Ab Initio Calculations of the Molecular Structures and the Electronic Properties of Phospha-Alkynes $R-C\equiv P$ ($R = H, CH_3, NH_2, OH, F$ and Cl)

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Z. Naturforsch. **39 a**, 169−174 (1984); received May 20, 1983

MO Calculations, Molecular Structures, Electronic Properties, Phospha-Alkynes

Results of ab initio SCF calculations on phospha-alkynes $R-C\equiv P$ with $R = H, CH_3, NH_2$, OH, F and Cl are reported. The geometries were optimized by the force method with analytical gradient employing double zeta (DZ) basis sets. Various molecular and one-electron properties are calculated with double zeta plus polarization functions (DZ+P) and compared with experimental ones. The effect of substituents is analysed in terms of computed properties.

1. Introduction

At present, it is well recognized that second-row atoms such as silicon and phosphorus can form $p\pi-p\pi$ multiple bonds with carbon, nitrogen and oxygen atoms [1]. New experimental techniques are now available for the synthesis of compounds containing carbon-phosphorus multiple bonds with a trivalent phosphorus [2]. A variety of unstable and stable phospha-alkynes have recently been prepared and spectroscopically studied by different groups [1−4]. Several theoretical studies [5−11] on the molecular and electronic structures of the unsubstituted phospha-alkyne HCP have already appeared. The most recent and accurate work on the HCP and FCP molecules [11] compares the effects of polarization and electron correlation on their geometrical parameters.

Because of the low thermal stability of many phospha-alkynes, microwave and photoelectron spectroscopy seems, among other experimental techniques, most likely to provide information about the structure of these transient species. For this reason, the present work is aimed primarily at a systematic determination of the molecular structure and the electronic properties of substitued phospha-alkynes $R-C\equiv P$, where $R=H, CH_3, NH_2$, OH, F and Cl, for which some experimental data are available [12−14].

In this work, we report the fully optimized geometries of these molecules calculated by means of ab initio methods employing a double-zeta (DZ) basis set. Furthermore, the influence of substituents on the electronic structure has also been examined by comparing the electronic charge distribution and the one-electron properties as calculated from a double-zeta plus polarization functions (DZP) basis set.

2. Details of Calculation

The calculations were carried out at the SCF level of theory. This has been accomplished employing two basis sets: the first was the (9s 5p/4s 2p) DZ basis of Huzinaga [15] and Dunning [16] for C, N, O and F atoms and the (11s 7p/6s 4p) DZ basis of Huzinaga [17] contracted according to Dunning and Hay [18] for P and Cl. A (4s/2s) basis for the hydrogen atoms was used with a scale factor of 1.2. In the second basis, a set of six cartesian d-like functions was employed with exponent 0.733 for C, 0.908 for N, 0.85 for O and 1.62 for F, and a set of p functions with exponent 0.9 for H. For P and Cl, two sets of d functions with exponents 0.43 and 0.12 for P and 0.165 and 0.68 for Cl were added (DZP basis).

The molecular geometries were optimized by the force method with analytical gradient [19] as implemented in the Monstergauss program [20]. The optimally conditioned minimization technique [21] was employed and all optimizations were terminated when the gradient length $g = \left(\sum_i^n (\partial E/\delta q_i)^2/n\right)^{1/2}$ was reduced below $5 \cdot 10^{-4}$ mdyne.

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3. Results and Discussion

The fully optimized geometries of HCP, CH_3CP, NH_2CP, FCP and ClCP determined by the DZ basis set are given in Fig. 1 and compared with available experimental values for HCP [12], CH_3CP [13] and FCP [14].

