Structure and Properties of 1-Phospha-allene ($H_2C{=}C{=}PH$). α-Carbon *versus* Phosphorus Protonation?

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Although 1-phospha-allenes ($>C{=}C{=}P-$) are generally only isolable when bulky groups are present, the first experimental data are now becoming available. *Ab initio* calculations are reported for this novel cumulene system ($H_2C{=}C{=}PH$) and four possible protonated analogues. The phospha-allene is configurationally stable with a large rotational barrier. The contribution of structures such as (**1b**) are minimal; in fact the C=C and C=P bonds are largely as in the uncumulated systems, in line with the failure to observe i.r. absorptions in the 1 600—2 300 cm^{-1} region. The α-carbon is the favoured site of protonation; this behaviour is contrasted with other cumulenes such as ketenimines or phosphaketenes. The proton affinity of 1-phospha-allene is calculated to be 193 ± 5 kcal mol^{-1} at MP4/6-31G**//HF/4-31G. The predicted reactivity of the phospha-allene in cycloadditions and with reagents HX is commented on.

The preparation of dico-ordinated phosphorus-containing compounds has in the past much intrigued the synthetic chemist for several reasons including the reluctance of P atoms to form *pπ–pπ* multiple bonds. Recently, several authors have been successful in designing efficient routes for the preparation of phosphacumulenes of general formula $X{=}C{=}P-$ ($X = -N$,[1–3a] O,[4a] C,[3,4b] $-P$[3b,5]). Although these compounds are in general only isolable because of the steric protection provided by bulky substituents, such as 2,4,6-tri-t-butylphenyl, they are however able to undergo a wide range of chemical transformations at the multiple bonds. As with other phosphorus-containing compounds in low co-ordination state, phospha-allenes appear to possess unusual physico-chemical properties. In this connection, theoretical studies are more than helpful in interpreting the new data, assignment of spectroscopic parameters, and in predicting reactive sites and thereby could stimulate further experimental work.

Recent theoretical studies[6] on model iminomethylenephosphine ($HP{=}C{=}NH$) and 1,3-diphospha-allene ($HP{=}C{=}PH$) suggested a difference between their chemical behaviour towards cycloaddition, addition, and metal complexation reactions. We now report on the 1-phospha-allenes (ethenylidenephosphines) ($>C{=}C{=}P-$) which are the phosphorus analogues of the ketenimines. The first substituted ethenylidenephosphines have recently been isolated by the groups of Yoshifuji[3a] and of Appel[4b] and some spectroscopic data are now available. Our aim in the present work is to examine in some detail the geometry, the vibrational frequencies, the configurational stability, the sites of protonation, and the reactivity towards some chemical reagents by means of *ab initio* calculations on the model molecule $H_2C{=}C{=}PH$. In particular, we wish to establish the similarities and the differences between phospha-allene and ketenimine ($>C{=}C{=}N-$) for which both extensive experimental[7] and theoretical[8–10] studies have previously been reported.

Geometries of stationary structures were determined employing the analytical gradient procedure[11] and the 4-31G basis set.[12] Improved relative energies were obtained from single-point calculations (with 4-31Gs geometries) which employ the 6-31G**[13a] and a double-zeta plus polarization[13b] basis sets. The correlation energies have also been taken into account *via* the Møller–Plesset perturbation theory to second, third, and fourth order[14] (with 6-31G** basis set).

The full harmonic force field (4-31G) for $H_2C{=}C{=}PH$ was computed by gradient difference using the VA05AD subroutines.[15] The harmonic frequencies and normal co-ordinates were calculated by the standard GF matrix method.[16] The calculations were performed making use both Monstergauss[17a] and Gaussian 80[17b] programs in their IBM/VM-CMS versions.

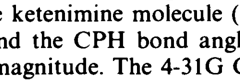
Optimized geometries are displayed within the text.

