Condon envelopes. While the PDS bands arise directly from electronic transitions of cations, PES measurements are made on neutral molecules, and the CNDO/S method was originally parametrized to study the singlet–singlet or singlet–triplet transitions of neutral molecules.

In the case of the A band, the CNDO/S transition energies, shown in Table III, are again predicted about 0.4 eV higher than observed. The calculations account fairly well for the substituent effects. Two chief predictions from the calculation are, first, that the substituent effects should be much smaller than for the I band, with a total range of about 0.5 eV, and, second, that the largest perturbation, a red shift, is expected with several outer-carbon substituents. These two theoretical expectations are seen to be borne out in the PDS results.

Conclusion

The two photodissociation bands observed in the conjugated diene radical cations show band shifts depending on the number and position of the methyl group substituents. The hole-transition bands show a blue shift with inner-carbon substitutions and a red shift with outer-carbon substitutions: These trends can be interpreted in terms of a nonbonding through-space interaction between the molecular orbitals of butadiene and the methyl groups. For the π–π^* transition bands, methyl group substitutions on the outer carbons give a red shift, while substitution on the inner carbons gives no clear band shifts. A comparison of PDS results, neutral spectroscopy, and ETS results for the UV transition shows considerable scatter, but a clear shift of 0.15 or 0.2 eV per methyl group can be discerned for substituents on the outer carbons. Calculational results for the two transitions using the CNDO/S-CI program show a good correlation with the experimental results.

Acknowledgment. We are most grateful to Professor Hans Jaffe for providing the CNDO/S program and for help in its use. We thank a referee for bringing ref 14 to our attention. The support of the National Science Foundation and of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Ethenylphosphine. Synthesis by Flash-Vacuum Thermolysis and Characterization by Photoelectron Spectroscopy[1]

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Contribution from the Laboratoire de Physico-Chimie Moléculaire, UA 474, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 Pau, and from the Laboratoire des Composés Thioorganiques, Ismra, Université de Caen, 14032 Caen, France. *Received September 29, 1987*

Abstract: Ethenylphosphine and prop-1-en-2-ylphosphine, obtained by flash-vacuum thermolysis of the corresponding Diels–Alder adducts, have been characterized by their photoelectron spectra. In both cases, the broad shape of the first two bands respectively at 9.65 and 10.85 eV for ethenylphosphine and at 9.50 and 10.3 eV for prop-1-en-2-ylphosphine can only be accounted for if we assume a free-rotating P–C bond. This conclusion was inferred from a complete theoretical study of the rotation process of the PH_2 group around the P–C bond. Two privileged forms were found: a syn form ($\phi = 0$, the lone pair of the phosphorus eclipsing the P–C bond) and a gauche form 3.5 kJ·mol^{-1} less stable ($\phi = 127°$), separated by low rotation barriers (8.19 and 10.74 kJ·mol^{-1}). Evaluation of the accurate ionization potentials according to a configuration interaction formalism has been achieved for ethenylphosphine in different conformations. The results of these calculations clearly indicate that during the rotation process the energy of the first two ionic states extends over a 0.4 eV interval.

1. Introduction

Although many spectroscopic and theoretical studies have been carried out on ethenylamine,[2] ethenol,[3] and ethenethiol,[4] ethenylphosphine has, to our knowledge, only recently been synthesized by flash thermolysis (FVT) of the corresponding Diels–Alder adduct.[5]

It was thus of interest to define the electronic and structural characteristics of these ethenylphosphines, by using flash thermolysis–UV photoelectron spectrometry coupling, as reported by our laboratory.[3i,6] These experimental data were compared to a complete quantum mechanical study of the internal rotation process and the ionic state energies of energetically favoured rotamers.

2. Photoelectron Spectra

Ethenylphosphine (**1**) and prop-1-en-2-ylphosphine (**2**) were obtained by the retro-Diels–Alder reaction of 9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine and 11-methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine (**3**) and (**4**), respectively, prepared by the reduction of the corresponding phosphonates[5] (Figure 1).

The photoelectron spectra of alkenylphosphines **1** and **2**, obtained by the flash thermolysis of **3** and **4**, respectively, are shown in Figures 2 and 3. In contrast to observations with ethenylamine, the nitrogen analogue of **1**,[3i] no change in the phosphine spectrum is observed, even after several minutes. Alkenylphosphines **1** and

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(1) "Application of Photoelectron Spectroscopy to Molecular Properties" Part 32. Part. 31: Guimon, C.; Pfister-Guillouzo, G. *Organometallics* **1987**, *6*, 1387.