In light of previous ab initio studies [11], the good agreement between calculated and experimental geometries is not surprising. It is useful to compare here the $C \equiv P$ bond distances previously determined by different methods of calculation. As seen in Table 1, the split-valence and double-zéta basis sets gave excellent $C \equiv P$ distances with a standard deviation of $4 \cdot 10^{-3}$ with respect to the experimental value. The effect of bond functions, local functions and polarization functions is to reduce the distance predicted at the DZ level by about 0.03 – 0.04 Å. In contrast, the electron correlation effect has tendency to lengthen this distance also by about 0.04 Å. So, in consequence of the opposite effects of polarization and correlation, it may be expected that the geometries obtained from split-valence or double-zéta basis sets are consistent with higher level calculations such as MP4/DZP. Therefore, we can use for the multiple bonds containing phosphorus atoms a basis set of split-valence or double-zéta quality for determining best geometrical parameters.

Except the STO-3G value, all theoretical dipole moments are appreciably overestimated compared to the experimental ones.

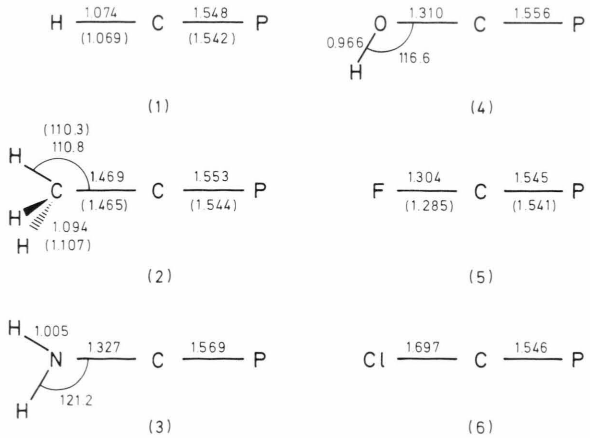

Fig. 1. Optimized geometries of phospha-alkynes determined by a DZ basis set. Bond lengths in Å and bond angles in degrees. Values in parantheses are experimental ones.

Table 1. Calculated geometry and dipole moment of HCP by different methods of calculation. Bond lengths in Å and dipole moments in Debye.

Method	$r(C\equiv P)$	$\Delta r(C\equiv P)$[a]	$r(C-H)$	μ	Ref.
STO-3G	1.471	−0.071	1.069	0.04	[8]
STO-3G/BFO[b]	1.552	0.010	–	–	[9]
STO-3G/BFM[b]	1.495	−0.047	–	–	[9]
STO-3G/BFD[b]	1.452	−0.090	–	–	[9]
3–21G	1.548	0.006	1.057	0.87	[22]
6–21G	1.549	0.007	1.059	0.90	[22]
4–31G	1.535	−0.007	1.056	0.51	[8]
4–31G/BFO[b]	1.506	−0.036	–	–	[9]
4–31G/BFD[b]	1.056	−0.036	–	–	[9]
LP-31G[c]	1.518	−0.024	1.050	–	[11]
DZ	1.544	0.002	1.058	0.67[d]	[7]
DZ	1.548	0.006	1.074	0.59	this work
STO-3G*	1.459	−0.083	–	–	[8]
3–21G*	1.513	−0.029	1.059	0.54	[22]
6–31G**	1.515	−0.027	1.063	0.62	[11]
DZP	1.508	−0.034	1.062	0.99	[6]
MP3/6–21G[e]	1.580	0.038	1.072	0.95	[11]
MP3/LP-31G[e]	1.553	0.011	1.050	–	[11]
Experimental[f]	1.542	–	1.069	0.39	[12]

[a] $\Delta r = r$ (calculated) − r (experimental).
[b] Mentioned basis set plus different types of bond functions.
[c] Local potentials for inner shells.
[d] Calculated with experimental geometry.
[e] Electron correlation obtained via third order Møller-Plesset perturbation Theory.
[f] From microwave spectroscopy.

Relative to HCP, the F and Cl atoms cause a very slight shortening of the $C \equiv P$ bond length, while the CH_3, NH_2, OH groups, which are all electron-donors, appear to lengthen significantly this distance (0.02 Å in NH_2CP). The same observation has also been made for the isoelectronic sulfido-borons $R-B\equiv S$ [23].

