J. Phys. Chem. A **1997,** *101,* 8319−8326

Structure and Vibrations of the C_2P and CNP Radicals and Their Cations Using Density Functional and Coupled Cluster Theories

Jamal El-Yazal,[†] Jan M. L. Martin,[†,‡,§] and Jean-Pierre François*,[†]

Department SBG, Institute for Materials Sciences (IMO), Limburgs Universitair Centrum, Universitaire Campus, B-3590 Diepenbeek, Belgium, and Department of Chemistry, Institute for Materials Sciences, University of Antwerp (UIA), Universiteitplein 1, B-2610 Wilrijk, Belgium

Received: February 19, 1997; In Final Form: July 23, 1997[⊗]

Energetically low-lying states of the C_2P and CNP molecular systems and their cations are studied. Geometries, harmonic frequencies, and dipole moments have been obtained at the density functional (using the Becke three-parameter Lee−Yang−Parr B3LYP functional) and coupled cluster theoretical levels in conjunction with correlation consistent basis sets. Single-point coupled cluster calculations for B3LYP geometries have been used to compute energy differences for the different states. For the C_2P radical, the global minimum is linear CCP($^2\Pi$) followed by cyclic C_2P($^2B_2$) at 5.5 kcal/mol, linear CCP($^4\Sigma^-$) (21.2 kcal/mol), cyclic C_2P($^4A_2$) (38.4 kcal/mol), and linear CPC($^2\Pi_g$) (88.0 kcal/mol). For the C_2P^+ cation the following sequence of states has been established: linear CCP^+($^1\Sigma^+$), cyclic C_2P($^1A_1$) (8.7 kcal/mol), cyclic C_2P^+($^3B_2$) (24.1 kcal/mol), linear CCP^+($^3\Pi$) (29.1 kcal/mol), and linear CPC^+($^1\Sigma^+{}_g$) (104.3 kcal/mol). For neutral PCN and PNC, the following sequence of states has been computed: linear PCN($^3\Sigma^-$); linear PNC($^3\Sigma^-$) (14.2 kcal/mol), linear PCN($^1\Delta$) (25.2 kcal/mol), cyclic CPN($^3A''$) (36.2 kcal/mol), cyclic CPN($^1A''$) (37.7 kcal/mol), and linear PNC($^1\Delta$) (38.8 kcal/mol). The ground state of the single ionized species is linear PNC^+($^2\Pi$) followed by linear PCN^+($^2\Pi$); the energy difference is very small: 0.8−1.4 kcal/mol. Cyclic CPN^+($^2A'$) lies much higher in energy (13.9 kcal/mol) and was found to be a local energy minimum at the doublet surface. Predictions for IR spectra of the species are given. The computed total atomization energies are 261.7 ± 1 kcal/mol for CCP($^2\Pi$) and 276.0 ± 1 kcal/mol for PCN($^3\Sigma^-$). Adiabatic ionization potentials (eV) are as follows: linear CCP($^2\Pi$) 9.05, cyclic C_2P($^2B_2$) 9.18, linear PCN($^3\Sigma^-$) 10.39, and linear PNC($^3\Sigma^-$) 9.73.

1. Introduction

The detection of phosphine, PH_3, in Jupiter's atmosphere by Ridgeway et al.[1] in 1976 was followed by the observation of two other phosphorus-bearing molecules in space. Turner and Bally[2] and Ziurys[3] detected in 1987 the PN molecule in the interstellar space; in 1990 Guelin et al.[4] reported the observation of PC in the envelope of a carbon star. The detection of these phosphorus-containing molecules stimulated the search for other phosphorus species in space as well as the study of potential production schemes for these species. Several experimental[5−7] and theoretical studies[8−14] have been published on ion−molecule processes which could lead to the interstellar production of phosphorus compounds (see also ref 15). An important result from Millar's study[16] is that phosphorus−carbon species such as C_2P and HC_2P might be detectable in warm dense clouds provided they are unreactive with oxygen atoms. Another phosphorus−carbon compound is the PCN molecule, which can be produced by the reaction of P^+, PH^+, and $PH_2{}^+$ with HCN.[17] An ab initio study of the PCN and PNC isomers and their cations has been published by Largo and Barrientos (LB).[17] Both isomers are found to be linear with $^3\Sigma^-$ ground states. PCN is the most stable isomer; PNC lies ca. 15 kcal/mol higher at the projected MP3 level and the isomerization barrier is estimated to be ca. 23 kcal/mol. Geometries and harmonic vibrational frequencies for the linear PCN and PNC isomers were computed at the UHF/6-31G* level. The singlet surface is characterized by two linear PCN and PNC structures ($^1\Delta$) together with a cyclic one ($^1A'$).

The PCN^+ and PNC^+ cations are found to be nearly isoenergetic when projected MP techniques are employed, although at the nonprojected MP4 level of theory, PCN^+ lies 11.7 kcal/mol below PNC^+. Geometries and harmonic frequencies for the linear PCN^+($^2\Pi$) and PNC^+($^2\Pi$) isomers were obtained at the UHF/6-31G* level.