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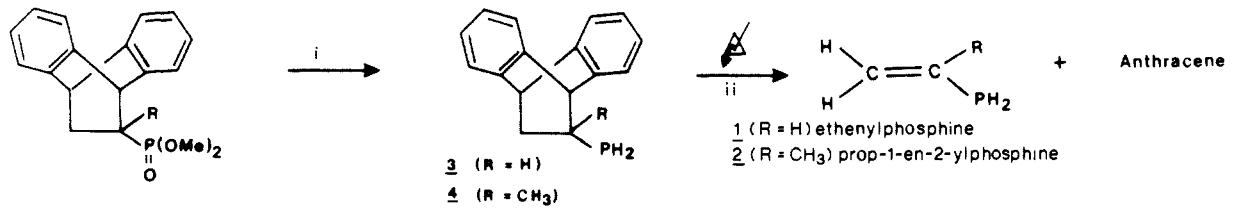
(3) (a) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399. (b) Nobes, R. H.; Radom, L.; Allinger, N. L. *J. Mol. Struct.* **1981**, *85*, 185 and references therein. (c) Ripoll, J. L. *Nouv. J. Chim.* **1979**, *3*, 195. (d) Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrup, P. A. *Helv. Chim. Acta* **1984**, *67*, 220. (e) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255. (f) Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580. (g) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025. (h) Rodler, M. *J. Mol. Spectrosc.* **1985**, *114*, 23. (i) Lafon, C.; Gonbeau, D.; Pfister-Guillouzo, G.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *Nouv. J. Chim.* **1986**, *10*, 69.

(4) Plant, C.; Mac Donald, J. N.; Boggs, J. E. *J. Mol. Struct.* **1985**, *128*, 353 and references therein.

(5) Lasnes, M. C.; Ripoll, J. L.; Thuillier, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1428.

(6) Lafon, C. Thèse de 3ème Cycle, Université de Pau, 1987.



i : LAH (ClSiMe$_3$)/THF ;

ii : FLASH VACUUM THERMOLYSIS (7.10^{-4} mbar, QUARTZ OVEN 2,5 x 20 cm, 550° for 1 700° for 2)

Figure 1. Synthesis of ethenylphosphine.

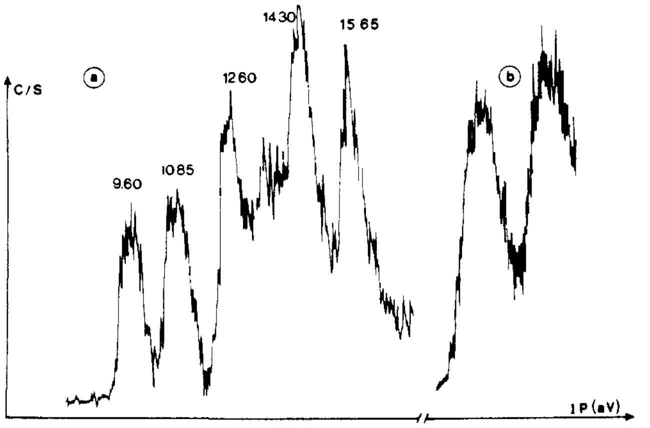


Figure 2. (a) Photoelectronic spectrum of ethenylphosphine [CH_2=C-HPH_2]. (b) Expanded two first bands (between 8.75 and 11.75 eV).

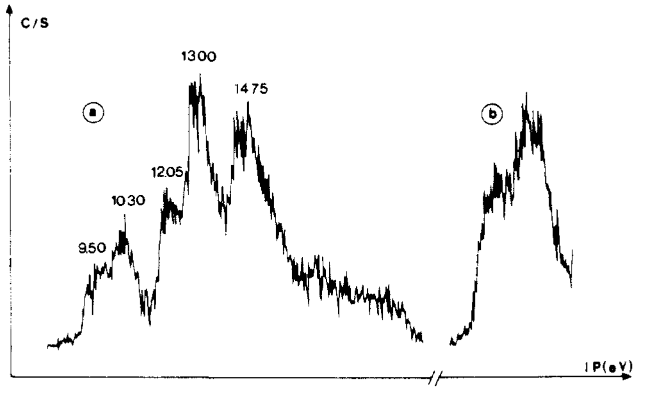


Figure 3. (a) Photoelectronic spectrum of prop-1-en-2-ylphosphine (2) [CH_2=C(CH_3)PH_2]. (b) Expanded two first bands (between 8.75 and 11.75 eV).

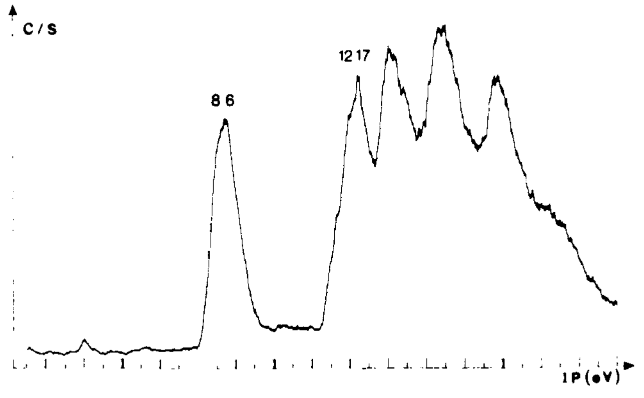


Figure 4. Photoelectronic spectrum of ethenylamine [CH_2=$CHNH_2$].