The computed moments of inertia and rotational constants are collected in Table 2 and those for HCP, CH_3CP and FCP are compared with the experimental values determined by microwave spectroscopy [12–14].

The calculated SCF energies using both DZ and DZP basis sets with DZ geometries are collected in Table 3. For the discussion of the electronic structure, the results obtained from DZP wave functions have been employed in all cases.

The magnitude and the ordering of the higher lying molecular orbitals is of interest since these data may, at the Koopmans' level of approximation, be directly correlated with the ionization potentials measured photoelectronspectroscopically.

Table 2. Calculated moments of inertia and rotational constants of phospha-alkynes. Values in parentheses are experimental ones.

	(1) HCP	(2) CH_3CP	(3) NH_2CP	(4) OHCP	(5) FCP	(6) ClCP
I_A[a]	–	3.16	1.49	0.70	–	–
I_B	25.47	102.03	96.12	94.72	97.63	174.23
I_C	25.47	102.03	97.62	95.43	97.63	174.23
$\Delta = I_C - I_A - I_B$	0.00	−3.16	0.01	0.01	0.00	0.00
A[b]	–	159 745.16	339 136.95	719 886.38	–	–
B	19 843.57 (19 976.05)[c]	4953.03 (4991.34)[d]	5257.40	5335.14	5176.50 (5257.80)[e]	2900.57
C	–	4953.03 (4991.34)	5177.14	5295.90	–	–

[a] amu. Å^2 units; [b] MHz units; [c] Ref. [12]; [d] Ref. [13]; [e] Ref. [14].

Table 3. SCF energies of phospha-alkynes with DZ and DZP basis sets (in atomic units).

Molecule	DZ	DZP
(1) $H-C\equiv P$	− 379.06049	− 379.11097
(2) $CH_3-C\equiv P$	− 418.09409	− 418.16284
(3) $NH_2-C\equiv P$	− 434.08981	− 434.16211
(4) $OH-C\equiv P$	− 453.89649	− 453.98692
(5) $F-C\equiv P$	− 477.88957	− 477.97238
(6) $Cl-C\equiv P$	− 837.91782	− 837.99732

The first three HOMO energies of each considered molecule are summarized in Table 4 and compared with earlier ab initio results and experimental ionization potentials of HCP [24], CH_3CP [25] and FCP [26].

Frost et al. [24] reported two adiabatic ionization potentials for HCP and assigned them as 10.79 eV (π) and 12.86 eV (n), respectively. Westwood et al. [25] observed four bands for CH_3CP and described them as 9.89 eV (π), 12.19 eV (n), 14.70 eV (CH_3) and 15.60 eV (CH_3). Finally, Kroto et al. [26] have shown that the first three ionization potentials of FCP are quite distinct and readily assigned as 10.57 eV (π), 13.55 eV (n) and 17.63 eV (π).

The calculated results in this work, on the whole, are in good agreement with previously reported studies in both quantitative and qualitative aspects. For all studied $R-C\equiv P$ compounds, the highest occupied orbitals are of π character. For R = H, CH_3, F and Cl, the two π orbitals are degenerated and mainly localized in the $C\equiv P$ bonds, while for

Table 4. Calculated (DZ P basis set) and experimental ionization potentials of phospha-alkynes (in eV).

Orbital nature	Calculated[a] IP (Koopmans)	Experimental IP	Orbital nature	Calculated IP (Koopmans)	Predicted IP (± 0.2 eV)[e]
HCP			NH_2CP		
$(\pi)^4$	10.60 (10.0)[b]	10.79[b]	$(\pi)^2$	8.35	8.50
$(n)^2$	13.42 (12.6)	12.86	$(\pi)^2$	9.81	10.00
$(\sigma)^2$	19.80 (20.0)		$(n)^2$	13.01	12.40
CH_3CP			OHCP		
$(\pi)^4$	9.69	9.89[c]	$(\pi)^2$	9.41	9.60
$(n)^2$	12.95	12.19	$(\pi)^2$	9.93	10.15
$(\sigma)^4$	16.14	14.70	$(n)^2$	13.34	13.00
FCP			ClCP		
$(\pi)^4$	10.55 (10.53)[d]	10.57[d]	$(\pi)^4$	10.13	10.30
$(n)^2$	14.20 (13.94)	13.55	$(n)^2$	13.75	13.20
$(\pi)^4$	20.31 (20.08)	17.63	$(\pi)^4$	14.59	14.00

[a] Values in parentheses are from previous ab initio calculations. [b] Ref. [24] and [5]. [c] Ref. [25]. [d] Ref. [26]. [e] Corrected values from orbital energies, see text.