The C_2P radical and its cation have been studied at the MP2 and MP4 levels of theory by Largo et al. (LBLU).[18] Linear CCP($^2\Pi$) was found to be the ground state but with cyclic C_2P($^2B_2$) lying just ca. 6 kcal/mol above. In the case of the cation, linear CCP^+($^1\Sigma^+$) is predicted to be the ground state whereas the energy difference with the cyclic C_{2v} symmetric state ($^1A_1$) is now higher than in the case of the neutral system, ca. 15 kcal/mol. Geometries and harmonic frequencies for the different C_2P and C_2P^+ states were obtained at the MP2/6-31G* theoretical level. Concerning the $C_2P^{(+)}$ and $CNP^{(+)}$ studies of Largo and collaborators (LBLU), two points should be raised: (1) the high degree of spin contamination for some states, and (2) unphysical MP2/6-31G* harmonic frequencies of C_2P (4375 cm^{-1} for the $^4A_2$ state) suggesting a breakdown of perturbation theory.

In one of our studies, it has been shown[19] that at the B3LYP/[4s3p2d1f] level, bond distances within a few milliangstroms of the experimental value could be obtained. It has been found that B3LYP/[3s2p1d] and B3LYP/[4s3p2d1f] harmonic frequencies are frequently in surprising good agreement with those computed at the CCSD(T) level and with the experimental values.[19−23] Hence, the very expensive CCSD(T) calculations of the harmonic frequencies could be avoided. However, the CCSD(T) method, in conjunction with the appropriate basis set,

---

* Corresponding author.

[†] Limburgs Universitair Centrum.

[‡] University of Antwerp.

[§] Present address: Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Kimmelman Building, Room 262, IL-76100, Israel.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S1089-5639(97)00614-2 CCC: $14.00

was used for calculating the relative energies of the different structures at the corresponding B3LYP geometries. In view of all these considerations, we found it worthwhile to reinvestigate the $C_2P^{(+)}$ and $CNP^{(+)}$ species.

2. Computational Methods

All DFT calculations were carried out using the GAUSSIAN 94 package[24] running on our two IBM RS/6000 Model 365 workstations. The B3LYP exchange-correlation functional[25-27] has been used throughout:

$$E_{xc} = E_x^{LDA} + c_0\,(E_x^{HF} - E_x^{LDA}) + c_x \Delta E_x^{B88} + E_x^{VWV} + c_c(E_x^{LYP} - E_x^{VWV}) \quad (1)$$

E_x^{LDA} is the standard local exchange functional, E_x^{HF} the exact Hartree−Fock exchange functional, ΔE_x^{B88} is Becke's gradient correction to the exchange functional,[25] E_x^{VWV} is the local correlation functional of Vosko, Wilk, and Nusair (VWN),[26] and E_x^{LYP} is the Lee−Yang−Parr correlation functional (LYP)[27] which also includes density gradient terms. The parameters c_0, c_x, and c_c have been optimized by Becke[25] by reference to experimental thermochemical data. The optimum values are $c_0 = 0.20$, $c_x = 0.72$, and $c_c = 0.81$.

CCSD(T) calculations were performed using the MOLPRO 96 package[28] running on our IBM RS/6000 workstations. The Dunning correlation-consistent basis set family[29,30] was employed in all our calculations.

1. The cc-pVDZ (correlation consistent polarized valence double zeta) basis set is a [3s2p1d] contraction of a (9s4p1d) primitive set for C and N, and a [4s3p1d] contraction of a (12s8p1d) primitive set for P;
2. The cc-pVTZ (correlation consistent polarized valence triple zeta) basis set is [4s3p2d1f] contraction of a (10s5p2d1f) primitive set for C and N, and a [5s4p2d1f] contraction of a (15s9p2d1f) primitive set for P;
3. The cc-pVQZ (correlation consistent polarized valence quadruple zeta) basis set is [5s4p3d2f1g] contraction of a (12s6p3d2f1g) primitive set for C and N, and a [6s5p3d2f1g] contraction of a (16s11p3d2f1g) primitive set for P.

Additionally, some geometry optimizations and harmonic frequency calculations were carried out at the CASSCF level (involving 12−14 valence electrons in all 12 valence orbitals) with the cc-pVDZ basis set using the SIRIUS/ABACUS program package[31] running on the aforementioned RS/6000 workstations.

3. Results and Discussion

3.1. Neutral C_2P. The optimized geometrical parameters and dipole moments for linear $CCP(^2\Pi)$, cyclic $C_2P(^2B_2)$, linear $CCP(^4\Sigma^-)$, cyclic $C_2P(^4A_2)$, and linear $CPC(^2\Pi_g)$ at our selected theoretical levels are presented in Table 1. The relative energies for the C_2P states are shown in Table 2. Harmonic frequencies for the C_2P isomers are collected in Table 3.

