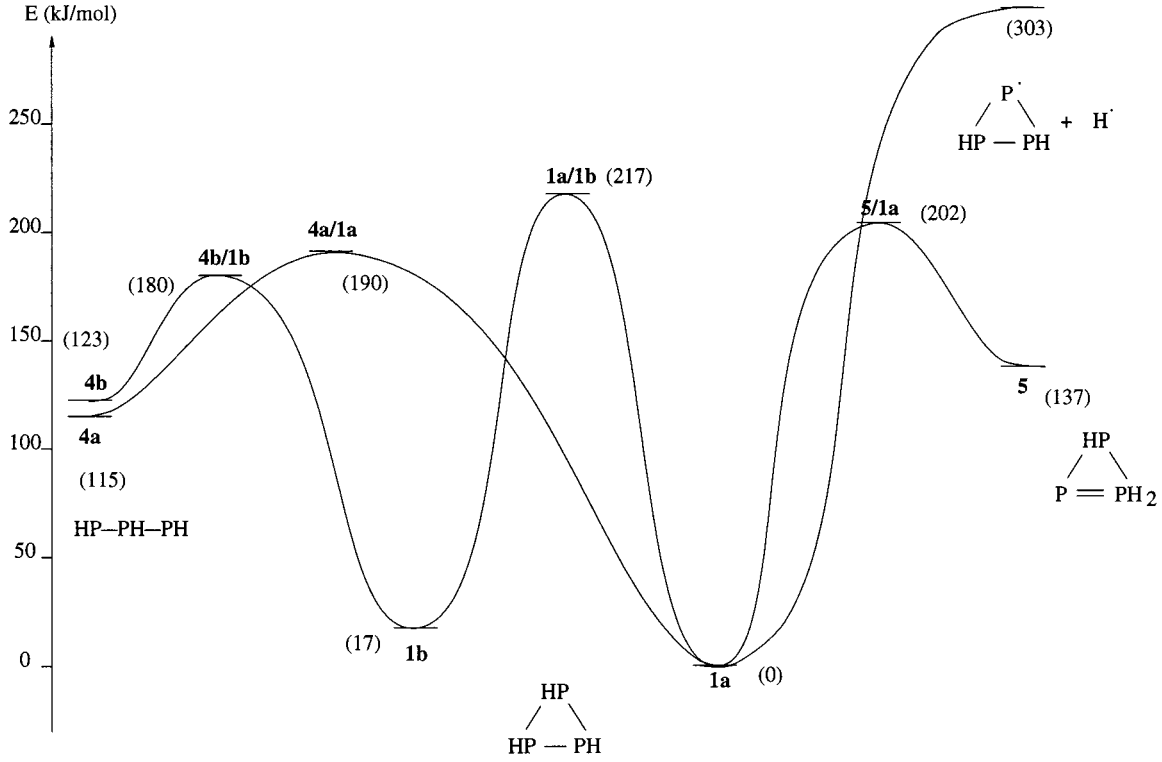

Figure 3. Relative energies calculated at QCISD(T) /6−311G(d,p) + ZPE/HF/6−31G(d,p) of TS and intermediate products of P_3H_3 ring isomerization in kJ/mol

