Theoret. Chim. Acta (Berl.) 35, 237—242 (1974)

# Near Hartree Fock Wave Function and Computed Molecular Properties of Methinophosphide, HCP

Colin Thomson

Department of Chemistry, University of St. Andrews, Scotland

Received October 17, 1973/June 18, 1974

A near Hartree Fock wave function for HCP has been calculated within the RHF approximation, using a large STO basis set and this is compared with geometry optimisation calculations using a polarised double zeta basis. The population analysis indicates a C≡P bond, and various one electron properties have been computed and compared with the limited experimental data.

*Key words:* Methinophosphide – HCP

## 1. Introduction

Methinophosphide, the phosphorus analogue of hydrocyanic acid, was first prepared in 1961 by Gier [1], and is the only isolated compound in which phosphorus is bonded to only one neighbouring atom, presumably through a carbon-phosphorus triple bond.

Although it is highly reactive at room temperature, the infrared [2] and microwave [3, 4] spectra were studied soon after it was prepared, showing that the molecule was linear with bond lengths: $R(\mathrm{HC}) = 1.067$ Å (2.0163 bohr) and $R(\mathrm{CP}) = 1.542$ Å (2.914 bohr). The values of its dipole moment, $(0.390 \pm 0.005\ \mathrm{D})$ is much smaller than the value of 3.00 D found for HCN. More recently, the u.v. and i.r. [5] absorption spectra of both HCP and DCP were studied, and the force constants and thermodynamic properties calculated from this data [6][1].

Recent work by Flygare and co-workers using the molecular Zeeman effect has resulted in much more detailed molecular information for a wide variety of molecules [7], and for HCP and DCP, experimental values of the molecular $g$-values, magnetic susceptibility anisotropies and the molecular quadrupole moments have been obtained [8]. Finally, a very recent report of the photoelectron spectrum has appeared [9].

There has only been one previous *ab-initio* calculation on HCP, in which various moderately sized gaussian basis sets were used in LCAO-MO-SCF calculations [10]. However, in the light of the recent experimental work [7–9], it seemed worthwhile to investigate HCP using a large STO basis set, particularly since the earlier calculation gave a dipole moment seriously in error. We have

---

[1] Since this work was completed, more accurate values of $R(\mathrm{HC}) = 2.0207$ bohr, $R(\mathrm{CP}) = 2.9099$ bohr have been obtained [19]. These are sufficiently close to the above values for the conclusions in this paper to remain valid.

therefore computed the equilibrium geometry and a variety of one-electron properties for the ground state of HCP and discuss the bonding in this interesting molecule.

## 2. Basis Set and Method of Calculation

Double zeta + polarization function (DZ + P) and Best Atom + polarization function (BA + P) basis sets were used, with exponents taken from our earlier calculations [11] or from the Clementi or McLean/Yoshimine tables [12]. The polarization function exponents were not optimized and the same set was used for both DZ and BA bases, these being taken from the work on HCN, PN [12] or BCC [11].

The $2p\sigma$, $2p\pi$, $3d\sigma$, and $3d\pi$ functions on H were taken from calculations on HCN [12]. In the light of previous work [13–15], it is not expected that polarization function optimization will affect the main conclusions reached in this paper.

Finally, a variety of one electron properties were computed for the BA + P wave function obtained for the experimental geometry. Calculations were carried out with the ALCHEMY programme [16] on an IBM 370/195, in the single configuration RHF approximation, for the ground state of the molecule.

## 3. Results of Energy and Wave Function Calculations

The ground state configuration of HCP is

$$(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2\,(6\sigma)^2\,(7\sigma)^2\,(2\pi)^4\quad {}^1\Sigma^+ .$$

The detailed results of the geometry optimization calculations are not given here but are available on request from the author.

The computed minimum energy configuration for the DZ + P basis was for $R(\mathrm{CH}) = 2.005$ bohr, $R(\mathrm{CP}) = 2.85$ bohr, with a total energy of $-379.13039$ hartree, and Virial Ratio $= -2.00007$. The computed bond lengths differ from experiment by only 0.011 and 0.06 bohr respectively, and thus reliable bond lengths can be computed with this smaller basis set, which should be useful for larger molecules. The BA + P calculations were carried out only for the experimental geometry, leading to a total energy of $-379.15740$ hartree, a lowering of 0.027 hartree over the lowest computed DZ + P energy. The difference between the calculated total energy and the Hartree-Fock energy of the molecule is estimated to be ~0.005 hartree by comparison with several previous calculations using BA + P basis sets [12]. The computed energy obtained in this work is 0.48 hartree (~13 eV) lower than the best energy in Ref. [10] of $-378.68$ hartree, the difference in energy being very large by chemical standards. However most of this difference is due to a poor description of the inner shells, and the valence region is not necessarily badly described in the earlier work. A comparison of the present wave function with the earlier work is given in Section 4. Table 1 gives the valence orbital energies for the experimental