2 are thus stable in the reaction conditions, and no isomerization into phosphalkene occurs. In identical conditions, ethenylamine was isomerized in several minutes into acetaldimine.

For the sake of comparison, the spectrum of ethenylamine obtained by the retro-Diels-Alder reaction of the corresponding amine precursor is shown in Figure 4.[3i]

Two rather broad and asymmetric bands are observed with ethenylphosphine (1) at 9.60 and 10.85 eV. The energy difference between these two bands (1.25 eV) is lower than that between the first two corresponding bands of ethenylamine (3.57 eV). This could result from a weaker $n_P \leftrightarrow \pi_{C=C}$ interaction than the $n_N \leftrightarrow \pi_{C=C}$ interaction of ethenylamine. Other bands are observed at 12.60, 14.30, and 15.65 eV.

The PE spectrum of prop-1-en-2-ylphosphine (2) also displays two broad bands at 9.5 and 10.30 eV, thus at lower potentials than those of ethenylphosphine (1). In the case of 2, the shape of the 9.50-eV band is much broader, while that at 10.30 eV is sharper. There is also a smaller difference (0.8 eV) between the first two bands of this molecule. Other ionizations are observed at 12.05, 13, and 14.75 eV.

3. Experimental Section

Photoelectronic spectra were recorded on an Helectros 0078 spectrometer connected to a microcomputer system supplemented by a digital analogic converter (DAC). The spectra consist of 512 data points and are recorded either between 4 and 18 eV (whole spectrum) or between 8.5 and 11.5 eV for the enhanced spectra. They are calibrated by using Xenon and Argon $^2P_{1/2}$ and $^2P_{3/2}$ bands (12.15, 13.43, 15.76 and 15.93 eV, respectively).

Reduction of the phosphonates and handling of phosphines 3 and 4 are carried out under inert atmosphere. Due to the great sensitivity of phosphines 3 and 4 toward oxygen and moisture, they are introduced on the flash vacuum thermolysis device immediately after their preparation. The phosphines 3 and 4 are thermolyzed at 823 and 973 K, respectively, under a pressure of 10^{-4} mbars in a 15-cm long and 2.5-cm internal diameter quartz oven. The gaseous flow provided by thermolysis is analyzed on the spectrometer directly coupled to the thermolysis device.

The calculations were performed with the MONSTERGAUSS program.[7] The split valence 4-31G basis set was used and augmented by one set of d polarization functions on phosphorus ($\delta_p^d = 0.57$).[8]

The molecular geometries were fully optimized at an SCF level with respect to all bond lengths and bond angles by the Broyden-Fletcher-Goldfarb-Shanno gradient method.[9] The detection of transition states was carried out by employing the Powell algorithm.[10] The stationary points were characterized by force constant analysis (number of negative eigenvalues). For the maxima a zero gradient (accuracy 10^{-4}) has been obtained.

In light of the size of the system we were led to use a method of pseudopotentials[11] (PSHONDO program[12]) for the rigorous calculation of ionization potentials. The pseudo potentials and the double-ζ quality basis set previously determined[13] were adopted including d polarization

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(7) Peterson, M.; Powier, K. MONSTERGAUSS (June 1981), Chemistry Department, Université of Toronto, Ontario, Canada.

(8) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Kutzelnigg, W.; Wallmeier, H. *Theor. Chim. Acta* **1979**, *51*, 261.

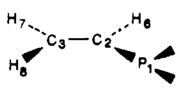
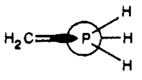
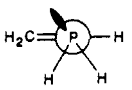
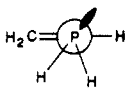
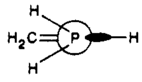
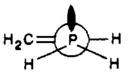
(9) Algorithm described by Fletcher (Fletcher, R. *Comput. J.* **1970**, *13*, 317).

(10) Algorithm described in *Numerical Methods for Nonlinear Algebraic Equations*; Gordon and Breach: London, 1970; Version 1981, p 87.

(11) (a) Durand, P.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283. (b) Barthelat, J. C.; Durand, P. *Gazz. Chim. Ital.* **1978**, *108*, 225.

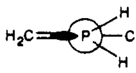
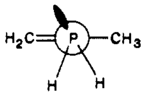
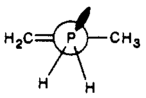
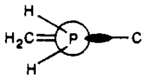
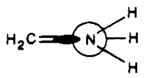
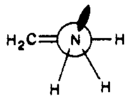
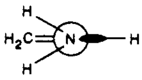
(12) (a) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111. (b) PSHONDO algorithm: a modified version of the HONDO package (program 338, Quantum Chemistry Program Exchange University of Indiana, Bloomington, IN 9701)—pseudopotentials adapted by J. P. Daudey.