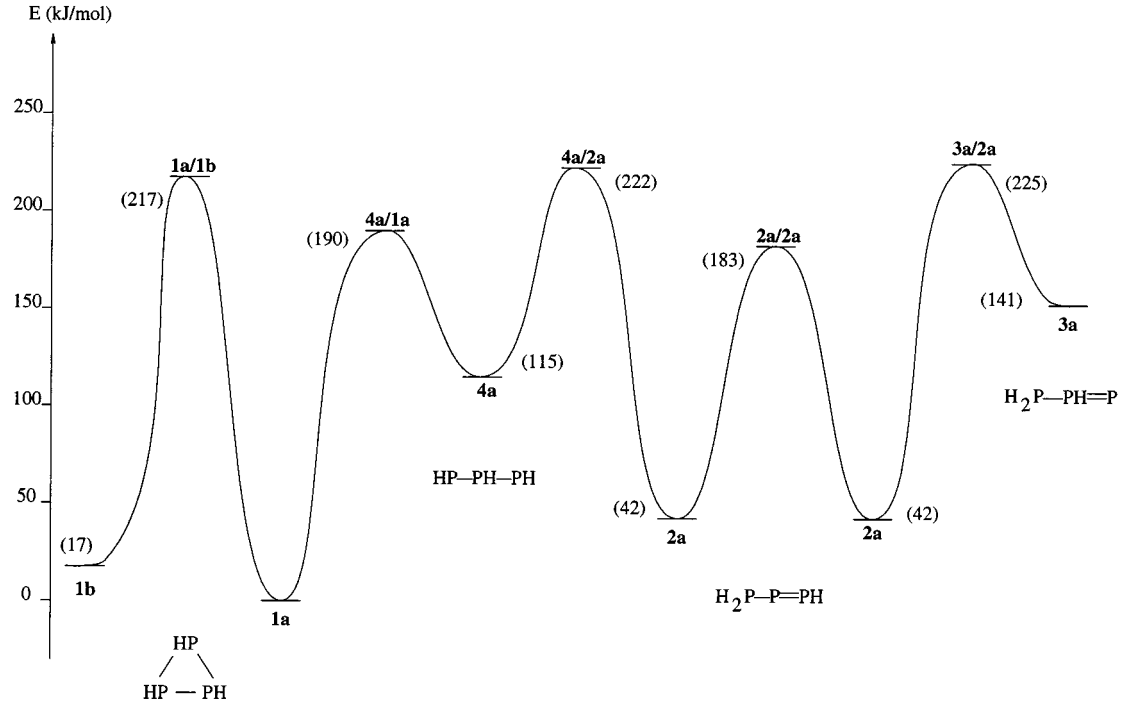

Figure 4. Relative energies calculated at QCISD(T) /6−311G(d,p) + ZPE/HF /6−31G(d,p) of TS and intermediate products of the rearrangements of acyclic P_3H_3 isomers in kJ/mol

taining only one P atom, physical properties differ only gradually.

Comparison of Triphosphirane Properties with Those of $(CH_2)_{3-n}(PH)_n$ with $n < 3$

Having established that the triphosphirane **1a** is the most stable form among P_3H_3 isomers, we now discuss some of its molecular properties and compare them with those of other three-membered rings built from PH and/or CH_2 groups (diphosphirane, phosphirane and cyclopropane).

Barrier of Inversion at Phosphorus

The inversion process at phosphorus in acyclic and cyclic molecules has been examined previously.[24,39,40] The semi-empirical finding that "the barrier in $(PH)_3$ is smaller than that in PH_3"[9][20] is a misleading artifact of the MNDO method. Our ab initio calculated inversion barriers, $\Delta_{inv}E$, are compiled in Table 3. The listed $\Delta_{inv}E$ values confirm that the phosphorus inversion barrier is about 100 kJ/mol larger in three-membered rings than in the corresponding acyclic molecules.[40] In the $(CH_2)_{3-n}(PH)_n$ series the barrier decreases with n (when σ^4-C is replaced by σ^3-P). How can this be explained? While "normal" (not T-shaped) TSs of σ^3-P have bond angles at phosphorus of around 120°, the three-membered ring only allows a Y-shaped TS with an endocyclic angle of around 60°. This bond-angle constraint rationalizes the pronounced destabilization of the $TS_{inv,P}$ in the rings relative to the related acyclic molecule [e.g. $(PH)_3$ vs. $HP(PH_2)_2$, cf. Table 3]. As the endocyclic bond angle at the inversion center increases (53° for phosphirane, 60° for diphosphirane, and 68° in the $TS_{inv,P}$ of **1a**) the phosphorus inversion barrier decreases.