Table 2 clearly shows that the linear $CCP(^2\Pi)$ isomer is the ground state at all selected levels of theory. At the B3LYP/cc-pVTZ level, the $CCP(^2\Pi)$ ground state is followed by the following states (in increasing order of energy): cyclic $C_2P(^2B_2)$, $\Delta = 7.5$ kcal/mol; linear $CCP(^4\Sigma^-)$, $\Delta = 23.6$ kcal/mol; cyclic $C_2P(^4A_2)$, $\Delta = 42.8$ kcal/mol; and linear $CPC(^2\Pi_g)$, $\Delta = 94.9$ kcal/mol. These results are confirmed by our single-point CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ calculations; the energy differences do not change greatly from B3LYP to CCSD(T). We note that the coupled cluster T_1 diagnostic,[32] giving a measure of the importance of nondynamical correlation effects, is well below the critical value of 0.08 for the CCSD(T) level of theory.[33] At the ROHF/cc-pVTZ level, the energy difference between the linear $CCP(^4\Sigma^-)$ and cyclic $C_2P(^2B_2)$ states is only 3.2 kcal/mol compared to 15.7 kcal/mol at the CCSD(T)/cc-pVTZ level.

TABLE 1: Geometrical Parameters (Å, deg) and Dipole Moments (debyes) for the C_2P Structures

geometrical parameters	B3LYP/cc-pVTZ	MP2/6-31G* (ref 18)
	$CCP(^2\Pi)$	
r_{CC}	1.3018	1.294
r_{CP}	1.6114	1.646
dipole moment	3.35	3.612[a]
	Cyclic $(^2B_2)$	
r_{CC}	1.3276	1.345
r_{CP}	1.7573	1.747
θ_{CPC}	44.39	45.3
dipole moment	2.34	2.535[a]
	$CCP(^4\Sigma^-)$	
r_{CC}	1.2453	1.236
r_{CP}	1.6750	1.673
dipole moment	0.13	0.502[a]
	Cyclic$(^4A_2)$	
r_{CC}	1.2854	1.304
r_{CP}	1.9195	1.907
θ_{CPC}	39.12	40.0
dipole moment	0.35	0.155[a]
	$CPC(^2\Pi_g)$	
r_{CP}	1.6892	1.670
dipole moment	0.0	0.0[a]

[a] Dipole moments were obtained with the MC-311G* basis set.[34]

It should be noted that even at the ROHF level, our results are in semiquantitative agreement with our CCSD(T) values; however, our ROHF values are qualitatively different from the UHF results of LBLU, due to the high spin contamination for the $^2\Pi$ wave function and neglible contamination for the $^2B_2$ state ($\langle S^2 \rangle$ expection values of LBLU are as follows: 0.916 ($^2\Pi$), 0.785 ($^2B_2$), 1.090 ($^2\Pi_g$), 4.224 ($^4\Sigma^-$), and 3.821 ($^4A_2$)). The problem appears to be remedied in the spin-projected PMP4 results of LBLU. The $^2B_2 - {}^2\Pi$ energy difference at our highest level of theory, CCSD(T)/cc-pVTZ+ΔZPE(B3LYP/cc-pVTZ), is found to be 5.0 kcal/mol which is very close to the G1 value of 6.1 kcal/mol reported by LBLU.

The optimized geometries at our highest theoretical level, B3LYP/cc-pVTZ (see Table 1), are generally in good agreement with those at the MP2/6-31G* level obtained by LBLU. At the B3LYP/cc-pVTZ level we found a substantial shortening of the CP distance (0.035 Å) in the linear $CCP(^2\Pi)$ ground state compared to the MP2/6-31G* value. There is also a good correspondence between the dipole moments at the B3LYP/cc-pVTZ and MP2/MC-311G* levels. A less good correspondence is seen for the dipole moments of linear $CCP(^4\Sigma^-)$ and cyclic $C_2P(^4A_2)$.

Harmonic frequencies for the C_2P isomers are listed in Table 3. For the linear $CCP(^2\Pi)$ ground state, even when scaled by 0.94,[35] the MP2/6-31G* frequencies of LBLU are in poor agreement with our B3LYP/cc-PVTZ results. This is probably due in large measure to the high spin contamination which affects the $^2\Pi$ wave function in the LBLU study. The values for the two different modes, corresponding to the two Renner−Teller components, are given in Table 3.

For the linear $CCP(^4\Sigma^-)$ isomer, the scaled MP2/6-31G* frequencies are clearly closer to our B3LYP/cc-pVTZ values. The a_1 frequencies for the cyclic $C_2P(^2B_2)$ isomer agree with those of LBLU at MP2/6-31G* (scaled).