Table I. Optimized Geometries–Forms **1–5** of Ethenylphosphine (Rotation–Inversion)[a]

	rotation				inversion
	form 1	form 2	form 3	form 4	form 5
					
ϕ	0	64	127	180	
$d_{C_2-C_3}$	1.3202	1.3184	1.3188	1.3185	1.3229
$d_{C_2-P_1}$	1.8303	1.8315	1.8276	1.8414	1.7670
$d_{P_1-H_4}$	1.4067	1.4066	1.4065	1.4055	1.3831
$d_{P_1-H_5}$					1.3851
$H_7C_3C_2$	122.17	122.01	121.89	121.94	121.84
$H_8C_3C_2$	122	122.42	122.52	122.48	122.88
$H_6C_2C_3$	119.49	119.38	118.82	118.56	119.59
$P_1C_2C_3$	121.46	125.99	126.99	126.93	127.97
$H_4P_1C_2$	97.77	99.68	97.23	98.23	121.23
$H_5P_1C_2$	97.77	97.54	97.60	98.23	119.58

[a] Bonds in Å, angles in deg.

Table II. $H_2C{=}CHPH_2$ - $H_2C{=}CHNH_2$ Energy Values (au)

	form 1	form 2	form 3	form 4	form 5	form 6	form 7
	 minimum $\phi = 0°$	 saddle point $\phi = 64°$	 minimum $\phi = 127°$	 saddle point $\phi = 180°$	 saddle point $\phi = 0°$	 minimum $\phi = 97.9°$	 saddle point $\phi = 180°$
E_{elect}	-515.192449	-514.916171	-515.125065	-514.861393	-204.657537	-205.029653	-204.567523
E_{NN}	96.331899	96.058752	96.265858	96.004948	71.735115	72.099383	71.646943
E_{tot}	-418.860549	-418.857419	-418.859207	-418.856446	-132.922422	-132.930270	-132.920580

and s diffuse type functions for phosphorus ($\zeta_d = 0.57$, $\zeta_s = 0.0348^{14}$). The energies of ionic states were evaluated by a configuration interaction method iteratively combining variation and perturbation (CIPSI algorithm[15]). A subspace S_0 was constructed iteratively in order to obtain a plurideterminant zero-order wave function. To evaluate remaining correlation energy a second-order Möller–Plesset perturbation method was used (all mono and biexcited determinants of S_0). At last 50 to 60 determinants were included in the variational wave function, 4.5×10^6–6×10^6 determinants thus being generated.

4. Characteristics of the Ground State

Ethenylphosphine. In the series of heterosubstituted alkenes $H_2C{=}CHX$ (X = OH, SH, NH_2), numerous publications have dealt with the identification of the most stable rotamers by using different spectroscopic techniques as well as the theoretical analysis of the internal rotation process.[2–4] In the case of X = PH_2, on the other hand, due to the lack of any synthetical procedure, there are no structural data and only one semiempirical study of this system.[16] To our knowledge, the only paper on this type of compounds deals with phosphino-substituted derivatives.[16] For these reasons we were led to undertake the analysis of the rotation process around the P–C bond, in order to determine the most stable conformation(s) and to compare theoretical results with the experimental data obtained. Different calculations were carried out with optimization of all geometric parameters and the search for stationary points on the potential energy hypersurface. We were thus able to show (Figure 5) the existence of two minima (forms 1 and 3) and two saddle points (forms 2 and 4). Letting ϕ define the dihedral angle between the lone pair of phosphorus and the C–C bond, the two ϕ values of the two minima are 0° and 127°, and for the two corresponding saddle points they are 64° and 180°. As noted previously,[17] in the energetically favored conformation the phosphorus lone pair eclipses the C–C bond, while the highest energy saddle point is characterized by an angle $\phi = 180°$.

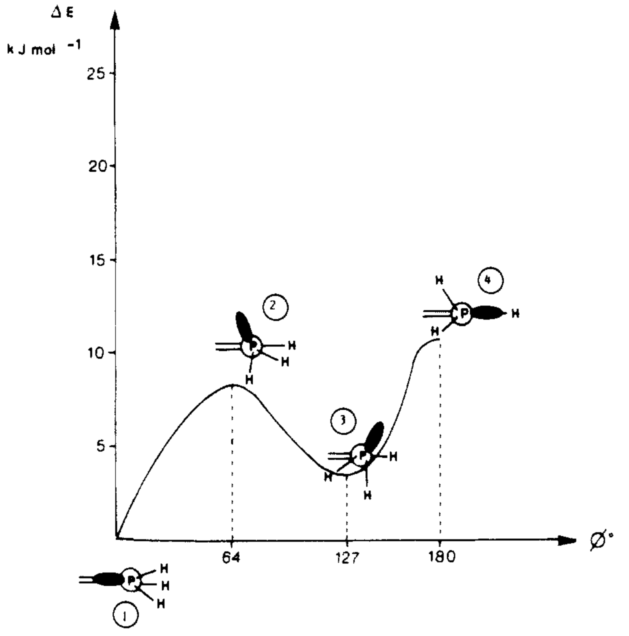


Figure 5. Rotation of the PH_2 group about the P–C bond. Relative energies as a function of ϕ.