Table 3. Inversion barriers at phosphorus in kJ/mol of σ^3-phosphorus in $(CH_2)_{3-n}(PH)_n$ rings (triphosphirane, $n = 3$; diphosphirane, $n = 2$; phosphirane, $n = 1$) and PH_3 calculated at different levels of theory[a]

Method[a]	$n = 1$	$n = 2$	$n = 3$	PH_3
MP2/6−31G(d,p)[a]	291	258	224	148
CISD/6−31G(d,p)	296	260	227	151
QCISD(T)/6−311G(d,p)[a]	280[c]	250	217	148
Experiment[b]				132

[a] Based on MP2(fc)/6−31G(d,p) geometries and corrected for zero-point energies. − [b] Estimated[51] experimental phosphorus inversion barrier. − [c] A. Göller and T. Clark (*Chem Commun.* **1997**, 1033) reported a value of 278 kJ/mol at CCSD(CT)/6-31+G(d)//MP2 /6-31+G(d) with C_s symmetry.

Ring Strain

The strain in a cyclic species arises from the enforced deformation of bond angles from their normal values in acyclic systems. To estimate the ring strain, different isodesmic reactions using reference molecules that are as strain-free as possible can be employed.[41][42] Here, simple bond separation reactions (Table 4) provide reasonable measures for ring strains. These values are somewhat sensitive to the computational methods. For cyclopropane, where experimental heats of formation are available, the calculated value using MP4SDTQ/6−311++G(3df,2p) + ZPE calculations compares quite well with the experimental data. From the results in Table 4, two important points can be concluded: (i) the ring strain decreases consistently on going from cyclopropane to triphosphirane; for each replacement of a CH_2 by a PH the ring strain is reduced by about 25 kJ/mol; (ii) for **1a**, variation of the calculated value with respect to the methods employed suggests that the isodesmic reaction considered might be slightly endothermic. The endothermicity obtained at MP4 is particularly interesting as lower level calculations[19,43,44] consistently predicted a small but significant exothermicity for reaction (1) (Table 4). In contrast to the conventional wisdom, corrections for zero-point vibration energies are found to be important: They change the energies of reactions (1) to (4) by up to 20 kJ/mol. The smaller ring strain in cyclophosphanes, relative to cyclopropane, is often interpreted as arising from two main factors; namely (i) the inherent ability of σ^3 phosphorus to form small rings owing to its sp^3 hybridization[9] and (ii) a larger concentration of its s electrons in the lone pair coupled with a greater use of its p electrons to form ring bonds.[19] In other words, formation of stronger ring-P bonds results in a partial compensation of the inherent destabilization due to bond angle deformation. Another question regards whether the endocyclic bond angle also has an effect on the ability of the lone pair of phosphorus to bind a proton.

Proton Affinities of Phosphorus

Table 5 lists the calculated proton affinities (PA) of related cyclic and acyclic phosphorus-containing molecules. A number of observations are worth mentioning: (i) Accurate calculations of PA with an absolute error of ±5 kJ/mol could only be achieved by using fairly large basis sets; for PH_3, the experimental value can be reproduced by calculations with the 6−311++G(3df,2p) basis set with either the MP4 or the QCISD(T) method. (ii) The relative trend in PAs can, however, be well established using lower level calculations; the difference in PAs between PH_3 and $PH(CH_3)_2$ is computed to be 112 ± 5 kJ/mol at the QCISD(T)/6−311G(d,p) + ZPE level whereas the experimental[45] difference is 113 kJ/mol. (iii) Comparison of calculated as well as experimental[45] PAs of PH_3, CH_3PHCH_3 and H_2PPHPH_2 shows that methyl substituents tend to increase the PA; the phosphanyl group also exerts a similar effect but to a lesser extent; while the PA is increased by 112 kJ/mol by two CH_3 groups (R = CH_3 in HPR_2), two PH_2 groups make it only 75 kJ/mol larger than in PH_3. (iv) In contrast, PAs in polyphosphaphosphiranes are quite close to each other; their PAs are around 800 kJ/mol, irres-

Table 4. Ring strain in kJ/mol of three-membered rings calculated from bond separation reactions[a]