TABLE 2: Relative Energies (kcal/mol) for the C_2P States at Different Levels of Theory and Electronic Energies (hartrees) (in Parentheses)

theoretical level	$^2\Pi$ CCP (lin)	$^2B_2$ cyclic	$^4\Sigma^-$ CCP (lin)	$^4A_2$ cyclic	$^2\Pi_g$ CPC (lin)
B3LYP/cc-pVTZ[a]	0.0 (−417.42678)	7.5	23.6	42.8	94.9
ROHF/cc-pVTZ[a]	0.0 (−416.32742)	7.9	11.1	35.2	115.0
CCSD(T)/cc-pVTZ[a]	0.0 (−416.77842)	5.5	21.2	38.4	88.0
T_1 diagnostic	0.036	0.024	0.051	0.044	0.045
CCSD(T)/cc-pVTZ[a] + ΔZPE[b]	0.0 (−416.77155)	5.0	21.4	37.9	86.1
UHF/MC-311G* (ref 18)	0.0	13.0	−13.7	32.4	103.1
MP4/MC-311G* (ref 18)	0.0	2.7	27.3	38.6	92.6
PMP4/MC-311G* (ref 18)	0.0	5.5	23.4	41.0	89.3
PMP4/MC-311G* + ΔZPE[c] (ref 18)	0.0	4.0 (6.1)[d]	22.3	39.3	86.9

[a] At B3LYP/cc-pVTZ optimized geometry. [b] Zero-point vibrational energy differences were obtained from the B3LYP/cc-pVTZ harmonic frequencies. [c] Zero-point vibrational energy differences were obtained from scaled MP2/6-31G* harmonic frequencies (factor 0.94, see ref 35).[d] G1 value in parentheses.

TABLE 3: Harmonic Frequencies (cm^{-1}) of the Different C_2P states and Infrared Intensities (km/mol) (in Parentheses)

theoretical level	harmonic freq (IR intensity)
	CCP($^2\Pi$)
B3LYP/cc-pVTZ	162 (π, 6); 275 (π, 0.6); 849 (σ, 2); 1727 (σ, 299)
MP2/6-31G* (scaled)[a,b]	286 (π, 0.001); 594 (π, 0.540); 960 (σ, 0.099); 1933 (σ, 1.000)
	Cyclic ($^2B_2$)
B3LYP/cc-pVTZ	354 (b_2, 139); 786 (a_1, 7); 1508 (a_1, 1)
MP2/6-31G* (scaled)[a,b]	418 (b_2, 1.000); 859 (a_1, 0.052); 1435 (a_1, 0.120)
	CCP($^4\Sigma^-$)
B3LYP/cc-pVTZ	327 (π, 4); 732 (σ, 17); 1765 (σ, 0.5)
MP2/6-31G* (scaled)[a,b]	343 (π, 0.113); 695 (σ, 1.000); 1637 (σ, 0.154)
	Cyclic ($^4A_2$)
B3LYP/cc-pVTZ	451 (b_2, 4); 543 (a_1, 7); 1697 (a_1, 7)
MP2/6-31G* (scaled)[a,b]	4113 (b_2, 1.000); 556 (a_1, 0.000); 1559 (a_1, 0.000)
	CPC($^2\Pi_g$)
B3LYP/cc-pVTZ	136 i (π_u, 9); 64 i (π_u, 5); 834 (σ_g); 881 (σ_u, 305)
CASSCF/cc-pVDZ	142 i (π_u); 71 i (π_u); 778 (σ_g); 803 (σ_u, 269)
MP2/6-31G* (scaled)[a,b]	155 (π_u, 0.562); 261 (π_u, 0.569); 846 (σ_u, 1.000); 818 (σ_g, 0.000)

[a] Reference 18; relative intensities are given in parentheses. [b] Scaled by 0.94 (ref 35).

TABLE 4: Geometrical Parameters (Å, deg) and Dipole Moments (debyes) for the C_2P^+ Structures

geometrical parameters	B3LYP/cc-pVTZ	MP2/6-31G* (ref 18)
	CCP$^+$($^1\Sigma^+$)	
r_{CC}	1.330	1.337
r_{CP}	1.5754	1.604
dipole moment	2.45	2.258[a]
	Cyclic ($^1A_1$)	
r_{CC}	1.2744	1.296
r_{CP}	1.7278	1.719
θ_{CPC}	43.28	44.3
dipole moment	1.57	1.853[a]
	CCP$^+$($^3\Pi$)	
r_{CC}	1.2495	1.240
r_{CP}	1.6443	1.636
dipole moment	0.26	0.028[a]
	Cyclic ($^3B_2$)	
r_{CC}	1.3275	1.342
r_{CP}	1.7782	1.775
θ_{CPC}	43.83	44.4
dipole moment	0.77	0.543[a]
	CPC$^+$($^1\Sigma_g^+$)	
r_{CP}	1.7222	1.749
dipole moment	0.0	0.0[a]

[a] Dipole moments were obtained with the MC-311G* basis set taking the center of mass at the origin.