The geometric parameters of these four stationary points (Table I) are rather close. Only a smaller PCC angle is observed in the most stable conformation in comparison to the three others. Phosphorus has a markedly pyramidal character of the same order for the four conformers. The sum of the angles around this atom is between 289.5° and 291.5°.

Similarly, the Mulliken populations of the four conformers are close. The values of only the most stable form are shown in Figure

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(13) Laboratoire de Physique Quantique, Toulouse, Ateliers, October 1981.

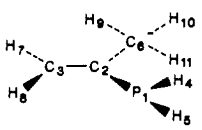
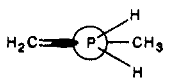
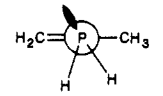
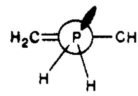
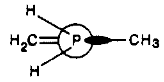
(14) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265 and references cited.

(15) (a) Huron, B.; Malrieu, J. P. Rancurel, P. *J. Chem. Phys.* **1973**, *58*, 5745. (b) Pelissier, M. Thèse, Université Paul Sabatier, Toulouse, France, 1980.

(16) Schmidt, H.; Schweig, A.; Mathey, F.; Muller, G. *Tetrahedron* **1975**, *31*, 1287.

(17) Gonbeau, D.; Pfister-Guillouzo, G. *Inorg. Chem.*, **1987**, 20.

Table III. Optimized Geometries and Total Energies for Forms **6**–**9** of Prop-1-en-2-ylphosphine

	form 6	form 7	form 8	form 9
	 minimum	 saddle point	 minimum	 saddle point
ϕ	0	64	127	180
$d_{C_2-C_3}$	1.3183	1.3180	1.3162	1.3161
$d_{C_2-P_1}$	1.8281	1.8278	1.8278	1.8271
$d_{C_2-C_6}$	1.5205	1.5204	1.5200	1.5204
$d_{P_1-H_4}$	1.4067	1.4034	1.4042	1.4055
$d_{P_1-H_5}$	1.4067	1.4052	1.4067	1.4055
$C_6C_2C_3$	122.31	121.49	121.96	121.77
$P_1C_2C_3$	118.25	121.27	123.94	123.79
$H_7C_3C_2$	122.12	121.97	121.77	121.88
$H_8C_3C_2$	122	122.35	122.41	122.37
$H_4P_1C_2$	97.72	97.61	97.60	98.46
$H_5P_1C_2$	97.72	98.21	97.23	98.46
$H_9C_6C_2$	110.08	110.86	110.91	110.94
$H_{10}C_6C_2$	111.03	111.04	111.07	111.75
$H_{11}C_6C_2$	111.02	111.42	111.16	111.15
E_{tot} (au)	−457.841841	−457.838040	−457.839856	−457.836346

[a] Bonds in Å, angles in deg.

6. Phosphorus has a positive character, and carbons bear a negative charge, the greatest on the carbon bonded to the phosphorus.

The same analysis of the nitrogen analogue ethenylamine showed a favored conformation with an angle ϕ of 97.9° between the nitrogen lone pair and the C–C bond.[3i,6] In terms of the interaction heteroatom lone pair $\leftrightarrow \pi_{C=C}$, this situation has to be compared to the least stable minimum of ethenylphosphine. The two saddle points of ethenylamine predicted by Dixon and Douglass[2b] could be unambiguously characterized (a single negative eigenvalue) at ϕ values of 0° and 180°.

Table II lists total energies, electronic and nuclear repulsion, for the stationary points associated with the rotational process around the C–P and C–N bonds. It may be seen that the energetically privileged conformation in both cases corresponds to the most favorable electronic balance, even though the interactions involved are obviously different.

For the conformations with a dihedral angle close to 90°, the essential stabilizing interaction involves the heteroatom lone pair and the $\pi^*_{C=C}$ orbital.

This stabilization is nevertheless weaker for the phosphorus than for the nitrogen derivative. For the same dihedral angle, this is expressed by a different localization on the carbon atoms in the molecular orbitals considered. This difference between ethenylphosphine and ethanylamine results from the fact that the P–C bond length ($\simeq$ 1.83 Å) is much greater than that of C–N ($\simeq$ 1.4 Å) and also from the less pronounced directional character of the phosphorus lone pair in comparison to that of nitrogen. As previously reported,[18] we observed an important s character for the phosphorus lone pair, directly related to the particularly pronounced pyramidal character of ethenylphosphine.