Reaction		CI[a,b]	CI[a,c]	MP4[a,d]	Exptl.[e]
cyclo-$(PH)_3$ (Triphosphirane) + 3 PH_3 → 3 H_2P-PH_2 (C_2)	(1)	−3.6	−0.5	6.2	
cyclo-$(CH_2)(PH)_2$ (Diphosphirane) + CH_4 + 2 PH_3 → 2 H_3C-PH_2 + H_2P-PH_2	(2)	−25.5	−24.7	−23.0	
cyclo-$(CH_2)_2(PH)$ (Phosphirane) + 2 CH_4 +3 PH_3 → 2 H_3C-PH_2 + H_3C-CH_3	(3)	−55.2	−54.5	−50.7	
cyclo-$(CH_2)_3$ (Cyclopropane) + 3 CH_4 → 3 H_3C-CH_3	(4)	−85.4	−83.1	−74.6	−75.7

[a] Based on MP2/6−31G(d,p) geometries and including ZPE correction. − [b] QCISD(T) /6−311G(d,p). − [c] QCISD(T) / 6−311++G(d,p). − [d] MP4SDTQ /6−311++G(3df,2p). − [e] Based on experimental heats of formation at 0 K (kJ/mol): cyclopropane, 70.9; CH_4, −66.8 and CH_3-CH_3, −68.4 from the literature.[50]

pective of the number of P atoms within the ring. (v) Comparing PA($H_3C-PH-CH_3$) with PA(phosphirane) on the one hand and PA($H_2P-PH-PH_2$) with PA(triphosphirane, **1a**)[46] on the other hand, clearly emphasizes that the strong effect of methyl and the weaker effect of the phosphanyl groups on PA is virtually offset in the cyclic structures. It is remarkable that the PA value of **1a** is very near to that of PH_3. The behavior of phosphirane toward protonation thus differs from that of aziridine, its nitrogen analog, which has a much larger PA (about 70 kJ/mol) than NH_3.[47][48] It is also worth noting that a stable phosphiranium cation has been isolated and characterized recently.[46][49]

Table 5. Calculated proton affinities of cyclic, $(CH_2)_n(PH)_{3-n}$, and acyclic, $H-(CH_2)_n(PH)_{3-n}-H$, molecules with $n < 4$

Compound	QCISD(T)[a,b]	MP4SDTQ[a,c]	Exptl[e]
Phosphirane	813	802	
Diphosphirane	811	799	
Triphosphirane	803	777	
PH_3	800	778[d]	782
$H_3C-PH-CH_3$	912		895
$H_2P-PH-PH_2$	875		

[a] Proton affinities based on MP2/6−31G(d,p)-optimized geometries (see Figure 5) and corrected for ZPE. − [b] Used basis set: 6−311G(d,p). − [c] Used basis set: 6−311++G(3df,2p). − [d] At QCISD(T)[a] /6−311++G(3df,2p) the PA is 777. − [e] Taken from ref.[38]

Heats of Formation

At the present time, accurate thermochemical data on phosphorus compounds are rather scarce. Heats of formation of small low-coordinated P species have been determined mainly by quantum-chemical calculations.[47] Therefore, it would be useful to evaluate this quantity for the three-membered rings and their protonated forms. Table 6 records our estimates for heats of formation at 0 K of neutral species, using heats of isodesmic reactions (1), (2) and (3) listed in Table 4 in conjunction with experimental[50] and theoretical values evaluated for the reference molecules. Heats of formation of the protonated species were determined from the data for neutral counterparts and proton affinities given in Table 5. At the level of theory considered, namely MP4SDTQ /6−311++G(3df,2p) + ZPE, absolute errors of about ±10 kJ/mol in heats of formation can be expected. We note that our estimate for phosphirane, $\Delta H°_{f0}$(phosphirane) = 86 ±10 kJ/mol, differs somewhat from the experimental value at 298 K (69 ± 2 kJ/mol; in the compilation of Lias et al.[50]).