For the cyclic $C_2P(^4A_2)$ isomer, it is not possible to compare our values with those of LBLU at the MP2/6-31G* level, since this method produces an anomalous high b_2 frequency (4113 cm^{-1}, scaled) suggesting its breakdown. Given that it is well-known that MP2 is essentially unusable for harmonic frequencies at $T_1 = 0.02$ or higher,[36,37] the anomalous harmonic frequencies obtained by LBLU are not surprising. It should be remarked that our values are comparable to those at the Hartree−Fock (HF) level: 337, 531, and 1885 cm^{-1} (LBLU). This is in agreement with the general observation (e.g. ref 38) that HF tends to give a more balanced treatment than MP2 for systems which are moderately multireference.

Finally, contrary to the results of LBLU at MP2/6-31G*, we found two imaginary frequencies for linear CPC($^2\Pi_g$). This result has also been confirmed at the CASSCF/cc-pVDZ theoretical level. This type corresponds to case (d) in the study of Renner−Teller potential energy surfaces of Lee et al.[39] According to the predicted IR intensities, the IR spectrum of the linear CCP($^2\Pi$) ground state isomer will be dominated by the C−C stretching mode; in the case of cyclic $C_2P(^2B_2)$ the b_2 bending mode turns out to be the most intense.

3.2. The C_2P^+ Cation. The geometrical parameters, optimized at the B3LYP/cc-pVTZ level, and dipole moments for linear CCP$^+$($^1\Sigma^+$), cyclic C_2P^+($^1A_1$), linear CCP$^+$($^3\Pi$), cyclic C_2P^+($^3B_2$), and linear CPC$^+$($^1\Sigma^+{}_g$), are presented in Table 4. For comparison the MP2/6-31G* results of LBLU are also given. The relative energies and harmonic frequencies for the C_2P^+ isomers at the selected theoretical levels are shown in Tables 5 and 6, respectively.

Table 5 shows that linear CCP$^+$($^1\Sigma^+$) is the ground state at all of our selected levels of theory; next comes cyclic C_2P^+($^1A_1$) at our correlated levels, followed by cyclic C_2P^+($^3B_2$), linear CCP$^+$($^3\Pi$), and linear CPC$^+$($^1\Sigma^+{}_g$). This sequence has also been found by LBLU at the (P)MP4/MC-31G* level of theory; it should be remarked that there are large deviations between the relative energies at the PMP4/MC-311G* (LBLU) and at the CCSD(T)/cc-pVTZ levels: $^1A_1 - {}^1\Sigma^+$, +78%; $^3\Pi - {}^1\Sigma^+$, +31%; $^3B_2 - {}^1\Sigma^+$, +30%; $^1\Sigma^+{}_g - {}^1\Sigma^+$, −22%, relative to the CCSD(T) values. From the geometrical parameters of C_2P and C_2P^+, collected in Tables 1 and 4, respectively, it can be seen that the geometry changes due to ionization show the same tendency both at the B3LYP/cc-pVTZ and MP2/6-31G* levels (LBLU). It can also be seen from Table 4 that the dipole moments for the C_2P^+ structures at the B3LYP/cc-pVTZ and

TABLE 5: Relative Energies (kcal/mol) for the C_2P^+ States at Different Levels of Theory and Electronic Energies (hartrees) (in Parentheses)

theoretical level	$^1\Sigma^+$ CCP$^+$ (lin)	$^1A_1$ cyclic	$^3\Pi$ CCP$^+$ (lin)	$^3B_2$ cyclic	$^1\Sigma_g^+$ CPC$^+$ (lin)
B3LYP/cc-pVTZ[a]	0.0	12.1	26.1	23.6	117.4
	(−417.08798)				
CCSD(T)/cc-pVTZ[a]	0.0	8.7	29.1	24.1	104.3
	(−416.44912)				
T_1 diagnostic	0.022	0.028	0.048	0.044	0.052
CCSD(T)/cc-pVTZ[a] + ΔZPE[b]	0.0	8.8	29.5	24.3	102.7
	(−416.44256)				
UHF/MC-311G* (ref 18)	0.0	19.0	−6.5	6.8	146.3
MP4/MC-311G* (ref 18)	0.0	15.5	47.2	32.7	81.8
PMP4/MC-311G* (ref 18)	0.0	15.5	38.1	31.3	81.8
PMP4/MC-311G* + ΔZPE[c] (ref 18)	0.0	15.6	38.5	31.6	80.9

[a] At B3LYP/cc-pVTZ optimized geometry. [b] Zero-point vibrational energy differences were obtained from the B3LYP/cc-pVTZ harmonic frequencies. [c] Zero-point vibrational energy differences were obtained from scaled MP2/6-31G* harmonic frequencies (factor 0.94, see ref 35).