For the conformations with a dihedral angle of 0° or 180°, stabilizing interactions occurred: (a) in σ between the heteroatom pair and the antiperiplanar σ bond (σ^*_{C-C} for ϕ = 180°, σ^*_{C-H} for ϕ = 0°); (b) in π between the π_{XH_2}, $\pi^*_{C=C}$ orbitals and $\pi^*_{XH_2}$, $\pi_{C=C}$.

The conformations of both ethenylphosphine and ethenylamine with a dihedral angle of 180° are the least electronically stable (Table II). In spite of a more favorable balance in σ in comparison to conformations with a dihedral angle of 0° (σ^*_{C-C} energy lower than σ^*_{C-H}), π interactions are much lower as a result of antibonding overlapping between hydrogens and the terminal carbon. This has to be compared to the situation of a methyl group adjacent to a double bond, where the eclipsed position of a C–H bond and the σ_{C-C} bond is always preferred to the staggered position.[19]

In the case of conformations with a dihedral angle of 0°, the most favorable balance for ethenylphosphine in comparison to ethenylamine results from the pyramidalization of phosphorus, which leads to a decrease in the stabilizing interactions lone pair $n_X \leftrightarrow \sigma_{C-C}$ and more effective stabilizing interactions $\pi_{C=C} \leftrightarrow \pi^*_{XH_2}$, $\pi^*_{C=C} \leftrightarrow \pi_{XH_2}$.

It should be pointed out that compensation effects occur for all rotation processes, between stabilizing factors arising from electronic interactions and nuclear repulsion effects. This leads to relatively low rotation barriers, particularly in the case of ethenylphosphine, where very low values of 8.21 and 10.76 kJ·mol^{-1} are obtained. The rotation barriers of ethenylamine are slightly higher at 20.59 and 25.44 kJ·mol^{-1}.

This study was extended by an analysis of the inversion process. The geometric parameters of the saddle point (form 5) we characterized are shown in Table I. The sp^2 hybridization of the phosphorus generates a shorter P–C bond as well as a more negative charge on the atom (Figure 6). The calculated barrier at 171.38 kJ·mol^{-1} is similar to that obtained in previous studies for PH_3[20] and PH_2NH_2[21] but slightly higher than the most recent values determined for PH_3.[22] These high values for the inversion barrier at phosphorus are reliable to our previous observations on the important pyramidal character of the phosphorus atom (see above). Planarization at phosphorus is energetically more costly than at nitrogen; this inability of phosphorus to become planar leads to poor π interactions for ethenylphosphine.

Prop-1-en-2-ylphosphine. Starting from the observation of the experimental spectrum of the C_α methylated derivative **2**, the consequences of the substitution on a possible change of the rotamers relative stabilities and barrier heights were checked. The analysis of the rotational process about the P–C bond was carried out with the methyl group in eclipsed position relative to the double bond, according to the well-known preferential arrangement.[19] Through optimization of parameters and characterization of stationary points, two minima and two saddle points were obtained (Table III). As for ethenylphosphine, the lowest minimum (form 6) corresponds to a dihedral angle ϕ = 0° and the saddle point

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Table IV. Ethenylphosphine: Ionization Potentials (eV) (Koopmans' Approximation[a])

form 1, ϕ = 0°, min		form 10, ϕ = 30°		form 11, ϕ = 90°		form 3, ϕ = 127°, min	
n_P	10.01	$\underline{n_P} - \pi_{C=C}$	9.73	$\underline{n_P} - \pi_{C=C}$	9.28	$\underline{n_P} - \pi_{C=C}$	9.35
$\pi_{C=C}$	10.51	$n_P + \underline{\pi_{C=C}}$	10.76	$n_P + \underline{\pi_{C=C}}$	11.57	$n_P + \underline{\pi_{C=C}}$	11.41
σ_{P-C}, σ_{C-H}	13.11	σ_{P-C}, σ_{C-H}	13.17	σ_{P-C}, σ_{C-H}	13.11	σ_{P-C}, σ_{C-H}	13.04
π_{PH_2}	14.48	π_{PH_2}	14.42	π_{PH_2}	14.03	π_{PH_2}	14.23
σ_{C-C}	15.61	σ_{C-C}	15.69	σ_{C-C}	15.78	σ_{C-C}	15.89

[a] IP (exp): 9.60 eV - 10.85 eV - 12.60 eV - 14.30 eV - 15.65 eV.

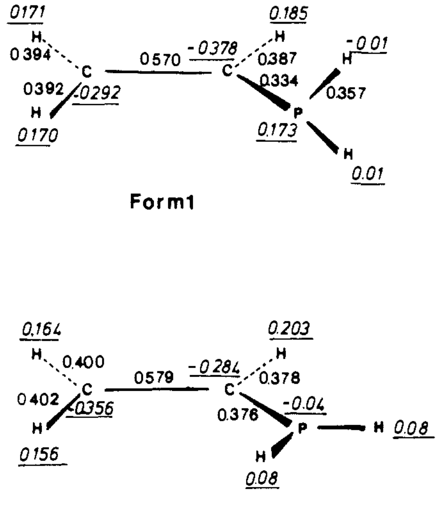

Figure 6. Mulliken population analysis net total charges (underlined) overlap populations.

with the highest energy occurs for ϕ = 180° (form 9). The intermediate saddle point and minimum (forms 7 and 8) have the same dihedral angle values.