R=NH_2 and OH there is a splitting of these orbitals (1.46 eV in NH_2CP and 0.52 eV in OHCP) and they are rather delocalized on the nuclear skeletons. That is doubtless due to the participation of the lone pairs of nitrogen and oxygen atoms to the conjugative interaction. So it might be expected that the photoelectron spectra of NH_2CP and OHCP contain two distinct bands corresponding both to the removal of π electrons. The lone pairs (n) of phosphorus atoms follow as the next high lying orbitals. The separation between π and n orbitals is not much different in all species. The $\pi - n$ separation of 2.07 eV in HCP was recently confirmed by results obtained from an emission spectrum of the cation HCP^+ [27]. In general, the calculations predict rather large values for the $\pi - n$ separation. This fact can arise from the rearrangement of the electronic distribution and correlation, which are neglected in Koopmans' approximation.

In Fig. 2, the molecular orbital correlation diagram for the first two ionization potentials of phospha-alkynes is presented.

Compared with the isoelectronic sulfido-borons $R-B\equiv S$ compounds [23], there is for the phospha-alkynes an overall shift to lower ionization potentials. So, the $C\equiv P$ group appears to be less electronegative than the $B\equiv S$ group. Apart from the splitting of the degeneracy (π^4 to $2\pi^2$) in NH_2CP and OHCP as above mentioned, the replacement of H by any of the considered substituents R destabilizes the π orbitals (by 0.05 – 2.25 eV). The decreasing order of π orbital energies is H > F > Cl > CH_3 > OH > NH_2, and this destabilization may be easily rationalized in terms of the π-donor ability of substituents (+M effect). Recently, Appel et al. [4] and Burckett-St. Laurent et al. [2] have independently observed a value of 8.65 eV and 8.68 eV, respectively, for the first bands in the photoelectron spectrum of C_6H_5CP, and these authors assigned it as π(CP). Thus, the conjugative effect destabilizes significantly the π orbitals. It is worth noting that the calculated π(CP) energy of 8.35 eV obtained with the 4–31 G basis set [2] is nearly the same as that of NH_2CP (DZP basis set, see Table 4).

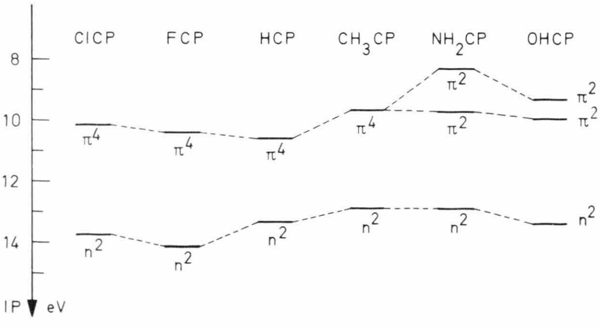

Fig. 2. Molecular orbital correlation diagram for the first π and n ionization potentials of phospha-alkynes. π^4 indicate the degenerated orbitals.

For the n orbital energies, the observed ordering F > Cl > H > OH > NH_2 > CH_3 is arising from the electron-withdrawing ability of the substituents (+I effect). This n(P) orbital is thus particularly inductively stabilized by F-substitution. Using obtained polynominal correlations between calculated and experimental ionization potentials of HCP, CH_3CP and FCP, we can estimate more realistic values of ionization potentials for NH_2CP, OHCP and ClCP. The predicted values are listed in the last column of Table 4.