TABLE 6: Harmonic Frequencies (cm^{-1}) of the Different C_2P^+ States and Infrared Intensities (km/mol) (in Parentheses)

theoretical level	harmonic freq (IR intensity)
	CCP$^+$($^1\Sigma^+$)
B3LYP/cc-pVTZ	88 (π, 0.54); 878 (σ, 4); 1826 (σ, 822)
MP2/6-31G* (scaled)[a,b]	156 (π, 0.001); 770 (σ, 0.013); 1728 (σ, 1.000)
	Cyclic ($^1A_1$)
B3LYP/cc-pVTZ	222 (b_2, 135); 937 (a_1, 66); 1762 (a_1, 43)
MP2/6-31G* (scaled)[a,b]	353 (b_2, 1.000); 917 (a_1, 0.304); 1617 (a_1, 0.060)
	CCP$^+$($^3\Pi$)
B3LYP/cc-pVTZ	205 (π, 7); 304 (π, 10); 808 (σ, 29); 1829 (σ, 170)
CASSCF/cc-pVDZ	195 (π, 6); 282 (π, 10); 781 (σ, 22); 1749 (σ, 163)
MP2/6-31G* (scaled)[a,b]	254 (π, 0.032); 325 (π, 0.034); 785 (σ, 0.080); 1742 (σ, 1.000)
	Cyclic ($^3B_2$)
B3LYP/cc-pVTZ	757 (b_2, 13); 758 (a_1, 2); 1535 (a_1, 0.51)
MP2/6-31G* (scaled)[a,b]	738 (b_2, 1.000); 782 (a_1, 0.239); 1482 (a_1, 0.023)
	CPC$^+$($^1\Sigma_g^+$)
B3LYP/cc-pVTZ	173 i (π_u, 0.55); 812 (σ_g); 976 (σ_u, 596)
CASSCF/cc-pVDZ	175 i (π_u); 731 (σ_g); 884 (σ_u, 397)
MP2/6-31G* (scaled)[a,b]	299 (π_u, 0.509); 665 (σ_g, 0.0); 938 (σ_u, 1.00)

[a] Reference 18, relative intensities are given in parentheses. [b] Scaled by 0.94 (ref 35).

MP2/6-31G* levels of theory are in good agreement with each other.

The harmonic frequencies of the C_2P^+ isomers, collected in Table 6, show a good correspondence between our B3LYP values and those of LBLU at the MP2/6-31G* (scaled) level except for CPC$^+$($^1\Sigma^+{}_g$). The IR spectrum of CCP$^+$($^1\Sigma^+$) will be dominated by the C−C stretching mode.

At the B3LYP/cc-pVTZ and CASSCF/cc-pVDZ theoretical levels, two imaginary frequencies have been found for CPC$^+$($^1\Sigma^+{}_g$) in contrast to the MP2/6-31G* level where all frequencies are real. This shows that CPC$^+$($^1\Sigma^+{}_g$) should be considered as a saddle point of order 2 at our selected theoretical levels.

3.3. Thermochemistry of CCP($^2\Pi$). The direct and corrected total atomization energies (kcal/mol) for CCP in its $^2\Pi$ ground state are given in Table 7. For CCP($^2\Pi$) at the CCSD)(T)/cc-pVDZ level from a B3LYP/cc-pVDZ reference geometry, a direct total atomization energy $\sum D_e = 228.1$ kcal/mol has been found. We will now apply Martin's[40] correction formula

$$\Delta E_{corr} = a_\sigma \Delta n_\sigma + b_\pi \Delta n_\pi + c_{pair} \Delta n_{pair} \tag{2}$$

where Δn_σ, Δn_π, and Δn_{pair} represent the changes of the numbers of σ-bonds, π-bonds, and valence pairs, respectively; the coefficients a_σ, b_π, and c_{pair} are specific to the basis set, electron correlation method, and level of theory for the reference geometry.

While no coefficients specific for B3LYP/cc-pVDZ geometries are available, we can assume them to be close to the CCSD(T) ones, and therefore the following values have been taken: $a_\sigma = 0.346$, $b_\pi = 0.481$, $c_{pair} = 9.407$. This leads us here to a correction of 29.88 kcal/mol, or to a corrected $\sum D_e =$ 258.0 kcal/mol. Extending the basis set to cc-pVTZ gives a direct total atomization energy $\sum D_e = 248.6$ kcal/mol, and a corrected $\sum D_e = 260.2$ kcal/mol.

For CCSD(T)/cc-pVQZ with a B3LYP/cc-pVTZ geometry, a direct $\sum D_e = 256.7$ kcal/mol is found, and a corrected $\sum D_e = 261.7$ kcal/mol, where 1−2 kcal/mol is probably a realistic error estimate.

The convergence properties of results obtained with a sequence of correlation-consistent basis sets have been studied by Dunning and co-workers.[41] These authors have used a geometric approximation, as discussed in ref 42, to extrapolate the computed results to the infinite basis set limit. Applying the approximation to the energy values yields an extrapolated CCSD(T)/cc-pV∞Z energy of 261.06 kcal/mol, which is in excellent agreement with the corrected CCSD(T)/cc-pVQZ value. We therefore propose 261.7 ± 1 kcal/mol as our best estimate for the total atomization energy of CCP in its $^2\Pi$ ground state.