Examination of the geometric parameters for the four prop-1-en-2-ylphosphine rotamers is above all indicative of angular deformations in comparison to ethenylphosphine (Table III). This is evidenced by a decreased CCC angle relative to the CCH angle and principally a closing of the CCP angle. The pyramidal character of phosphorus, however, remains unchanged. Similarly, charge distributions on the atoms are only slighly disturbed, with phosphorus remaining positive, and the methyl carbon bearing the highest negative charge.

The rotation barrier heights of 9.97 and 14.41 kJ·mol^{-1} are higher than in ethenylphosphine but remain relatively low.

5. Theoretical Evaluation of Ionization Potentials

Ethenylphosphine. The existence of two rotamers, close in energy (ΔE = 3.62 kJ·mol^{-1}) and separated by rather low rotation barriers (8.21 and 10.76 kJ·mol^{-1}), has been inferred from the theoretical study.

Bearing in mind the conditions used to obtain the molecule (temperature close to 823 K) the coexistence of the two rotamers and even the possibility of free rotation of the system have to be considered. By using Koopmans' approximation, the ionization potential values of the two favored rotamers (forms 1 and 3) and of the two intermediate forms with 30° and 90° dihedral angles (forms 10 and 11) were evaluated (Table IV). It was verified that the 60° and 180° dihedral angles were associated with ionization potential values similar to those obtained for the dihedral angles of 120° and 0°. In the gauche conformations there is only a weak interaction between the ethylene system and the phosphorus lone pair: the energies of the last two occupied orbitals are energetically close and localized, respectively, on the n_P pair of phosphorus and the $\pi_{C=C}$ system.

At deeper energies, characteristic orbitals relevant to σ_{P-C} and σ_{C-H} and then π_{PH_2} and σ_{C-C} bonds are predicted.

In rotamers with notable phosphorus lone pair ↔ double bond interaction, the last two molecular orbitals are delocalized throughout the system, and there is a considerable energy separation.

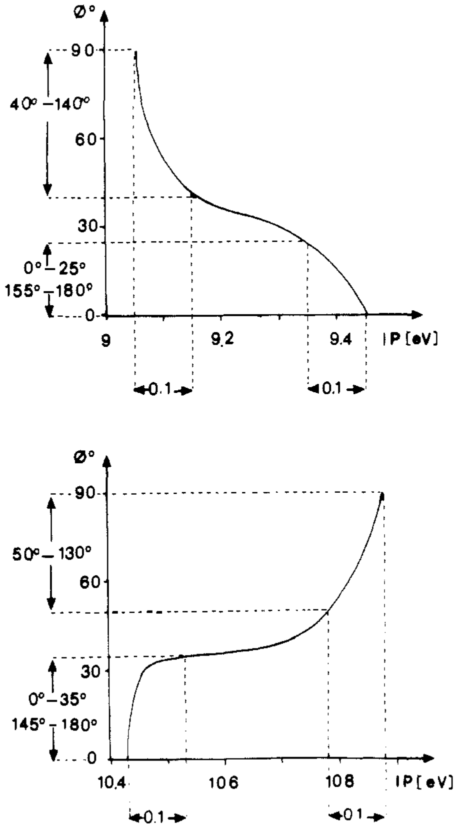

Figure 7. Ethenylphosphine: variation of ionization potentials as a function of dihedral angle ϕ.

On the basis of these data alone, it is difficult to account for the experimental spectrum within the Koopmans' approximation, especially the energy position of the first two bands. A rigorous calculation of the energies of the first two ionic states of forms 1, 3, 10, and 11 was thus carried out with a configuration interaction (CI) formalism. Ionization potential values are listed in Table V. For the most stable conformation 1 and the rotamer at 30°, a noticeable decrease in the energy of the first ionic state is observed, in comparison to Koopmans' evaluation, as a result of the participation of polarization effects (localization on the phosphorus lone pair). The energy of the second ionic state is only slightly modified (equilibrium between polarization and correlation effects).

Concerning the conformations corresponding to a strong interaction between the phosphorus lone pair and the ethylene system, weak polarization effects are observed for the first ionic state, while a substantial correction arising from the specific correlation of the ion occurs for the second state.

It thus appears that, for a 0-90° (90-180°) variation of the dihedral angle, the first ionization potential varies from 9.45 to 9.05 eV and the second from 10.43 to 10.88 eV.

