Electronic Structure of Phospha-alkenes

By COLIN THOMSON*
(*Department of Chemistry, University of St. Andrews, St. Andrews* KY16 9ST)

Summary *Ab-initio* STO-3G and STO 4-31G calculations of the equilibrium geometry of the phospha-alkenes $CH_2{=}PH$, $CF_2{=}PH$, and $CH_2{=}PCl$ have been carried out and the results compared with recent experimental work on these molecules.

ALTHOUGH elements of the 2nd row of the Periodic Table are usually reluctant to form stable compounds involving a $p\pi$–$p\pi$ multiple bond, the recent synthesis of the phospha-alkenes $CH_2{=}PH$, $CF_2{=}PH$, and $CH_2{=}PCl$ shows that this type of bond is stable under certain conditions.[1]

Prior to the work of Hopkinson *et al.*,[1] the only characterised compound containing an isolated multiple bond of this type was $HC{\equiv}P$,[2] and we have studied this molecule theoretically in an earlier paper.[3] The present note describes the results of *ab-initio* calculations on the geometry and dipole moment of these interesting molecules.

The calculations were carried out using the Gaussian 70 programmes with both STO-3G and STO 4-31G basis sets.[4] Since the QCPE version of the programme does not include *d*-orbitals, these were not added to the basis set. Various studies have shown their inclusion to be necessary to describe the charge distribution rather accurately, but they do not make much difference to geometrical predictions, and for this reason we expect the qualitative conclusions of this study to be valid.

Table 1.

Computed geometries, energies, and dipole moments of phospha-alkenes with STO-3G and STO 4-31G basis sets

Molecule	Basis	R(CP)/Å	R(PX)/Å	∠CPX	D/Debye	E/a.u.[b]
$H_2C{=}PH$	3G	1·62	1·39	97·0	0·357	−375·9883
	43-1G	1·67	1·47	98·0	1·08	−379·8149
$H_2C{=}PCl$[a]	3G	1·65	2·11	99·2	3·254	−830·0383
$F_2C{=}PH$	3G	1·67	1·39	92·6	2·60	−570·91108
	43-1G	1·74	1·67	94·4	1·024	−570·25194

[a] Calculations with the 4-31G basis set gave convergence problems and were not pursued in view of the expense.
[b] 1 a.u. of energy = $4{\cdot}3598 \times 10^{-18}$ J.

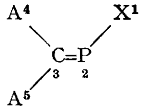
Table 1 gives the computed total energies, bond lengths, and bond angles for these molecules. We have assumed r(C–H) = 1·09 Å, and optimized the remaining parameters. Hopkinson *et al.*[1] obtained several of their structural parameters from work on related species, and some of our values are significantly different.

The CPH bond angle is different in $CF_2{=}PH$ and $CH_2{=}PH$, the true value probably being *ca.* 93° for $CF_2{=}PH$, and *ca.* 97° for $CH_2{=}PH$, both less than the value of 100° calculated by Hopkinson. This difference is probably real.

The P–Cl bond length of 2·11 Å is close to the value observed in PCl_3, and the P–C bond length is also close to that expected.

Table 2

Computed relative charge distributions in



Molecule	Basis	q_1	q_2	q_3	q_4	q_5
$H_2C{=}PH$	3G	−0·13	+0·38	−0·35	+0·05	+0·05
	4-31G	−0·06	+0·31	−0·67	+0·21	+0·22
$H_2C{=}PCl$	3G	−0·38	+0·55	−0·32	+0·09	+0·07
$F_2C{=}PH$	3G	−0·12	+0·31	+0·06	−0·12	−0·12
	4-31G	0	+0·31	+0·42	−0·36	−0·36

Perhaps rather more interesting is the computed energy level order. The highest occupied MO (HOMO) is a π orbital in $CH_2{=}PH$, $CH_2{=}PCl$, and $CF_2{=}PH$, whereas in methylenamine, $CH_2{=}NH$,[5] the HOMO is a σ-orbital. These results should be of interest when the photoelectron spectrum is measured.

In Table 2 we also present the computed relative atomic charge distributions for both basis sets (where applicable) and the optimized geometries. The large differences between the basis sets are expected, but it is clear that there is a substantial positive charge on phosphorus, and this is unlike the situation in $CH_2{=}NH$. In addition the H atom attached to P has an appreciable negative charge. The computed dipole moments are smaller than for $CH_2{=}NH$, probably *ca.* 1 D for $CH_2{=}PH$ and $CF_2{=}PH$, and *ca.* 4D for $CH_2{=}PCl$.

Finally, we have computed the barrier both to in-plane inversion and out-of-plane rotation of the C–P–X fragment. In the case of $CH_2{=}PH$, the in-plane barrier is *ca.* 0·19 hartree (570·5 kJ mol^{-1}) for the STO-3G basis and 0·13 hartree (341 kJ mol^{-1}) for the 4-31G basis, both values being much larger than the value of *ca.* 107 kJ mol^{-1} for $CH_2{=}NH$. The perpendicular barrier was rather similar, 0·18 hartree (472 kJ mol^{-1}) for the STO-3G basis, and 0·12 hartree (315 kJ mol^{-1}) for the 4-31G basis. In the case of $CF_2{=}PH$ the barriers for the STO-3G basis calculations were 0·12 hartree (315 kJ mol^{-1}) for the in-plane inversion and 0·19 hartree for the out-of-plane motion. The in-plane barrier for $CH_2{=}PCl$ was substantially bigger at 0·22 hartree (578 kJ mol^{-1}).

It will be interesting to see if further experimental work on these interesting molecules confirms these predictions.

(*Received*, 21*st February* 1977; *Com.* 150.)

---

[1] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J.C.S. Chem. Comm.*, 1976, 513.
[2] T. E. Gier, *J. Amer. Chem. Soc.*, 1961, **83**, 1769; J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170.
[3] C. Thomson, *Theor. Chim. Acta*, 1974, **35**, 237.
[4] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, 'Gaussian 70,' QCPE 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.
[5] R. Macauley, L. A. Burnelle, and C. Sandorfy, *Theor. Chim. Acta*, 1973, **29**, 1.