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The Electronic Structures of HCP and FCP: A Comparison of the Results of SCF Calculations with Several Different Basis Sets, and the Inclusion of Electron Correlation

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Ab initio calculations using a variety of basis sets and including electron correlation via the MP3 method are reported for HCP and FCP and their positive ions. Comparisons are made with the available experimental data.

Key words: HCP – FCP – Basis sets – Correlation.

1. Introduction

During the last few years, several phosphaalkynes $RC\equiv P$ have been produced experimentally, starting with phosphaethyne [1], which was prepared in 1961 by Gier. These compounds are the phosphorus analogues of the cyanides $RC\equiv N$, but are much less stable than the cyanides, on account of the well-known reluctance of second-row elements to form multiple bonds [2]. However, the use of photoelectron spectroscopy and microwave spectroscopy to characterise these species has opened up a whole new field of study of the reactions of compounds containing the $-C\equiv P$ grouping, and in the most recent work $N\equiv C-C\equiv P$, $HC\equiv C-C\equiv P$, $CH_2=CHC\equiv P$, $C_6H_5C\equiv P$ and $F-C\equiv P$ have all been observed [3].

Since the experimental observation of $HC\equiv P$, a variety of theoretical calculations on this molecule have appeared, the first of these by Robert et al [4], followed by a more accurate calculation by Thomson [5], who used a Slater orbital basis

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sets of essentially $DZ+P$, and $BA+P$ quality. In this work, a variety of one electron properties were computed, and subsequently Botschwina et al [6] computed the force constants and vibration frequencies. Pople and co-workers [7] have also reported calculations on this molecule.

On the other hand, there has been only one calculation on FCP, using the 4-31G basis set [8], and these authors calculated the bond lengths to be $R(\mathrm{FC}) = 1.2995$ Å, $R(\mathrm{C{\equiv}P}) = 1.5365$ Å.

With the advent of gradient techniques for calculation of the equilibrium geometry [9], and the development of techniques for inclusion of electron correlation [10], it seemed worthwile to compare the results of calculations on these two molecules and their positive ions using a variety of basis sets, with the relatively limited experimental information on these species. We report the results of such a study in the present paper.

2. Method of Calculation

The calculations were carried out using the VAX 11/780 version of Gaussian 80 [11], modified for Release 2.0 (and subsequent releases) of the VAX VMS operating system by one of us (C.T.). The bond lengths were optimized for the linear geometry using the gradient method as implemented in Gaussian 80. The wave function for the closed shell ground state was obtained by the Restricted Hartree–Fock method and for the open shell cation by the Unrestricted Hartree–Fock method. Some calculations were also carried out using the local potential method available in Gaussian 80, which utilises the Coreless Hartree–Fock potential of Goddard et al. [12].

The calculations were carried out using a variety of basis sets ranging in quality from the minimal STO-3G basis set [13] through the split valence 6-21G basis [14], and finally including polarization functions with the 6-31G* or 6-31G** bases.

The local potential basis set LP-31G can also be augmented with polarization functions and the results for all these calculations are given in Table 1.

Calculations including correlation via Møller–Plesset perturbation theory to third order [15] and geometry optimization were restricted to the LP-31G [16] and 6-21G basis sets, but single point MP3 calculations were carried out at the optimal SCF geometries for the LP-31G**, and 6-31G** basis sets. In Table 1, we present the computed energies, bond lengths, atomization energy, dipole moment and rotational constants and the relevant experimental quantities. The dipole moments are only calculated for the SCF wave functions.

3. Results and Discussion

The calculated values for the bond lengths in the neutral molecules are in reasonable agreement with experiment, although the C≡P bond length is far

Table 1. Calculated and experimental properties of HCP and FCP

Molecule	Basis	Total Energy[a]	Atomisation Energy[b]	*Rl*[c]	*R*(C—P)	Dipole moment[d]	Rotational constant[e]
HCP	STO-3G	−374.80066	1643	1.069	1.472	0.040	21 761
	6-21G	−379.02557	1271	1.059	1.549	0.905	19 873
	6-21G[f]	−379.19703	804	1.072	1.580	0.947	19 127
	LP-31G	−12.49407	522	1.050	1.518	—	20 650
	LP-31G[f]	−12.59915	780	1.050	1.553	—	19 810
	LP-31G**	−12.54284	790	1.050[g]	1.553[g]	—	—
	LP-31G**[f]	−12.69117	963	1.050[g]	1.553[g]	—	—
	6-31G**	−379.10568	621	1.063	1.515	0.619	20 684
	6-31G**[f]	−379.34210	859	1.063[g]	1.515[g]	—	—
	Experiment [19]	—	1090 [7]	1.067	1.542	0.390	19 974
FCP	STO-3G	−472.26671	1501	1.315	1.478	0.402	5402
	6-21G	−477.70229	1120	1.299	1.556	0.190	5149
	6-21G[f]	−477.98892	740	1.323	1.590	0.316	4945
	LP-31G	−35.90185	375	1.272	1.522	—	5377
	LP-31G[f]	−36.05617	625	1.280	1.561	—	5194
	LP-31G**	−35.98592	582	1.280[g]	1.561[g]	—	—
	LP-31G**[f]	−36.21436	889	1.280[g]	1.561[g]	—	—
	6-31G*	−477.93809	530	1.265	1.517	0.034	5519
	6-31G*[f]	−478.35908	910	1.265[g]	1.517[g]	—	—
	Experiment [20]	—	—	1.285	1.541	0.279	5258

[a] Atomic Units (1 a.u. = 27.21 ev).

[b] kJ mol^{-1}.