Table 6. Heats of formation of polyphosphaphosphiranes, *cyclo*-$(CH_2)_n(PH)_{3-n}$ (with n = 1, 2, and 3), and their protonated forms ($\Delta H°_{f0}$ at 0 K in kJ/mol)

Molecule considered	$\Delta H°_{f0}$[a]	Reference molecule	$\Delta H°_{f0}$[b]
Triphosphirane	70 ± 10	PH_3	13.3
Triphosphirane − H^+	821 ± 10	H_3C-PH_2	−8.1
Diphosphirane	85 ± 10	H_2P-PH_2	38.7
Diphosphirane − H^+	814 ± 10	H^+	1528.0
Phosphirane	86 ± 10		
Phosphirane − H^+	812 ± 10		

[a] Based on heats of isodesmic reactions (1), (2) and (3) listed in Table 4 and proton affinities given in Table 5 obtained from MP4SDTQ /6−311++G(3df,2p) + ZPE calculations. − [b] Values from the literature.[50][52]

Ionization and Excitation Energies

The vertical excitation energies as well as the geometries of the ionized structures give additional insight into the electronic structure of these rings. In contrast to cyclopropane, where the ring opens after ionization, the radical cation minimum of **1a** is cyclic **1a**$^{+\cdot}$ (Figure 5). The lengths of the P−P bonds that are *trans*-substituted are only slightly longer in **1a**$^{+\cdot}$ than in **1a**. In contrast, the *cis*-substituted P−P distance is clearly (0.103 Å) shorter in the radical cation. This can be rationalized by the reduced repulsion of the less populated *cis*-oriented phosphorus lone pairs, which form a 3-electron/2-center π bond in **1a**$^{+\cdot}$. The en-

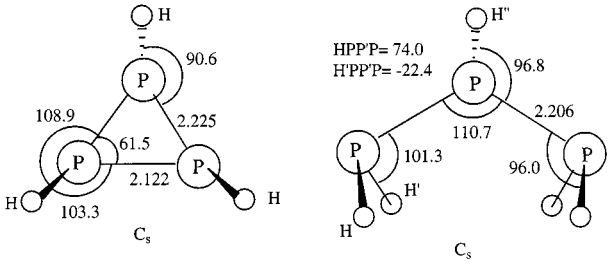

Figure 5. Minimum structure of the *cyclo*-$(PH)_3$ radical cation optimized at UMP2(fc) /6−31G(d,p) and and of the best triphosphane, $PH_2-PH-PH_2$, minimum structures at RMP2(fc) /6−31G(d,p)

ergy decrease due to geometrical relaxation, measured by the difference between vertical and adiabatic ionization energies, is only 0.25 eV in **1a**$^{+\cdot}$.

Separate calculations on some simple phosphanes indicate that IE_as calculated at QCISD(T)/6−311++G(d,p) + ZPE level are consistently underestimated by about 0.3 eV. Taking this correction into account, we estimate the values: IE_a = 9.3 ±0.3 eV for both **1a** and diphosphirane and IE_a = 9.5 ±0.3 eV for phosphirane (Table 7). The latter value agrees well with the available experimental estimate of 9.4 ±0.1 eV.[50] Thus, adiabatic ionization energies of three-membered P rings are rather independent of the number of P atoms. Note that the IE_a = 9.87 eV of PH_3[50] is somewhat larger than for the polyphosphaphosphiranes. The first vertical electronic excitation energies of P rings are listed in Table 7. CIS/6−311++G(d,p) calculations, which include only singly excited configurations, provide only upper bounds for this property; usually, an overestimation of 0.5 eV relative to the experimental value is expected.[26] More realistic estimates assume a systematic correction of 0.5 eV to CIS values. With the basis set employed, no Rydberg states could be identified. It is apparent that the first transition energy decreases with increasing number of P atoms. A shift of the absorption bands toward longer wavelength region is noticeable.