If we also examine the curve giving the variation of calculated ionization potentials as a function of the dihedral angle, it may be seen (Figure 7) that (a) for the first ionic state at a 0.1-eV energy difference on the low-energy side (9.05–9.15 eV), there

Table V. Ethenylphosphine: Calculated Ionization Potentials (eV), CIPSI[a]

	form 1, ϕ = 0°, min	form 10, ϕ = 30°	form 11, ϕ = 90°	form 3, ϕ = 127°, min
first IP	9.45	9.29	9.05	9.10
second IP	10.43	10.46	10.88	10.80

[a] IP (exp): 9.60 eV - 10.85 eV.

Table VI. Prop-1-en-2-ylphosphine: Ionization Potentials (eV) (Koopmans' Approximation)

form 6, ϕ = 0°, min		form 8, ϕ = 127°, min	
n_P	9.91	$\underline{n_P} - \pi_{C=C}$	9.22
$\pi_{C=C}$	10.14	$n_P + \underline{\pi_{C=C}}$	10.99
σ_{P-C}, σ_{C-H}	12.80	σ_{P-C}, σ_{C-H}	12.69
π_{CH_3}, π_{PH_2}	14.13	π_{CH_3}, π_{PH_2}	14.02
σ_{C-C}, σ_{CH_3}	14.25	σ_{C-C}, σ_{CH_3}	14.26
π_{PH_2}, π_{CH_3}	15.86	π_{PH_2}, π_{CH_3}	15.76
σ_{C-C}, σ_{CH_3}	16.06	σ_{C-C}, σ_{CH_3}	16.44

is a corresponding population of rotamers whose dihedral angle varies between 40 and 140°, and at a 0.1-eV difference on the high-energy side (9.35–9.45 eV), there is a population of rotamers whose dihedral angle varies between 0 and 25° and 155 and 180° and (b) for the second ionic state at a 0.1-eV energy difference between 10.43 and 10.53 eV, rotamer energies whose dihedral angle varies between 0 and 35°, and 145–180° are associated and between 10.78 and 10.88 eV rotamers whose dihedral angle varies between 50 and 130° may be attributed. The intermediate range of 0.25 eV corresponds to a more restricted population.

The rather broad shape of the first two band leads, to account for the experimental spectrum, to the proposal of a free rotating system in the operating conditions.

Prop-1-en-2-ylphosphine. As a result of the conditions used to obtain the compound and of the evaluated barriers, we were led as above to consider for prop-1-en-2-ylphosphine either the coexistence of two rotamers or free rotation. Nevertheless, due to the large size of the system, the theoretical evaluation of the ionization potentials was carried out only on a simple Koopmans level and only for the two most stable rotamers. This approach minimized the effect of methylation, since the high degree of stabilization of the ionic state was not taken into account.

As expected, the results obtained for conformer 6 (Table VI) indicate that after methylation there is a greater decrease in the second ionization potential (0.35 eV) than in the first (0.1 eV). At deeper energies, ionization potentials characteristic of σ_{P-C}, σ_{C-H} bonds and then those associated with the systems π_{PH_2}, π_{CH_3} and σ_{C-C}, σ_{CH_3} are evaluated.

The interaction between the phosphorus lone pair and the σ_{C-C} bond of conformer 8 is strong. The effect of methylation, in comparison to conformer 6, is a decrease in the first and second ionization potentials of about 0.13 eV and 0.4 eV.

If free rotation is to be considered, estimating corrections beyond Koopmans of the same order of magnitude as for ethenylphosphine, the resulting effects of an α-methylation can be predicted as follows: (a) a broadening of the first band as a result of the more pronounced methylation effect for the rotamers near 90° (ionizations on the low energy side) and (b) a shift of the second band toward low energies with a more pronounced effect for the rotamers near 90° (ionizations on the high energy side).

These comments agree with observations in the experimental spectrum of two neighboring bands with, in comparison to ethenylphosphine, a broadening of the band associated with the first ionic state and, inversely, a sharper band corresponding to the second ionic state. Also for this compound, the shape of the spectrum can be interpreted only if we consider a free rotating system.

6. Conclusion

This study has led to the definition of the electronic and structural characteristics of ethenylphosphine, a compound only recently synthesized. The most stable rotamer in this system is a form minimizing the interaction between the phosphorus lone pair and the $\pi_{C=C}$ bond. The structure of the second less energetically stable rotamer is close to that of ethenylamine. Nevertheless the calculated rotation barriers are very low. Experimentally, generating this molecule by flash thermolysis, we conclude to the observation of a free-rotating system by PES in the operating conditions.

The results obtained for the α-methylated derivative (relative to the phosphino group of ethenylphosphine) are consistent with these conclusions.

Note Added in Proof. In a very recent paper P.v.R. Schleyer et al.[23] communicate a theoretical investigation on ethenylphosphine in excellent agreement with our results.

Registry No. 1, 58436-39-8; **2**, 2049-57-2; **3**, 109051-00-5; **4**, 113322-97-7; 9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine, 50560-12-8; 11-methyl-9,10-dihydro-9,10-ethanoanthracen-11-ylphosphine, 113322-98-8; anthracene, 120-12-7.