The calculated net charges and overlap populations of phospha-alkynes are reported in Table 5. The phosphorus atoms in all R–CP compounds are predicted to be positively charged. The net charges on the carbon atoms are shown to be dependent on the substituent, and the sequence CH_3 > H > NH_2 > Cl > OH > F appeared as a result of mixing of inductive and mesomeric effects. It is well known that the charge distribution derived from Mulliken population analysis is strongly dependent upon the basis sets. Indeed, the 6–31 G* basis set gave a charge of −0.37 for carbon in HCP whereas it is positive (0.14) in FCP [11].

A detailed breakdown of the π and n populations and charges within CP groups is collected in Table 6. Except for CH_3CP, all other substituents preferently attract σ electrons from C and P atoms, while back-donating π electrons to the CP groups. The σ-attraction is largest in FCP while the π-donation is largest in NH_2CP. Totally, the CP group charge remains negative in NH_2CP whereas it is near to zero in OHCP and becomes positive in FCP and ClCP. It is striking to note that compared to HCP, all substituents depopulate the $C\equiv P$ bond. The increased diffuseness of the $C\equiv P$ bond by substituents has already been concluded from photoelectron data [25].

Table 7 summarizes some computed one-electron properties of phospha-alkynes. They include the dipole moment, the quadrupole moment, the $\langle r^2 \rangle$

Table 5. Net charges and overlap populations of phospha-alkynes in DZ P basis set. Numbers of molecules stand for those given in Figure 1.

	(1) X=H	(2) X=C	(3) X=N	(4) X=O	(5) X=F	(6) X=Cl
Net charges						
C	−0.381	−0.429	−0.330	−0.142	−0.021	−0.146
P	0.233	0.228	0.196	0.157	0.169	0.285
X	0.148	−0.169	−0.306	−0.310	−0.148	−0.139
H	–	0.123	0.220	0.296	–	–
Overlap populations						
C−P	1.642	1.450	1.390	1.420	1.484	1.206
C−X	0.742	0.849	0.774	0.670	0.518	0.772
X−H	–	0.772	0.776	0.682	–	–

Table 6. σ, π populations of C, P atoms and σ, π charges of CP bond in phospha-alkynes (DZ P basis set).

	HCP	CH_3CP	NH_2CP	OHCP	FCP	ClCP
C (σ)	4.439	4.453	4.327	4.202	4.097	4.180
C (π)	0.971	0.988	0.831	0.891	0.962	0.983
C ($\bar{\pi}$)	0.971	0.988	1.172	1.049	0.962	0.983
P (σ)	8.717	8.737	8.566	8.579	8.610	8.599
P (π)	3.025	3.017	3.371	3.235	3.110	3.058
P ($\bar{\pi}$)	3.025	3.017	2.867	3.029	3.110	3.058
CP (σ)[a]	−0.156	−0.190	0.107	0.219	0.293	0.221
CP (π)[b]	0.004	−0.005	−0.202	−0.126	−0.072	−0.041
CP ($\bar{\pi}$)[b]	0.004	−0.005	−0.039	−0.078	−0.072	−0.041
CP_t[c]	−0.148	−0.200	−0.134	0.015	0.149	0.139

[a] CP (σ) = 13 − C (σ) − P (σ)

[b] CP ($\pi/\bar{\pi}$) = 4 − C ($\pi/\bar{\pi}$) − P ($\pi/\bar{\pi}$).

[c] CP_t = CP (σ) + CP (π) + CP ($\bar{\pi}$).

Table 7. Molecular electronic properties of phospha-alkynes (DZ P basis set) in atomic units.