Table 7. Calculated adiabatic ionization energies and vertical excitation energies of polyphosphaphosphiranes (eV)

Molecule	First ionization energies[a]	First vertical excitation energies[b]
Triphosphirane	8.97	5.5 (f = 0.010)[d] (9.3 ±0.3) ($^1A'' \leftarrow {}^1A'$)
Diphosphirane	9.00	5.7 (f = 0.320) (9.3 ±0.3) ($^1B \leftarrow {}^1A$)
Phosphirane	9.18	6.4 (f = 0.015) (9.5 ±0.3) ($^1A'' \leftarrow 1A'$)

[a] Calculated values from QCISD(T)/6−311++G(d,p) + ZPE level based on MP2/6−31G(d,p) geometries. In parentheses are corrected IE_a; see text. − [b] Experimental value.[50] − [c] Calculated values from CIS/6−311++G(d,p) level and corrected by −0.5 eV for overestimation; see text. − [d] In parenthesis are oscillator strengths.

NMR Properties of Triphosphirane and Related Molecules

Table 8 shows, for the $PH(PH_2)_{2-n}(CH_3)_n$ molecules with n = 0, 1, and 2, that the magnetic shielding, $\sigma(^{31}P)$, decreases with decreasing electron density around the ^{31}P nucleus. This is in agreement with a more general study.[16] Since the range of the phosphorus valence in this set of molecules, characterized by the sum of Wiberg bond indices, ΣWBI(P), is small (2.8−3.1), no significant correlation with $\sigma(^{31}P)$ can be established. The bond-angle sum at phosphorus, Σα, ranges from 236.5° in phosphirane, $(PH)(CH_2)_2$, to 303.5° in $(PH)_3$. In contrast to the atomic charges, which do not correlate with the chemical shifts in these cyclic molecules, the bond angles are roughly related to $\sigma(^{31}P)$. The square of the correlation coefficient is 0.82 for the σ − Σα and 0.74 for the σ − α(P) relationship. Despite the fact that these relationships are rough, they indicate that the unusually large ^{31}P shieldings in the small rings are due to the small bond angles at σ^3-P. The similarity of $\sigma(^{31}P)$ of the two symmetry equivalent atoms in **1a** and the phosphorus atoms in diphosphirane can therefore be rationalized by compensation of two effects: (i) the more electronegative endocyclic substituents reduce $\sigma(^{31}P)$ (charge changes from −0.06 to +0.11) and (ii) the contracted endocyclic bond angle, which increases magnetic shielding [angle α(P) changes from 59.8° to 53.3°].

Table 8. Absolute NMR isotropic magnetic shielding, σ[a] charges, q[b] valence,[c] and coordination[d] of phosphorus in optimized[e] geometries

Molecule[e]		σ[a]	q[b]	val[c]	Σα[d]	α(P)[d]
1a, P1	C_s	570	−0.06	3.01	249.3	60.4
1a, P2	C_s	599	−0.06	3.01	251.9	59.8
$(\mathbf{P}H)_2(CH_2)$ ring	C_2	599	0.11	2.94	242.6	53.3
$(\mathbf{P}H)(CH_2)_2$ ring	C_s	636	0.20	2.87	236.5	46.9
PH_3	C_{3v}	561	−0.17	2.99	283.7	99
$H\mathbf{P}(PH_2)_2$	C_s	457	−0.11	3.01	303.4	110.4
$H\mathbf{P}(CH_3)PH_2)$	C_1	423	0.11	2.97	297.7	104.1
$H\mathbf{P}(CH_3)_2$	C_s	403	0.29	2.91	294.5	99.7

[a] Magnetic shielding at phosphorus, σ, computed at GIAO / B3LYP /6−311G(d) //RMP2(fc) /6−31G(d,p). Details at http://www.ccc.uni-erlangen.de/sharc/ in NMR-SHARC format. The corresponding NMR chemical shifts, δ, can be derived with δ(X) = δ(PH_3, reference) − [σ(PH_3) − σ(X)], using σ(PH_3) = 561 from the table. − [b] Charge at phosphorus from Mulliken population analysis. − [c] Sum of Wiberg bond indexes at B3LYP /6−31G(d,p). − [d] Bond angle sum of the phosphorus bonds, Σα, and endocyclic (HPH and CPC, respectively) bond angle at phosphorus, α(P). − [e] NMR properties, population analysis and geometric properties for global minimum structures at RMP2(fc) /6−31G(d,p); see Figures 1 and 5.