Results and Discussion

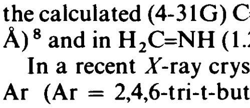
(1) *Geometry*.—The 1-phospha-allene molecule (**1**) is calculated to have C_s symmetry. The $H_2C{=}C$ moiety is nearly the same as that of the ketenimine molecule ($H_2C{=}C{=}NH$).[8] The PH bond length and the CPH bond angle are both in their ordinary order of magnitude. The 4-31G C=P bond length of 1.657 Å is situated in between those in $HN{=}C{=}PH$ (1.718 Å) and $HP{=}C{=}PH$ (1.644 Å)[6] and quite close to that of 1.672 Å in $H_2C{=}PH$.[6] By comparison, note that the difference between the calculated (4-31G) C=N bond lengths in $H_2C{=}C{=}NH$ (1.219 Å)[8] and in $H_2C{=}NH$ (1.256 Å)[6] is somewhat larger.

In a recent *X*-ray crystallographic study on the $Ph_2C{=}C{=}P-Ar$ (Ar = 2,4,6-tri-t-butylphenyl) compound, Appel *et al.*[4b] reported the values of 1.31 Å for C=C and 1.63 Å for C=P. We note that the sums of the C=C and C=P distances in both cases are almost the same.

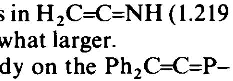
(2) *Configurational Stability*.—Like ketenimines, 1-phospha-allenes are axially dissymmetrical. However, according to the computed barriers to rotation (47.5 kcal mol^{-1} at 4-31G and 48.5 kcal mol^{-1} at DZP//4-31G, see Table 1) with the transition structure (**2**), 1-phospha-allene is rather stable towards configurational change. This barrier to rotation can be compared



(**1**)



(**2**)



(**3**)

Table 1. Calculated total (a.u.) and relative (kcal mol^{-1}) energies of three forms of 1-phospha-allene at both 4-31G//4-31G and DZP//4-31G levels

	Total energies		Relative energies	
	4-31G//4-31G	DZP//4-31G	4-31G	DZP
(**1**)	−417.601 36	−418.134 31	0.0	0.0
(**2**) (rotation)	−417.525 53	−418.056 94	47.6	48.5
(**3**) (inversion)	−417.476 84	−418.000 26	78.1	84.1

with related systems: 42 kcal mol^{-1} (DZP//4-31G) in diphospha-allene (HP=C=PH),[6] 75.3 kcal mol^{-1} in phosphaethene (H_2C=PH, 4-31G//4-31G),[18] 60 kcal mol^{-1} in diphosphene (HP=PH, DZP//3-21G).[19] A similar situation has already been met for the H_2C=C=NH/H_2C=NH pair of molecules where the barrier to inversion is 13.9 and 32.4 kcal mol^{-1} at 6-31G**//4-31G, respectively.

For 1-phospha-allene (**1**), the interconversion process *via* the rotation transition structure (**2**) is noticeably favoured relative to the inversion transition structure (**3**) by *ca.* 30—36 kcal mol^{-1} (see Table 1); for comparison the difference is only 6 kcal mol^{-1} (4-31G) in H_2C=PH[18] and 10 kcal mol^{-1} (DZP) in HP=PH.[19]

The Figure displays the orbital correlation diagram calculated at DZP//4-31G level for the LUMOs and four HOMOs of different structures including three forms (**1**)—(**3**) of H_2C=C=PH, both perpendicular (**4**) (minimum) and linear (**5**) (inversion transition structure) forms of H_2C=C=NH, and finally H_2C=PH (**6**) and H_2C=NH (**7**).

The linearization of the hydrogen atom on the phosphorus in H_2C=C=PH (**1**)—(**3**) destabilizes both π and n HOMOs. However, the rotation of the PH bond in H_2C=C=PH (**1**) to (**2**) and the inversion of the nitrogen atom in H_2C=C=NH (**4**) to (**5**) create two opposite effects: the one destabilizing the highest occupied orbitals (n character in H_2C=C=NH and π-character in H_2C=C=PH) and the other stabilizing the immediately subsequent occupied orbitals (π in H_2C=C=NH and n in H_2C=C=PH).

Very recently, an activation free energy of 20.3 kcal mol^{-1} has been reported[20] for the *Z–E* isomerization in the bis-(2,4,6-tri-t-butylphenyl)diphosphene (ArP=PAr). It can be expected that the aromatic rings could stabilize appreciably the n-orbitals by the inductive effect and tend to limit the destabilization of the π-orbitals by conjugation.

