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Gas-Phase Structure and Stability of Alkynylphosphines and Allenylphosphines: Photoelectronic Study[1]

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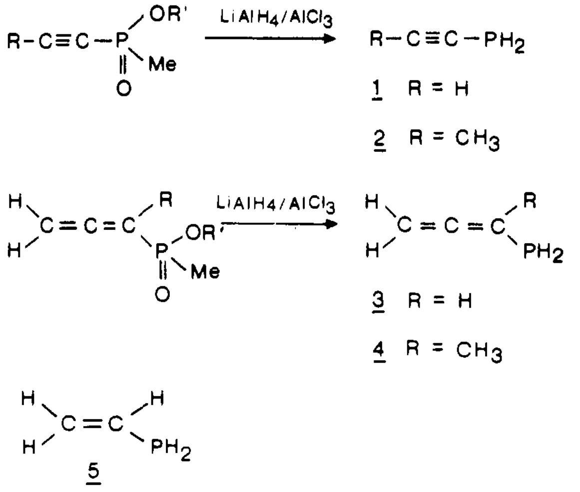
Compounds bearing a heterosubstituted double or triple bond such as ethenol, ethynol, ethenamine, or ethynamine have been the subject of extensive theoretical investigations.[2] However, due to the high instability of these compounds, the experimental characterizations of the unsubstituted parent molecules have been performed either in matrix[3] or in the gas phase by mass or photoelectron spectroscopy[4] (PES). To our knowledge similar studies on phosphorus compounds are limited to ethenylphosphines.[5] We report here our results on the gas-phase structure and reactivity of alkynyl- and allenylphosphines monitored by photoelectron spectroscopy.

PE Spectra of Alkynyl- and Allenylphosphines

Alkynyl- and allenylphosphines are cleanly produced by mild reduction with dichloroalane ($AlHCl_2$) in tetraglyme of the corresponding alkynyl- or allenylphosphonates, respectively.[6] The reductions are performed on a vacuum line directly connected, via a cryogenic trap, to the PES inlet. In this way the volatile phosphines are continuously distilled from the reaction mixture to the cryogenic trap (100 K). After subsequent heating of the trap to the suitable temperature, the analysis of the phosphines is completed by recording the PE spectra of the gaseous flow. This gaseous flow may also be trapped on a cold finger fitted to an NMR tube, bypassing the PES inlet. The NMR spectra of each reduced phosphine can thus be recorded and compared with reported data.[6] Under these conditions, ethynylphosphine (**1**) and 1-propynylphosphine (**2**) appear to be pure, as well as 1,2-propadienylphosphine (**3**) and 1-methyl-1,2-propadienylphosphine (**4**).[7]



The PE spectra of ethynylphosphine (**1**) and of 1-propynylphosphine (**2**) (obtained for respective trap temperatures of 188 and 200 K) are displayed in Figure 1. No impurities, except for small amounts of phosphine PH_3, are detected at different trap temperatures, demonstrating the selectivity of the phosphonate reduction.

The spectra of 1,2-propadienylphosphine (**3**) and 1-methyl-1,2-propadienylphosphine (**4**) obtained at trap temperatures 213 and 223 K are given in Figure 2.

Discussion

The known PE spectrum of ethenylphosphine (**5**)[5] has been analyzed on the basis of the free rotation of the phosphino moiety, contrary to the cases of ethenol and ethenamines for which only one rotamer was characterized in the gas phase.[4a,b] These experimental results were assessed by quantum calculations on the rotation of the heteroatomic substituent.

The same approach has been followed for the analysis of the PE spectra of ethynyl- and allenylphosphines. The favored gas-phase conformation is inferred from analysis of the spectra supported by calculations of the rotation barrier heights. Owing to the size of the studied molecules, these calculations have been carried out within the MNDO formalism.