[c] R(C—H) for HCP, R(C—F) for FCP: Values in Å.

[d] Debye.

[e] MHz.

[f] Including electron correlation via third order Moller-Plesset Perturbation Theory.

[g] Single point calculation at this geometry.

too short for the STO-3G basis set, and somewhat short for the LP-31G and 6-31G** basis set. The latter result is somewhat surprising. The inclusion of correlation with the split valence or LP-31G basis set makes little difference to the bond lengths. The computed values are in reasonable agreement with earlier calculations not employing gradient methods [5–7].

The dipole moment on the other hand is very sensitive to the basis set, as noted previously [5], and only the previous $BA+P$ calculation has succeeded in reproducing the small value observed for HCP. On the other hand the computed value for FCP is closer to the experimental value with the 6-21G basis set. The low value obtained in the 6-31G* calculation is probably a consequence of the short bond lengths obtained with this basis set.

The photoelectron spectra of both HCP [17] and FCP [8] have been reported, and the experimental values for the first few ionisation energies are given in Table 2 together with the calculated values obtained from the orbital energies using Koopmans' theorem. We have also calculated the adiabatic ionization

Table 2. Calculated and experimental photoelectron spectrum of HCP and FCP

Molecule	Basis	Orbital energies[a]			Total energy of cation[a]	First ionisation potential[b]
		2Π	7σ	6σ		
HCP	STO-3G	0.2838	0.3731	0.6276	−374.50172	0.2989
	6-21G	0.3843	0.4851	0.7362	−378.68555	0.3400
	6-21G[c]	0.3814	0.4913	0.7344	−378.73139	0.4656
	LP-31G	0.3989	0.4892	0.7390	12.09389	0.4002
	LP-31G[c]	0.3788	0.4860	0.7426	12.22110	0.3781
	LP-31G**[d]	0.3738	0.4921	0.7346	12.16579	0.3771
	LP-31G**[cd]	—	—	—	12.23802	0.4532
	6-31G**	0.3852	0.4896	0.7290	−378.76366	0.3420
	Experiment [17]	0.3966	0.4726	—	—	0.3966
		3Π	9σ			
FCP	STO-3G	0.2680	0.3926	0.5671	−471.94093	0.3261
	6-21G	0.3882	0.5179	0.7398	−477.26580	0.4365
	6-21G[c]	0.3852	0.5221	0.7320	−477.49585	0.4931
	LP-31G	0.3956	0.5250	0.7573	−35.54435	0.3575
	LP-31G[c]	0.3900	0.5292	0.7569	−35.65826	0.3971
	LP-31G**[d]	0.3765	0.5260	0.7566	−35.65179	0.3341
	LP-31G**[cd]	—	—	—	−35.83418	0.3802
	6-31G*	0.3852	0.5159	0.7619	−477.50031	0.4378
	Experiment [8]	0.3885	0.4980	0.6554	—	0.3883

[a] Atomic Units (1 a.u. = 27.21 eV).

[b] Difference in calculated neutral molecule and cation energies in atomic units.

[c] Including electron correlation via third order Moller-Plesset Perturbation Theory.

[d] Single point calculation at LP-31G plus correlation geometry.

potential as the difference between the energies of the neutral molecule and the cation, both geometries being optimzed.

The ground state valence confirmations of HCP and FCP are depicted below

$$(5\sigma)^2(6\sigma)^2(7\sigma)^2(2\Pi)^4 \ \text{HCP}$$

$$(6\sigma)^2(7\sigma)^2(8\sigma)^2(2\Pi)^4(9\sigma)^2(3\Pi)^4 \ \text{FCP}$$

and the first photoelectron bond is assigned to ionization from the 3Π orbital (FCP) or the 2Π orbital (HCP). The composition of the wave function shows this orbital to be mainly localised in the C≡P group, a result in accordance with the vibrational structure in the P.E.S., assigned to the C≡P stretching mode [17]. The experimental adiabatic and vertical ionization potentials coincide for this band, but our calculated values differ substantially (Table 2) since the bond lengths in the cation are substantially different: for the 6–31G** basis set R(H—C) = 1.072 Å, and R(C≡P) = 1.586 Å, leading to a significant difference betweeen the two ionization potentials. The second band corresponds to ionization from the 7σ orbital which is largely localised on P, and the third band arises from ionization from an σ-orbital made up of roughly equal contributions from C and P.

In the case of FCP, the composition of the 3Π and 9σ orbitals is similar to that found for the corresponding orbitals in HCP, but the origin of the third band is different, since in FCP it arises from a Π orbital, which is essentially a lone pair on fluorine. These calculations are therefore in reasonable agreement with experiment and the previous work using the 4-31G basis [8].

The adiabatic ionization potentials, however, differ from the first vertical ionization potential by only 0.02 a.u. in the case of HCP, but by 0.12 a.u. for FCP. The emission spectra of HCP^+ has recently been observed [18], and the increase in the length of the C≡P bond found in the calculations is also inferred from the experiments.

A Mulliken population analysis gives the charge distribution on the atoms, and leads to a charge of ~0.1e for the charge on the phosphorus atom in both molecules (for the 6-31G* basis set). However, in HCP the carbon is negatively charged (−0.37e) whereas in FCP it is positively charged (0.14e). The fluorine has a large negative charge of −0.24. This charge distribution is less exaggerated than in the 4-31G calculations [8].

In conclusion, we have shown that the results of calculations with several different basis sets are in reasonable agreement with one another and with experiment for these molecules, and the inclusion of electron correlation does not make very much difference to the results. However, the minimal basis set STO-3G seems to lead to unacceptably large errors in these cases.

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