From the energetic data of (**1**) and (**2**) as presented in Table 1 and the Figure, we may predict that for the radical cation H_2C=C=PH$^{+\bullet}$, both perpendicular and planar structures are close in energy. The radical cation might even have the planar configuration as a minimum.

(3) *Electronic Structure.*—The ground-state electronic configurations of 1-phospha-allene (**1**) and ketenimine (**4**) are as follows:

H_2C=C=PH (**1**): $(1a'')^2(7a')^2(8a')^2(2a'')^2(9\text{-}12a')^8(3a'')^2(4a'')\ldots$
H_2C=C=NH (**4**): $(1a'')^2(7a')^2(8a')^2(2a'')^2(9a')^2(3a'')\ldots$

As mentioned above, the HOMO in (**1**) as well as in H_2C=PH (**6**) is the π-orbital of the C=P bond (with the largest coefficient on the P atom) while in (**4**), as well as in H_2C=NH (**7**), the HOMO is the n-orbital of the nitrogen atom. Unlike HP=C=NH and HP=C=PH where the π_{CP} and n_P HOMOs are quasi-degenerate,[6] a significant n–π separation of 0.6 eV in (**1**) has been calculated. Nevertheless, this orbital energy difference is much smaller than that of 3.15 eV observed in ketenimine (**4**) (see Figure). It is also worth noting that both n and π orbitals in H_2C=C=PH (**1**) are little perturbed with respect to those of the uncumulated H_2C=PH (**6**), in clear contrast to the situation in H_2C=C=NH (**4**). As seen in Table 2, the overlap population of the C=P bond in (**1**) is nearly equal to that of (**6**).

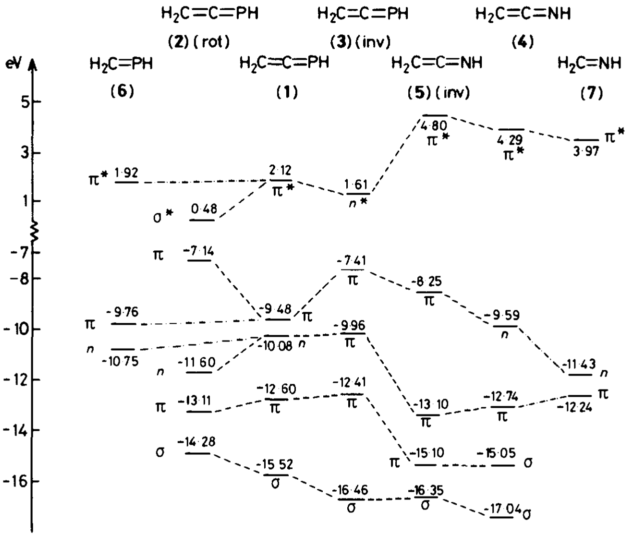


Figure. Orbital correlation diagram for the LUMO and some HOMOs in three forms (**1**)—(**3**) of H_2C=C=PH, two forms (**4**) and (**5**) of H_2C=C=NH, H_2C=PH (**6**), and H_2C=NH (**7**) calculated at the DZP/4-31G level

The following is the decrease in the C=P bond populations in different compounds:[6] H_2C=C=PH (1.16) ~ H_2C=PH (1.18) > HPC=PH (0.86) ~ HNC=PH (0.85). The P atom in (**1**) is less positively charged than that in (**4**) but the charge of 0.13 is still significantly positive by comparison with those of 0.02e$^-$ in HP=C=PH and −0.01e$^-$ in HN=C=PH.[6] This electronic distribution is consistent with the n.m.r. data. The observed ^{31}P chemical shift, δ_P 72 p.p.m., in Ph_2C=C=PAr[3a] is not very low by comparison with those of phospha-alkenes (>C=P–, usually δ_P > 200 p.p.m.). In contrast, the peaks in the carboimidophosphenes (–N=C=P–) are situated at high field, δ_P *ca.* −65 to 100 p.p.m.[1,3]

The α-carbon is the most negatively charged atom in the 1-phospha-allene (**1**) and the charge on this carbon decreases in the following sequence: H_2C=PH (−0.49) > H_2C=C=PH (−0.34) > HP=C=PH (−0.14) > HN=C=PH (−0.06). In summary, the cumulation with a C=C double bond products little modification on the electronic structure of the C=P bond.