In the spectrum of the ethynylphosphine (**1**) (Figure 1), three narrow and well-resolved bands are observed at 9.77, 10.81, and 11.83 eV. This does not mean that there is a single rotamer: actually, due to the local cylindrical symmetry of the acetylenic triple bond, all the conformers have the same energy, whatever the position of the phosphorus lone pair relative to the two π orbitals. This results from the exact counterbalance between the nuclear repulsion and the electronic energy (although these two energies vary for each conformation). Moreover, the orbital

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(7) In a previous paper[6] it was reported that 1,2-propadienylphosphine (**3**) was invariably contaminated by traces (≃10%) of 1-propynylphosphine (**2**) on the basis of ^{31}P NMR spectra. The similar contamination of **3** in this experiment is likely, and our PE spectrum of **3** (Figure 2a) could be complicated by the presence of minor amounts of **2** (shoulder at 9.2 eV and small peak at 11.17 eV in Figure 2a). However, the PE spectrum of the allenylphosphine **4**, which cannot undergo such an isomerization, also exhibits a shoulder on the low-energy side of the first band (8.9 eV) and a small peak at 10.7 eV on the high-energy side. Owing to this latter observation, the spectra of both **3** and **4** have been analyzed by assuming that the small amounts of isomeric **2** in the spectrum of **3** would not be discernible and that the observed broad first bands were actually due to the allene isomers **3** and **4**.

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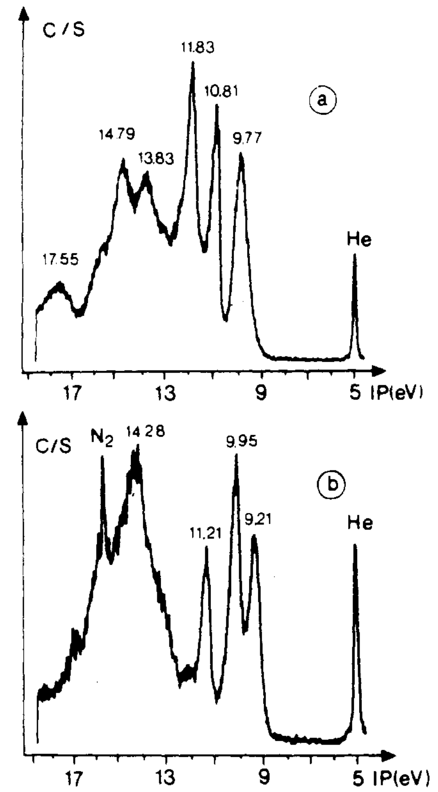

Figure 1. Photoelectron spectra of (a) ethynylphosphine (**1**) and (b) 1-propynylphosphine (**2**).

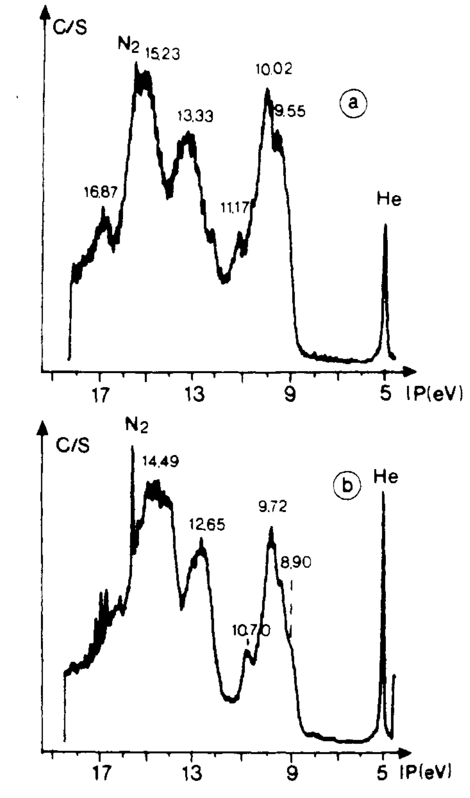

Figure 2. Photoelectron spectra of (a) 1,2-propadienylphosphine (**3**) and (b) 1-methyl-1,2-propadienylphosphine (**4**).