Table 1. Valence orbital energies of HCP for different basis sets[a]

| Orbital | BA + P | DZ + P | (951/52/3) [10] |
|---|---|---|---|
| $5\sigma$ | $-0.9668$ | $-0.9592$ | $-0.9482$ |
| $6\sigma$ | $-0.7305$ | $-0.7277$ | $-0.7056$ |
| $7\sigma$ | $-0.4952$ | $-0.4828$ | $-0.4594$ |
| $2\pi$ | $-0.3835$ | $-0.3710$ | $-0.3491$ |
| $3\pi$[b] | $+0.0818$ | $+0.1084$ | — |

[a] Computed at the experimental geometry.
[b] Virtual orbital.

geometry for the DZ + P, BA + P bases and also for the Gaussian (951/52/3) basis of Ref. [10]. The orbital energies of the valence orbitals are lowered only slightly with respect to the smaller basis set calculations. The first ionization potential measured by PES is 10.79 eV, in good agreement with the present calculations. However, the calculations in Ref. [10] give a value more than 1 eV too low. The second I.P. is also in reasonable agreement with experiment. The calculated dissociation energy [15] is 0.254 hartree (6.92 eV) for the DZ + P calculation and 0.250 hartree (6.81 eV) for the BA + P. The agreement between the two calculations is encouraging, despite the significant difference in the total energy. It is likely that the computed value is within ~0.1 eV of the Hartree-Fock value which, however, does not include any correlation contributions to the true dissociation energy. HCP is isoelectronic with PN, SiO, and AlF, and the Molecular Extra Correlation energy for this series of molecules has been estimated as 4.6, 3.0, and 1.4 eV respectively. However, it is not a simple matter to estimate this quantity for HCP, but it is likely to be closest to the value for PN. If we assume it to be ~5 eV (~0.2 hartree), we can estimate the atomization energy of HCP to be ~0.45 hartree or ~11–12 eV. Note that the MECE is about the same magnitude as the Hartree-Fock contribution. It is, however, to be noted that for 2nd row atoms, the relativistic contribution to the total energy is large: for P it is 0.79 hartree [17]. However, it is likely that it is comparable in the atom and in the molecule and thus cancels in the calculations of the dissociation energy.

## 4. Population Analysis

The gross atomic population for the two basis sets and the work of Ref. [10] are compared in Table 2. There are large differences between the small GTO basis and the larger STO basis which once again emphasis the unreliability of population analyses with basis sets of less than DZ + P quality [11, 13, 14]. The differences between the DZ + P and BA + P results are small, the largest basis predicting very nearly the same charge on phosphorus, but a small transfer of electron density from H to C. Rather surprisingly, this makes a considerable difference to the dipole moment whose computed value of 0.353 D for the BA + P basis is in good agreement with the experimental value of 0.39 D. It is apparent from an analysis of the contributions to $\mu$ that this decrease is

Table 2. Gross atomic populations $G_i$ in HCP and dipole moment $\mu$ at experimental geometry for different basis sets

| | BA + P | DZ + P | (951/52/3) [10] |
|---|---|---|---|
| $G_H$ | 0.925 | 0.805 | 0.774 |
| $G_C$ | 6.313 | 6.442 | 6.307 |
| $G_P$ | 14.761 | 14.753 | 14.919 |
| $\mu$ (Debye) | − 0.353 | − 0.998 | − 0.11 |

attributable to a different composition of the $7\sigma$ orbital which has a significantly lower population on H in the BA + P case.

Examination of the contributions to the various orbitals from the basis functions gives the following description of the valence orbitals. The $3\sigma$ orbital is predominantly a localised $(2s)^2$ electron pair on P, and the $4\sigma$ orbital corresponds to a $(2p_z)^2$ lone pair on P. The $5\sigma$ orbital corresponds to the C–P $\sigma$-bond although it is, of course, not completely localised. $6\sigma$ is a combination of $1s$(H), $2p_z$(C), and $3s$(P), and can be roughly ascribed to the H–C bond. The $7\sigma$ orbital, however, corresponds to essentially a lone pair $(3p\sigma)^2$ on phosphorus and the bonding is completed by the delocalised $2\pi$ orbital, mainly concentrated between C and P. Hence the structure is very like that of H–C≡N; i.e. H–C≡P with triply bonded phosphorus. Comparison with the small basis set GTO calculations, shows that in the latter, the charge on H and P is the opposite way round.

## 5. One Electron Properties

Recent experimental work has yielded values for some one-electron properties [4–9], and Table 3 gives the computed values for the experimental geometry and the BA + P wave function.

The coordinate origin is the centre of mass of the molecule. We have used the symbols and definitions given by Schaefer [17], following earlier work by McLean and Yoshimine [18].

The BA + P dipole moment is close to the experimental value as expected [15], whereas the smaller basis sets give large errors in $\mu$. The expectation values of $\langle 1/r \rangle$ are proportional to the diamagnetic shielding of each nucleus, and these are relatively insensitive to the basis set. The values obtained are predictions, since no experimental values are available.