(4) *Molecular Properties.*—The dipole moment of 1.44 D of (**1**) is slightly larger than the value of 1.02 D for H_2C=PH at the same DZP//4-31G level (Table 3). That is no doubt due to the small but positive contribution of the negative charge at the β-carbon in (**1**) in reinforcing the dipole $\overset{-}{C}$——$\overset{+}{P}$. In contrast, the dipole moment of (**4**) is found to be smaller than that of 2.18 D of H_2C=NH.[6] Table 2 indicates that this

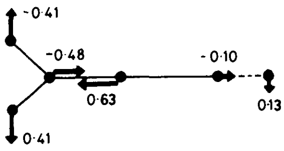
Table 2. Net charges and overlap populations (DZP//4-31G)

	$H_2C{=}PH$ (**6**)	$H_2C{=}C{=}PH$ (**1**)	$H_2C{=}C{=}NH$ (**4**)	$H_2C{=}NH$ (**7**)
Net charges				
α-C		−0.099	−0.241	
β-C	−0.494	−0.343	0.063	−0.195
P or N	0.173	0.126	−0.273	−0.253
H (P or N)	0.006	0.051	0.200	0.199
Overlap populations:				
C=C		1.376	1.296	
C=P or C=H	1.084	1.164	1.512	1.378
P–H or N–H	0.698	0.654	0.754	0.694

Table 3. Calculated molecular properties of $H_2C{=}C{=}PH$ and $H_2C{=}C{=}NH$ at DZP//4-31G level

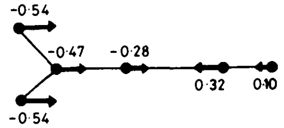
	$H_2C{=}C{=}PH$ (**1**)	$H_2C{=}C{=}NH$[a] (**4**)
Dipole moment μ/D	1.44	1.74 (1.97)
Second moment (a.u.) $\langle r^2 \rangle$	−56.1	−39.8 (−54.9)
Potential (a.u.) $1/r$ (C_β)	−14.70	−14.72 (−14.72)
$1/r$ (C_α)	−14.68	−14.65 (−14.67)
$1/r$ (P or N)	−54.15	−18.34 (−18.30)
Electric field gradient (a.u.)[b]		
q_{xx} (P or N)	−0.341	−0.341
q_{yy} (P or N)	−0.627	−0.459
q_{zz} (P or N)	0.968	0.800
η[c]	0.295	0.146

[a] In parentheses are the values obtained for $H_2C{=}C{=}NH$ with a CI/DZP wave function taken from ref. 9. [b] In principal axis systems. [c] Asymmetric parameters.



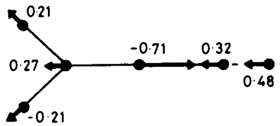
ν_3 1987 cm^{-1} (A')

(**8**)



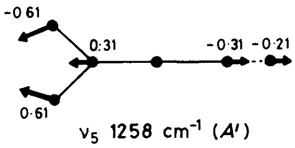
ν_7 789 cm^{-1} (A')

(**9**)



ν_3 2290 cm^{-1} (A')

(**10**)



ν_5 1258 cm^{-1} (A')

(**11**)

reduction could arise from a partial cancellation of the dipoles of the N–H bond and the whole C=C=N group. The second moment $\langle r^2 \rangle$ shows that the extent of the charge distribution in the ketenimine (**4**) is about two-thirds as large as that of 1-phospha-allene (**1**). The $\langle 1/r \rangle$ values indicate that the potential at the carbon nucleus remains unchanged in both positions (α and β) and in both structures (**1**) and (**4**). Finally, the electric field gradient g_{zz} of the P atom in (**1**) is predicted to be the smallest value among those of the molecules considered, namely: $H_2CC{=}PH$ (0.968) < $HPC{=}PH$ (1.123) < $HNC{=}PH$ (1.131) < $H_2C{=}PH$ (1.384). This decrease for $H_2C{=}C{=}PH$ suggests a similar decrease of the ionic character of the C=P bond through cumulation: $H_2C\overset{-}{C}{-\!-}\overset{+}{P}H < HP\overset{-}{C}{-\!-}\overset{+}{P}H < HN\overset{-}{C}{-\!-}\overset{+}{P}H < H_2\overset{-}{C}{-\!-}\overset{+}{P}H$. In other words, the resonance structures (**1a** and **b**) are only minor contributors to the overall structure of the 1-phospha-allene molecule by comparison with other phosphacumulenes.