energies are unchanged for all the conformations considered. As a result, for this acetylenic compound with a freely rotating phosphino moiety, the first three observed ionization potentials are described as linear combinations of the acetylenic π orbitals and the phosphorus lone pair. It is worth noticing that for the two rotamers for which the phosphorus lone pair interacts strongly with only one of the acetylenic π orbitals, the IP of the other unperturbed π orbital is 10.81 eV (to be compared with 11.40 eV for C_2H_2). This shift is due to the destabilizing inductive effect of the phosphino moiety (≃0.6 eV). The broader following bands observed for **1** at 13.83, 14.79, and 17.55 eV are in turn assigned to the ionizations of ($\pi + \sigma_{PH}$), (σ_{PC}, σ_{CC}), and σ_{CH} orbitals, respectively. Upon methylation of the triple bond, the first three bands are shifted for **2** to 9.21, 9.95, and 11.21 eV, while the very broad following band centered at 14.28 eV does not clearly indicate the position of the separate components. These spectra are consistent with the reported spectrum of *tert*-butylethynylphosphine (9.05, 9.75, and 11.10 eV).[8]

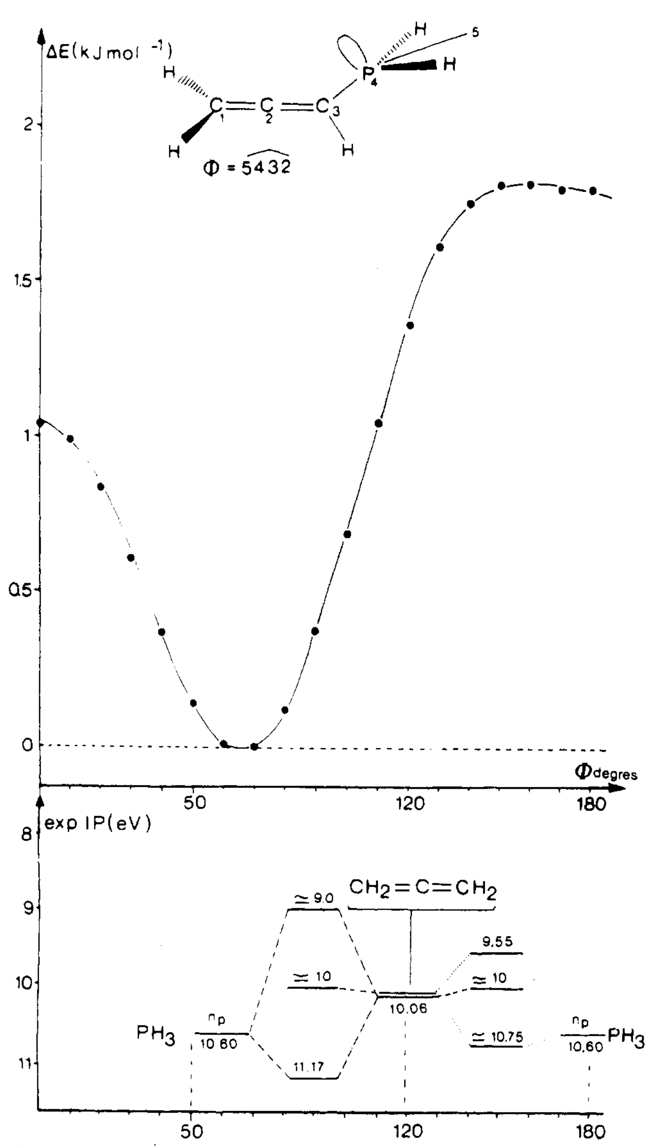

Figure 3. Energy curve (kJ/mol) of the different conformers of 1,2-propadienylphosphine with the dihedral angle φ and variation of the IP's with the conformation.