The adiabatic ionization potentials of the two lowest states of neutral C_2P are given in Table 8. At the highest level in our calculations, CCSD(T)/cc-pVQZ, we find an adiabatic ionization potential IP = 9.04 eV for the linear CCP($^2\Pi$) and 9.15 eV for the cyclic $^2B_2$ isomer. If we apply the Woon−Dunning extrapolation,[42] we find the following extrapolated IP's: 9.05 eV for linear CCP($^2\Pi$) and 9.18 eV for the cyclic ($^2B_2$) isomer; these values are in excellent agreement with the CCSD(T)/cc-pVQZ + ΔZPE values. We therefore propose 9.05 and 9.18 eV as our best estimates for the adiabatic ionization potential of linear CCP($^2\Pi$) and cyclic C_2P($^2B_2$), respectively. Our value for the cyclic structure is in good agreement with that published by LBLU (9.10 eV); a deviation of 0.70 eV has been found for linear CCP($^2\Pi$).

3.4. Neutral PCN and PNC. The optimized geometrical parameters and dipole moments for the triplet and singlet states at the B3LYP/cc-pVTZ theoretical level are given in Table 9. UHF/6-31G* results of LB are also given for comparison. The relative energies for the PCN and PNC states at the selected theoretical levels are listed in Table 10. Harmonic frequencies can be found in Table 11.

Linear PCN($^3\Sigma^-$) is the ground state at our selected theoretical levels, followed by linear PNC($^3\Sigma^-$). Linear PCN($^1\Delta$) comes next, followed by cyclic PCN($^3A''$), cyclic PCN($^1A'$), and linear PNC($^1\Delta$) at our highest level, CCSD(T)/cc-pVTZ. We remark

TABLE 7: Direct and Corrected Total Atomization Energies (kcal/mol) for the Ground State of C_2P

	$C_2P(^2\Pi)$			
ΣD_e	CCSD(T)/cc-pVDZ// B3LYP/cc-pVDZ	CCSD(T)/cc-pVTZ// B3LYP/cc-pVTZ	CCSD(T)/cc-pVQZ// B3LYP/cc-pVTZ	CCSD(T)/cc-pV∞Z
direct	228.1	248.6	256.7	261.06[a]
corrected	258.0	260.2	261.7	

[a] Woon−Dunning extrapolation (ref 42).

TABLE 8: Adiabatic Ionization Potentials (eV) for the Two Lowest C_2P States

	$C_2P(^2\Pi)$				
state	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ cc-pV∞Z[b] + ΔZPE[a]	PMP4/ MC-311G* + ΔZPE[c]
$CCP(^2\Pi)$	8.68	8.96	9.04	9.05	8.35
cyclic ($^2B_2$)	8.93	9.10	9.15	9.18	9.10

[a] Zero-point energy differences were obtained from the B3LYP/cc-pVTZ harmonic frequencies. [b] Woon−Dunning extrapolation (ref 42). [c] LBLU,[18] zero-point energy differences were obtained from scaled MP2/6-31G* harmonic frequencies (factor 0.94, ref 35).

TABLE 9: Geometrical Parameters (Å, deg) and Dipole Moments (debyes) for the PCN and PNC States

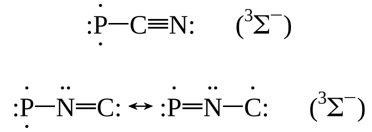
geometrical parameters	B3LYP/cc-pVTZ	UHF/6-31G*[a]
	$PCN(^3\Sigma^-)$	
r_{PC}	1.7237	1.7224
r_{CN}	1.1697	1.174
dipole moment	2.68	2.42
	$PCN(^3\Sigma^-)$	
r_{PN}	1.6649	1.680
r_{NC}	1.1875	1.170
dipole moment	2.48	2.16
	$PCN(^1\Delta)$	
r_{PC}	1.7019	
r_{CN}	1.1756	
dipole moment	2.55	
	Cyclic ($^3A''$)	
r_{PC}	1.8789	1.936
r_{PN}	2.1134	2.110
θ_{CPN}	34.07	33.4
dipole moment	1.54	
	Cyclic ($^1A'$)	
r_{PC}	1.8394	
r_{PN}	1.7021	
θ_{CPN}	42.88	
dipole moment	2.37	
	$PNC(^1\Delta)$	
r_{PN}	1.6395	
r_{NC}	1.1967	
dipole moment	2.32	

[a] Reference 17.

that the coupled cluster T_1 diagnostic,[32] giving a measure of the importance of nondynamical correlation effects, is well below the critical value of 0.08 for the CCSD(T) level of theory.[33] Our relative energies at CCSD(T)/cc-pVTZ of 14.2 (PNC, $^3\Sigma^-$) and 36.2 kcal/mol (cyclic $^3A''$) are in good agreement with those of LB at the PMP3/MC-311G* level, namely, 15.0 and 39.4 kcal/mol, respectively. The unprojected MP values of LB are less reliable due to spin contamination for PCN in its $^3\Sigma^-$ ground state ($\langle S^2\rangle = 2.308$).