$$\underset{(\mathbf{1})}{H_2C{=}C{=}PH} \longleftrightarrow \underset{(\mathbf{1a})}{H_2C{=}\overset{-}{C}{-}\overset{+}{P}H} \longleftrightarrow \underset{(\mathbf{1b})}{H_2\overset{-}{C}{-}C{\equiv}\overset{+}{P}H}$$

The situation in ketenimine (**4**) is somewhat different. The sequence of $q_{zz}(^{14}N)$ values is: $HNC{=}NH$ (0.662) < $H_2CC{=}NH$ (0.800) < $H_2C{=}NH$ (1.117). Consequently, an increasing ordering of ionic character may be noted: $H_2\overset{+}{C}{-\!-}\overset{-}{N}H < H_2C\overset{+}{C}{-\!-}\overset{-}{N}H < HP\overset{+}{C}{-\!-}\overset{-}{N}H < HN\overset{+}{C}{-\!-}\overset{-}{N}H$.

(5) *Vibrational Frequencies.*—The 4-31G harmonic frequencies are collected in Table 4. It is well established that harmonic force fields of molecules containing first-row atoms (H, C, N, O, F) calculated at SCF level of theory with double-zeta or split-valence basis set provide vibrational frequencies systematically overestimated by about 10% with respect to the experimental values.[21] On the other hand, it was recently shown that the stretching frequencies of P=X multiple bonds are slightly underestimated by 4-31G calculations.[22,23] For this reason, we consider here an average scale factor of ν(predicted)/ν(4-31G) = 0.9 for the vibrational modes of the $H_2C{=}C$ moiety in order to predict more realistic frequencies (Table 4).

In their experimental works, Yoshifuji *et al.*[3] have reported an i.r. (KBr) spectrum of the $Ph_2C{=}C{=}P{-}Ar$. The most striking feature of this i.r. spectrum is that there are no significant bands in the region 1 600—2 300 cm^{-1}, in clear contrast to other cumulenes such as Ph–N=C=P–Ar[1–3] where strong bands were observed in the same region and usually assigned to the antisymmetrical stretching of the –P=C=N– group. Results from Table 4 indicate that there are two distinct stretching frequencies both belonging to the C=C=P skeleton of (**1**). The first at 1 987 cm^{-1} (4-31G value) can be assigned to the stretching of C=C bond and the second at 789 cm^{-1} to the stretching of the C=P bond. The normal co-ordinates corresponding to these modes of vibration can be in shown in schematic form in (**8**) and (**9**).

Similar calculations[24] on ketenimine (**4**) provide the following data in (**10**) and (**11**) for the C=C=N stretching frequencies (4-31G values). After correction with a scale factor of 0.9, the asymmetric stretching frequency (**10**) becomes ν_{CCN} 2 091 cm^{-1} and this value is in good agreement with the experimental frequency of 2 040 cm^{-1} previously reported for $H_2C{=}C{=}NH$ (**1**) in an Ar matrix.[25]

The difference in both molecules (**1**) and (**4**) is quite clear. No

Table 4. Harmonic vibrational frequencies (4-31G) of $H_2C=C=PH$

		Wavenumber (cm^{-1})[a]	Assignment
A'	ν_1	3 299 (2 969)	CH stretching (symmetric)
	ν_2	2 194	PH stretching
	ν_3	1 987 (1 788)	C=C stretching
	ν_4	1 561 (1 405)	HCC bending (symmetric)
	ν_5	1 097 (987)	H_2C wagging
	ν_6	1 018	HPC bending
	ν_7	789	C=P stretching
	ν_8	400	CCP bending (out of plane)
A''	ν_9	3 375 (3 076)	CH stretching (asymmetric)
	ν_{10}	1 102 (992)	HCC bending (asymmetric)
	ν_{11}	814	H(+)H(−)C and PH(+) out-of-plane
	ν_{12}	373	CCP bending (in-plane)

[a] Values in parentheses are the predicted frequencies with an average scale factor of $\nu_{predicted}/\nu_{4-31G} = 0.9$ for the $H_2C=C$ moiety, see text.