Summary and Conclusions

We explored the P_3H_3 potential energy surface by ab initio methods, MP2/6−31G(d,p), with particular focus on ring-chain rearrangements of triphosphirane **1**. Further-

more, molecular properties of **1** are compared with those of other polyphosphaphosphiranes and cyclopropane. A number of conclusions emerge from this theoretical study: (i) The cyclic *trans*-triphosphirane (**1a**) is by far the most stable P_3H_3 isomer; the most stable open-chain isomer is phosphanyldiphosphene, which lies about 42 kJ/mol above **1a**. The cyclic form is increasingly favored upon successive replacement of C by P in polyphosphaphosphiranes, $(CH_2)_{3-n}(PH)_n$ (n = 1−3). (ii) The energy ordering of P_3H_3 isomers is (in kJ/mol): **1a** (0) > phosphanylphosphene (42) > phosphorane (115) > cyclic PH−P=PH_2 (137) > phosphanylphosphinidene (141). (iii) Isomer **1a** is almost a strain-free ring; it even exhibits a small stabilization relative to three separated P−P single bonds. In contrast to cyclopropane, ring strain in phosphirane has essentially vanished. (iv) As the ring strain decreases from phosphirane to triphosphaphosphirane, the phosphorus inversion barrier, $\Delta_{inv}E$, also decreases. $\Delta_{inv}E$ of *cyclo*-$(PH)_3$ is only 224 kJ/mol. (v) Isomer **1a** has a proton affinity, PA, that is almost identical to that of PH_3, PA(**1a**) = 777 ±10 kJ/mol. The values for diphosphirane (799 ±10 kJ/mol) and phosphirane (802 ±10 kJ/mol) are somewhat larger, but they are far smaller than the corresponding values of their open-chain counterparts. This reduced PA appears to be due to the bonding characteristics of the three-membered rings. (vi) Another special feature of the carbon−phosphorus triangles is that the calculated adiabatic ionization energies, IE_a, are rather similar for all polyphosphaphosphiranes (IE_a = 9.5 ±0.3 eV for phosphirane; 9.3 ±0.3 eV for diphosphirane and **1a**). The first UV absorption band shifts toward shorter wavelength on going from phosphirane to triphosphirane. (vii) The heats of formation are computed to be ($\Delta H°_{f0}$ at 0 K in kJ/mol): 70 ± 10 *trans*-triphosphirane, 821 ± 10 protonated triphosphirane, 85 ± 10 *trans*-diphosphirane, 814 ± 10 protonated diphosphirane, 86 ± 10 phosphirane, and 812 ±10 protonated phosphirane. (viii) The ^{31}P-NMR-chemical shifts of the C_s-symmetric *trans*-triphosphirane are predicted to be at δ = −249 for one phosphorus and δ = −278 for the two *cis*-substituted nuclei. (ix) In contrast to phosphirane, triphosphirane undergoes preferentially either a ring-opening by P−P bond breaking or a 1,2-hydrogen shift, but not a combined motion. Ring-opening is, in the gas phase, the more favored reaction path but the energy barrier for this process is still rather large [213; at QCISD(T)/6−311G(d,p) //RMP2(fc)/6−31G(d,p) 190 kJ/mol]. The TS of ring-opening profits from stabilization by a three-center π bond completely formed in triphosphaallyl, PH=PH=PH. For the parent triphosphirane the conversion into the open-chain phosphanyldiphosphene is a two-step process in which the 1,2-H shift is the most energy-demanding step.

Acknowledgments

The authors are indebted to the Fund for Scientific Research Flanders (FWO) and the KULeuven Research Council (GOA program) for continuing support.

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Received June 7, 1999
[I99206]