The molecular quadrupole moment $\theta$ is in good agreement with the experimental value measured recently by Flygare and co-workers [8]. $\xi_s$ and $\xi_r$ are computed lower and upper reference values for the magnetic susceptibility [18]. The values of $\xi_\perp$ and $\xi_\parallel$ are obtained using the experimental value of $\xi_\perp - \xi_\parallel$. The computed values seem reasonable for these quantities.

The molecular $g$-factors are also related to $\xi_\perp - \xi_\parallel$ and were measured by Flygare *et al.* [8]. The computed value of $g$, using the observed $\xi_\perp - \xi_\parallel$, is $-0.039$ which is in good agreement with the observed value of $-0.041$. The

Table 3. Computed one electron properties of HCP using BA + P basis and experimental geometry

| Property | Calculated value | Experiment |
|---|---|---|
| Diamagnetic shielding | | |
| $\sigma_H^d$ (ppm) | 125 | — |
| $\sigma_C^d$ (ppm) | 36 | — |
| $\sigma_P^d$ (ppm) | 1001 | — |
| Molecular quadrupole moment | | |
| $\theta(10^{-26}\ \mathrm{esu \cdot cm^2})$ | 4.81 | 4.4 |
| Magnetic susceptibility (erg/gauss$^2 \cdot$ mole) | | |
| $\xi_s$ | $-7.465 \times 10^{-5}$ | — |
| $\xi_r$ | $-1.192 \times 10^{-5}$ | — |
| $\xi_{\parallel}$ | $-3.57 \times 10^{-5}$ | — |
| $\xi_{\perp}$ | $-2.73 \times 10^{-5}$ [a] | — |
| Molecular $g$ value | $-0.039$ | $-0.041$ |
| Field gradients | | |
| $q$(H) | 1.021 | — |
| $q$(C) | 0.467 | — |
| $q$(P) | $-0.537$ | — |
| Deuteron quadrupole coupling constant (kHz) | | |
| $qQ$ | 656 | $233 \pm 40$ |

[a] Using observed value of $\xi_{\perp} - \xi_{\parallel} = 8.4 \times 10^{-6}$ erg/gauss$^2$ mole.

electric field gradients are very sensitive to the basis set, as noted previously and our values may not be very reliable. The computed value of the deuteron quadrupole coupling constant is 656 kHz, which is about twice the value observed in DCP of $233 \pm 40$ kHz [8] which again indicates the difficulty of calculating this sensitive property.

In summary, these calculations give good agreement with experiment for the dipole moment, ionization potential, molecular quadrupole moment and molecular $g$-value for this interesting molecule. It is hoped that the calculations will stimulate further experimental work on this and similar intermediates.

*Acknowledgements.* We are indebted to Dr. A. D. McLean for the copy of the ALCHEMY programme, and to the Science Research Council for a grant of computer time on the Rutherford Laboratory IBM 370/195.

## References

1. Gier, T. E.: J. Am. Chem. Soc. **83**, 1769 (1961)
2. Dodd, R. E., Little, R.: Spectrochim. Acta **16**, 1083 (1960)
3. Sheridan, J., Tyler, J. K., Aynsley, E. F., Dodd, R. E., Little, R.: Nature **185**, 96 (1960)
4. Tyler, J. K.: J. Chem. Phys. **40**, 1170 (1964)
5. Johns, J. W. C., Shurvell, H. F., Tyler, J. K.: Can. J. Phys. **47**, 893 (1969)
6. Shurvell, H. F.: J. Phys. Chem. **74**, 4257 (1970)

7. Flygare, W. H., Benson, R. C.: Mol. Phys. **20**, 225 (1971)
8. Hartford, S. L., Allen, W. C., Norris, C. L., Pearson, E. F., Flygare, W. H.: Chem. Phys. Letters **18**, 153 (1973)
9. Frost, D. C., Lee, S. T., McDowell, C. A.: Chem. Phys. Letters **23**, 472 (1973)
10. Robert, J.-B., Marsmann, H., Absar, I., Van Wazer, J. R.: J. Am. Chem. Soc. **93**, 3320 (1971)
11. Thomson, C.: J. Chem. Phys. **58**, 216 (1973)
12. McLean, A. D., Yoshimine, M.: Suppl. IBM J. Res. Develop. (1967)
13. Thomson, C., Wishart, B. J.: Theoret. Chim. Acta (Berl.) **31**, 347 (1973)
14. Thomson, C.: J. Chem. Phys. **58**, 841 (1973)
15. Yoshimine, M., McLean, A. D.: Intern. J. Quantum Chem. **1** S, 313 (1967)
16. McLean, A. D.: IBM Tech. Rept. RA **18** (1971)
17. Schaefer, H. F., III: Electronic structure of atoms and molecules. New York: Addison-Wesley 1972
18. McLean, A. D., Yoshimine, M.: J. Chem. Phys. **45**, 3676 (1966)
19. Strey, G., Mills, I. M.: Mol. Phys. **26**, 129 (1973)

Dr. C. Thomson
Department of Chemistry
University of St. Andrews
St. Andrews, Fife, KY 16 9 ST, Scotland