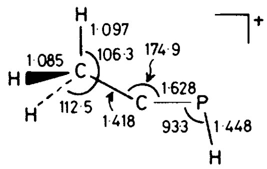
stretching mode involving the whole C=C=P group in (**1**) exists, while there are two in (**4**), one symmetrical and one asymmetrical. In 1-phospha-allene (**1**), both C=C stretching (**8**) and C=P stretching (**9**) are nearly independent of each other. The C=P stretching frequency of 789 cm^{-1} in (**1**) is smaller than that of 1 146 cm^{-1} calculated for phosphaethene $H_2C=PH$.[23] This independence can be considered as a consequence of the non-interaction, geometric and electronic, between C=C and C=P bonds in the cumulated structure (**1**) (see above).

Interpreting this observed difference in the i.r. spectrum, Yoshifuji *et al.*[3a] have suggested that there is only a small contribution of the resonance form (**1b**) (see above) to (**1**). As shown above from the electric field gradients, our results more or less support this assumption. Nevertheless, this assumption appears to be not satisfactory in interpreting the behaviour of ketenimines.[26] From symmetry considerations, the C=C stretching mode (**8**) of (**1**) may be active in the Raman. Further i.r. investigations of 1-phospha-allenes as well as comparative theoretical studies on different phosphacumulenes including the calculations of vibrational intensities (from dipole moments) are necessary in order to understand this important and interesting point.

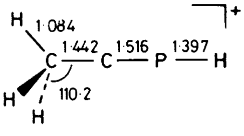
(6) *Protonation Sites and Proton Affinities.*—We consider here seven possible structures of the protonated $H_2C=C=PH$: β-carbon protonation, (**12**) (minimum) and (**13**) (saddle point); α-carbon protonation, (**14**), (**15**) (minima), and (**16**) (saddle point); and phosphorus protonation, (**17**) (minimum) and (**18**) (saddle point). The corresponding total energies and proton affinities calculated at different levels are listed in Tables 5 and 6, respectively.

Some points are noteworthy. (a) The ordering of the computed proton affinities (PA) is: PA [α-C, (**14**)] > PA [P, (**17**)] > PA [β-C, (**12**)], and hence the α-carbon constitutes the preferred site of protonation in 1-phospha-allene in contrast to the case of ketenimine (**4**) where the ordering (6-31G**//4-31G) is PA (β-C, 231.8 kcal mol^{-1}) > PA (N, 217.4 kcal mol^{-1}) > PA (α-C, 175.2 kcal mol^{-1}).[27] That is also different from the case of $H_2C=PH$ (**6**) where *P*-protonation has recently been predicted as favoured over *C*-protonation: PA (P, 190 kcal mol^{-1}) > PA (C, 179 kcal mol^{-1}, results at MP4/6-31G**).[28]

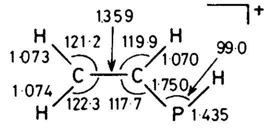
(b) At the MP4/6-31G** level, the calculated energy difference between (**14**) and (**17**) is 10 kcal mol^{-1} while that between (**12**) and (**17**) is only 2 kcal mol^{-1}. The correlation energy tends thus to reduce the separation between protonated species. These rather small energy gaps could obviously be reduced again by substituents and, consequently, all possible protonated species could be observed. Combined with the negative contribution of the zero-point vibrational energy by *ca.* 7 kcal mol^{-1} to the PA, we can estimate a proton affinity of 193 ± 5 kcal mol^{-1} for the α-C-site of $H_2C=C=PH$.