	HCP	CH_3CP	NH_2CP	OHCP	FCP	ClCP
Dipole moments[a]						
μ	0.441	1.552	3.116	2.212	0.765	0.185
Quadrupole moments[b]						
Q_{xx}	−1.855	−1.757	−0.499	−3.552	−0.515	−1.749
Q_{yy}	−1.855	−1.757	−5.712	−3.068	−0.515	−1.749
Q_{zz}	3.711	3.514	6.162	6.620	1.030	3.498
$\langle r^2 \rangle$	−41.310	−55.142	−51.117	−50.237	−51.640	−66.877
Electric field gradients[b]						
q_{xx} (P)	−0.677	−0.573	−1.352	−0.702	−0.282	−0.485
q_{yy} (P)	−0.677	−0.572	0.720	0.126	−0.281	−0.487
q_{zz} (P)	1.354	1.145	0.632	0.576	0.562	0.972
η	0.000	0.001	0.065	0.640	0.001	0.001
Magnetic shielding						
xx (C)	−5.256	−5.364	−5.398	−5.384	−5.380	−5.447
yy (C)	−5.256	−5.364	−5.398	−5.390	−5.380	−5.447
zz (C)	−4.174	−5.963	−3.866	−3.848	−3.826	−3.739
$1/r$ (C)	−14.687	−14.691	−14.663	−14.623	−14.586	−14.632
xx (P)	−18.168	−18.201	−18.162	−18.191	−18.201	−18.209
yy (P)	−18.168	−18.201	−18.275	−18.237	−18.201	−18.209
zz (P)	−17.810	−17.765	−17.744	−17.734	−17.730	−17.718
$1/r$ (P)	−54.147	−54.167	−54.181	−54.162	−54.133	−54.137

[a] Dipole moments in Debye units.

[b] Principal axis systems.

value, the electric field gradient on P and the magnetic shielding on C and P. As already seen in Table 1, the present DZP dipole moment of 0.441 D for HCP appears to be the best calculated value when compared to the experimental one of 0.39 D [12]. From the net charges shown in Table 5, the dipole moment of HCP is pointing toward the P atom. The computed value of 1.552 D for CH_3CP is close to the dipole moment of 1.499 D measured from Stark effect experiments [13]. Since the polarity of the C≡P bond is almost the same in both HCP and CH_3CP, the dipole moment of the latter is thus essentially due to the polarity of three C−H bonds. Finally, the DZP value of 0.795 D is appreciably overestimated with respect to the experimental dipole moment of 0.279 for FCP [14].

The quadrupole moment $Q_{zz} = 4.9$ Buckinghams for HCP calculated in this work may be compared with the earlier ab initio value of 4.81 [6] and the experimental value of 4.4 [28]. The quadratic moment $\langle r^2 \rangle$ indicates the compact or diffuse character of the total charge distribution of a molecule. The quantity of $\langle r^2 \rangle = 41.310$ for HCP is almost the same as 41.456 for the isoelectronic species HBS determined with the same DZP basis set [23].

The $\langle 1/r \rangle$ values, for their part, are proportional to the diamagnetic shielding of the considered nucleus. The obtained results indicate that they are rather little sensitive to the substituents. The average diamagnetic shielding (σ_{av}) at the phosphorus nucleus in HCP is calculated to be 961 ppm, which is reasonably close to the value of 1001 as previously reported [6].

The electric field gradients are of interest in connection with the nuclear quadrupole moments (eQq). Unfortunately, there are as yet no available experimental data of nuclear quadrupole moments of phosphorus atoms (^{31}P). However, we can note that the present field gradient $q_{zz} = 1.354$ of ^{31}P in HCP amounts to more than twice the previous value of 0.537 [6]. All calculated q_{zz} values in substituted phospha-alkynes are smaller than that in HCP; this decrease suggests an increase of the ionic character of the C≡P bond through substitution with the ordering of $CH_3 < NH_2 < OH < F$. The unusually large value of the asymmetric parameter (η) in OHCP seems to indicate that the electronic repartition around the P atom is far from rotationally symmetric. Further nuclear quadrupole resonance (NQR) experiment on the phospha-alkynes is very desirable, and it is hoped that the quadrupole data predicted in this work might assist in spectroscopic analysis.

Acknowledgements

The author wishes to thank Prof. L. G. Vanquickenborne for constant encouragement and advice and is indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid).

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