The PE spectrum of 1,2-propadienylphosphine (**3**) exhibits a rather broad and poorly resolved first band (Figure 2). Obviously, it cannot be analyzed as originating from a single rotamer in the gas phase unless the presence of minor amounts of isomeric **2** is ruled out.[7]

Contrary to the ethenylphosphine case,[5] only one rotamer (in which the phosphorus lone pair interacts with the $\pi_{C_2=C_3}$ orbital, i.e. dihedral angle 5432 = 70° in Figure 3) is found to be at an energy minimum. Were this rotamer the only one in the gas phase, the observed spectrum should contain three different bands with the same intensity: the first and third would be associated with the ($\pi_{C_2=C_3} \pm n_p$) orbitals and the second one with $\pi_{C_1=C_2}$ (orthogonal to the conjugated $\pi_{C_2=C_3}$ bond). The IP of this latter

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[8] Cabelli, D. A.; Cowley, A. H.; Dewar, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3290.

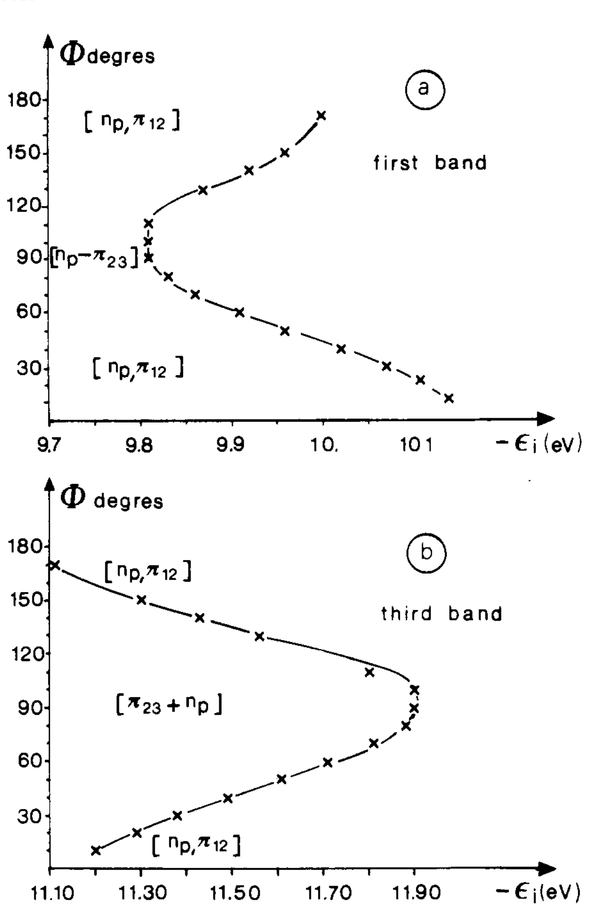

Figure 4. Calculated first and third MO energies ($-\epsilon_i$) as a function of the conformation (ϕ = 5432).

orbital should be found rather close to the known positions of other allenic compounds ($\simeq$10.06 eV[9]), owing to the β location of $\pi_{C_1-C_2}$ relative to the phosphino substituent.[10] With such a small rotation barrier of 2 kJ/mol^{-1} (see Figure 3), the phosphino moiety can actually rotate freely. In order to assess the influence of this free rotation on the experimental IP's, we have analyzed the molecular orbital (MO) energies (MNDO calculations) for several conformations. Although within Koopmans' approximation these MO energies are overestimated, especially for the ionization of the phosphorus lone pair, their variation with the conformation is helpful in the analysis of the experimental spectrum.