(**12**)



(**13**)



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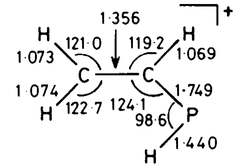
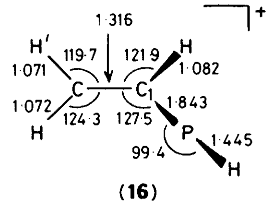
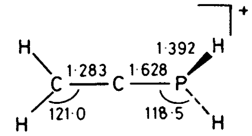


(**15**)

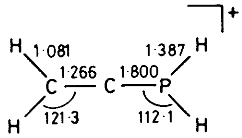


(**16**)

$HC_1CH' = -2°$
$PC_1CH = 3°$
$HPC_1C = 90°$



(**17**)



(**18**)

(c) The local minimum of the β-carbon-protonated species has a bent *E*-structure (**12**). The linear structure (**13**) is a saddle point and lies at 30 kcal mol^{-1} (DZP//4-31G) above (**12**). The species (**12**) is also the *P*-protonated $H_3CC{\equiv}P$. At the 4-31G//4-31G level, the corresponding PA is 159.4 kcal mol^{-1} which is larger than that of 134 kcal mol^{-1} obtained for $H{-}C{\equiv}P$[28] at 3-21G//3-21G. It is, however, shown that the *P*-protonation of phosphaethyne HCP is strongly disfavoured with respect to the *C*-protonated derivative by *ca.* 45 kcal mol^{-1}[28] (3-21G).

(d) The *cis*-conformer (**15**) of the α-carbon-protonated species

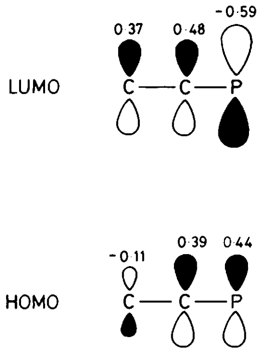
Table 5. Calculated total energies (a.u.) of neutral and protonated 1-phospha-allene (**1**) considered at different levels

Species[a]	HF/4-31G	HF/DZP	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4SDQ/6-31G**
(**1**) (neutral)	−417.601 36 (0.0)	−418.134 31 (0.0)	−418.127 47 (0.0)	−418.500 03 (0.0)	−418.527 01 (0.0)	−418.534 39 (0.0)
(**12**) (β-C protonated)	−417.891 49 (−182.0)	−418.428 90 (−184.8)	−418.423 41 (−185.77)	−418.792 81 (−183.7)	−418.823 17 (−185.8)	−418.833 04 (−187.4)
(**13**) (β-C protonated)	−417.856 69 (−160.2)	−418.380 00 (−154.1)				
(**14**) (α-C protonated)	−417.930 11 (−206.2)	−418.463 94 (−206.8)	−418.458 51 (−207.7)	−418.815 59 (−198.0)	−418.847 13 (−200.8)	−418.853 18 (−200.0)
(**15**) (α-C protonated)	−417.927 22 (−204.4)	−418.461 26 (−205.1)	−418.455 70 (−205.9)	−418.813 36 (−196.6)	−418.844 83 (−199.4)	−418.851 08 (−198.7)
(**16**) (α-C protonated)	−417.891 26 (−181.9)	−418.423 45 (−181.4)				
(**17**) (P protonated)	−417.897 73 (−185.9)	−418.437 19 (−190.0)	−418.434 46 (−192.6)	−418.798 90 (−187.5)	−418.828 72 (−189.3)	−418.836 13 (−189.3)
(**18**) (P protonated)	−417.813 94 (−133.3)	−418.343 93 (−131.5)				

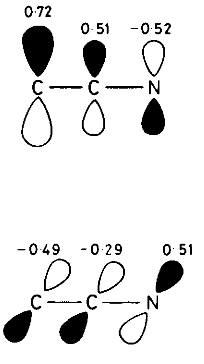
[a] The numeration of the species and the 4-31G-optimized geometries are given in the text.

Table 6. Relative energies (kcal mol^{-1}) between the neutral and protonated 1-phospha-allene species at different levels.