For all the conformations studied, the energy of the π MO associated with the second band of the spectrum is nearly invariant and is calculated to be around 10.20–10.30 eV. This π MO corresponds to the π_{23} double bond when ϕ = 180 or 0° and to the π_{12} double bond when ϕ = 90° (Figure 3). On the other hand, the MO's associated with the first and third bands (Figure 4) are described as the antisymmetric and symmetric combinations of the phosphorus lone pair either with the π_{12} bond for ϕ in the vicinity of 180 or 0° or with the π_{23} bond for ϕ around 90°. Accordingly, the energy of the first MO is found to vary between 9.8 and 10.10 eV. For the third MO and for ϕ values between 50 and 120°, the energy is close to 11.8–11.9 eV but decreases sharply to 11.10 eV for $\phi < 50°$ or $\phi > 120°$. From these calculations it is thus predicted that the first band of the spectrum should be broad but shapeless with a ~0.4-eV width. The third band should be wider with a marked shoulder on the high-energy side accounting for one third of the total population of conformers. Although these MO energies are not accurate, they account fairly well for the observed spectrum (Figure 3, bottom). For the rotamers with $\phi < 50°$ or $\phi > 120°$, there is a weak (n_p–π_{23}) interaction: the π_{23} orbital is slightly destabilized by an inductive effect of the phosphino substituent (0.5–0.6 eV), while the phosphorus lone pair orbital has only a weak spatial interaction with the coplanar π_{12} orbital in the β position. The broad band between 9.55 and 10.75 eV for **3** and that between 9.31 and 10.0 eV for **4** are thus associated with these rotamers. For the other set of conformations, i.e. those where $50° < \phi < 120°$, the first three bands are split to a greater extent: the first one is hidden in the broad signal at 9.55 eV and only appears as a very weak shoulder around 9 eV, while the well-resolved shoulder at 11.17 eV is due to the third band of this conformer's population.

From this study we find that, as for ethenylphosphine (**5**),[5] the free rotation of the phosphino moiety in allenylphosphines plays an important role in interpreting the PE spectra. The favored rotamer is found to have the phosphorus lone pair interacting with the $\pi_{C_2-C_3}$ orbital, the presence of the orthogonal π orbital of the allenic skeleton raising the energy of the gauche conformations.

Stability of Alkynyl- and Allenylphosphines in the Gas Phase

As already reported,[6] phosphines **1**–**4** can be kept for several weeks in pure form at −20 °C in the absence of air. It should be mentioned that these phosphines are much more stable than their amino analogues. Actually, different attempts to record the PE spectrum of 1,2-propadienylamine under flash thermolytic conditions[11] have only led to the known 2-propen-1-imine,[12] while the spectrum of its phosphorus analogue could be obtained at room temperature. Moreover, to our knowledge ethynylamine could only be observed by matrix IR and mass spectrometry and proved to be highly unstable, giving rise to acetonitrile.[4] On the contrary, we have heated **1** and **5** to 1000 K in the gas phase; no other product could be detected below this temperature. These results indicate that the phosphorus compounds are much more stable than their nitrogen analogues.

The reactivity of these unsaturated phosphines, from both an experimental and a theoretical point of view, is currently under investigation.

Experimental Section

Photoelectron spectra were recorded on an Helectros 0078 photoelectron spectrometer equipped with a 127° cylindrical analyzer and monitored by a microcomputer supplemented with a digital analog converter. The spectra are calibrated with the known ionizations of xenon (12.13 and 13.43 eV) and argon (15.76 and 15.93 eV). The IP's are accurate within 0.02 eV. The phosphonates were synthesized and reduced to the desired phosphines according to ref 6.

Calculations were performed using the AMPAC program[13] on a VAX computer.

Conclusion

Alkynyl- and allenylphosphines have been characterized in the gas phase. The analysis of their PE spectra and the results of MNDO calculations indicate that, as for the related ethenylphosphine, the phosphino moiety rotates freely around the P–C bond.

These compounds, unlike their amino analogues, appear to be very stable even at high temperature. Up to 1000 K, no isomerization is observed whereas ethenamine or ethynamine are quickly converted to an imine[4b] or acetonitrile, respectively, at room temperature. The reactivity of this class of molecules is being studied.

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