Species[a]	HF/4-31G	HF/DZP	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4SDQ/6-31G**
(**1**) (neutral)	0.0	0.0	0.0	0.0	0.0	0.0
(**12**) (β-C protonated)	−182.0	−184.8	−185.7	−183.7	−185.8	−187.4
(**13**) (β-C protonated)	−160.2	−154.1				
(**14**) (α-C protonated)	−206.2	−206.8	−207.7	−198.0	−200.8	−200.0
(**15**) (α-C protonated)	−204.4	−205.1	−205.9	−196.6	−199.4	−198.7
(**16**) (α-C protonated)	−181.9	−181.4				
(**17**) (P protonated)	−185.9	−190.0	−192.6	−187.5	−189.3	−189.3
(**18**) (P protonated)	−133.3	−131.5				



(19)



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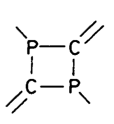

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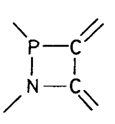

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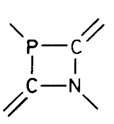

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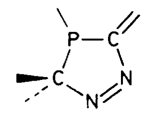

(24)

lies *ca.* 1 kcal mol^{-1} above the most stable (**14**). The interconversion (**15**) $\rightleftharpoons$ (**14**) *via* the transition structure (**16**) requires a barrier to rotation of 23.7 kcal mol^{-1} (DZP). Accordingly, both conformers can be observed as stable intermediates. By comparison with the couple $H_3C\text{-}PH^+/H_2C{=}PH_2^+$ (where the former lies *ca.* 12 kcal mol^{-1} above the latter[28]), it can be pointed out that the preferred α-carbon site of protonation in 1-phospha-allene (**1**) arises from the stabilizing effect of the vinyl group ($H_2C{=}C\text{-}PH^+/H_2C{=}C{=}PH_2^+$: the former lies 10—12 kcal mol^{-1} below the latter). Populating the vacant orbital of the P atom in the phosphenium cations (R_2P^+) by electrons from π-donor substituents should in fact stabilize them considerably. Experimentally, several diaminophosphenium cations $(R_2N)_2P^+$, have been prepared and they undergo cycloadditions, for example, like carbenes or silylenes.[29,30]

(7) *Chemical Reactivity.*—No experimental facts have been reported as yet on the chemical reactivity of 1-phospha-allenes. We attempt to predict here their reactivity and to compare them with those of ketenimines which are well established. First, it is useful to analyse the HOMOs and the LUMOs of both $H_2C{=}C{=}PH$ (**1**) and $H_2C{=}C{=}NH$ (**4**). They are schematized in (**19**) and (**20**), respectively. In (**1**), both HOMO and LUMO [see (**19**)] appear to be dominated by the C=P bond which possesses the largest orbital coefficients, whereas both C=C and C=N bonds in (**4**) have comparable MO coefficients. The picture of the CP moiety in (**19**) is very similar to that in $H_2C{=}PH$.[6]

(a) *Addition to HX.* Without a catalyst, the nucleophile part (X^-) of proton-acidic reagents HX can be predicted to add to the P atom; this is followed by a proton transfer to the α-C atom [equation (1)] within a concerted mechanism. With acidic

$$R_2C{=}C{=}PR + HX \longrightarrow R_2C{=}CH-PRX \qquad (1)$$

catalysis, the α-C-site protonation occurs first and the anionic nucleophile X^- adds to the phosphenium cation subsequently [equation (2)]. In both cases, the vinylphosphines will be

$$R_2C{=}C{=}PR + H^+ \longrightarrow R_2C{=}CH\text{-}PR^+ \xrightarrow{X^-} R_2C{=}CH-PRX \qquad (2)$$

obtained as primary adducts. Note that for ketinimines,[26] phosphaketenes RP=C=O,[4] and carboimidophosphenes RN=C=PR,[1-3] the α-carbons are electrophilic and are attacked by nucleophile to form azomethine or carbonyl derivatives in the first step.

(b) *Cycloadditions*. The dimerization of 1-phospha-allene can be expected to occur as a head-to-tail addition of two C=P moieties, leading to diphosphetane (**21**). This cycloadduct is usually obtained from 1,1-self-condensation of phospha-alkenes or phosphacumulenes.[1-6] Condensation of (**1**) to a polar multiple bond $\overset{+}{X}=\overset{-}{Y}$ such as C=N in carbodi-imides or isocyanates could also be predicted to generate the four-membered ring (**22**) rather than (**23**). As a matter of fact, both charge and orbital considerations act in favour (**22**).

Concerning 1,3-dipolar cycloaddition of 1-phospha-allene with diazomethane, for example, the five-membered ring (**24**) is predicted to be the adduct of the normal addition.

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