We note also the small energy difference of 1.1 kcal/mol, (CCSD(T)/cc-pVTZ) between the cyclic ($^1A'$) and $PNC(^1\Delta)$ isomers.

Our geometric parameters of $PCN(^3\Sigma^-)$ and $PNC(^3\Sigma^-)$ at the B3LYP/cc-pVTZ level are in good agreement with those of LB. There is also good agreement in the computed dipole moments. The CN bond distance in the $PCN(^3\Sigma^-)$ linear isomer (1.1617 Å at B3LYP/cc-pVTZ) is very close to that observed in the CN radical, 1.172 Å,[43] with a triple bond between the C and N atoms. Our B3LYP/cc-pVTZ CN distance in $PNC(^3\Sigma^-)$ (1.1875 Å) is somewhat longer than that in the CN radical. It is seen that the PC bond distance in PCN is somewhat shorter than typical P−C single-bond distances and much longer than P=C bond lengths (1.665 Å).[44] The PN bond distance in $PNC(^3\Sigma^-)$ is that of a typical single bond.[45,46] The bond distances are consistent with the following valence-bond structures:



$$:\overset{\cdot}{\underset{\cdot}{P}}-C\equiv N: \qquad (^3\Sigma^-)$$

$$:\overset{\cdot}{\underset{\cdot}{P}}-\overset{\cdot\cdot}{N}=C: \leftrightarrow :\overset{\cdot}{P}=\overset{\cdot\cdot}{N}-\overset{\cdot}{C}: \qquad (^3\Sigma^-)$$

The CN stretching mode for the $PCN(^3\Sigma^-)$ isomer at the B3LYP/cc-pVTZ level differs +266 cm^{-1} from the UHF/6-31G* value of LB. This large difference can be explained by spin contamination ($\langle S^2\rangle = 2.308$) that affects the UHF/6-31G* value and by neglect of electron correlation; it is well-known that inclusion of an appropriate electron correlation treatment is a prerequisite for an accurate treatment of triple bonds.[47,48] The PC stretching and PCN bending modes are in rather good agreement with those of LB. It is worth noting that according to our predicted IR intensities, the IR spectrum of the linear $PCN(^3\Sigma^-)$ isomer is dominated by the PC stretching mode, whereas at the UHF/6-31G* level, the CN stretching mode is predicted to be the most intense.

For the $PNC(^3\Sigma^-)$ isomer, all frequencies appear to be in good agreement with those of LB, except for the CN stretching mode where the difference is −236 cm^{-1}. The inclusion of an adequate electron correlation treatment for obtaining accurate frequencies for multiple bonds is clearly illustrated for the $PNC(^3\Sigma^-)$ isomer since the wave function at the UHF/6-31G* level is nearly spin-pure here, namely $\langle S^2\rangle = 2.062$.

The cyclic structure ($^3A''$) on the triplet surface is a transition state: the imaginary frequency, found at all our theoretical levels, is associated with the migration of the P atom from N to C. The geometrical parameters of the $^3A''$ structure at the B3LYP/cc-pVTZ level are in rather good agreement with those of LB at the UHF/6-31G* level.

In the IR spectrum of $PCN(^1\Delta)$, the CP stretching frequency will prevail over all other modes, whereas the CN stretching mode in $PNC(^1\Delta)$ is the most intense. The cyclic ($^1A'$) structure on the singlet surface is a local energy minimum: the vibrational frequencies are real at our selected theoretical levels.

3.5. The PCN^+ and PNC^+ Cations. The optimized geometric parameters and dipole moments for the doublet states at the B3LYP/cc-pVTZ level are presented in Table 12; the UHF/6-31G* results of LB are also given for comparison. Relative energies and harmonic frequencies for the different structures are listed in Tables 13 and 14, respectively. The CN bond length in the PCN^+ and PNC^+ species is increased by comparison to the neutral molecule; the PC and PN bond lengths are now noticeably shorter, being more close to P=C or P=N

TABLE 10: Relative Energies (kcal/mol) for the PCN and PNC States at Different Levels of Theory and Electronic Energies (hartrees) (in Parentheses)

theoretical level	$^3\Sigma^-$ PCN (lin)	$^3\Sigma^-$ PNC (lin)	$^1\Delta$ PCN (lin)	^{3}A″ cyclic	^{1}A′ cyclic	$^1\Delta$ PNC (lin)
B3LYP/cc-pVTZ	0.0 (−434.19651)	12.9	26.1	36.8	40.5	38.9
CCSD(T)/cc-pVTZ[a]	0.0 (−433.53514)	14.2	25.2	36.2	37.7	38.8
T_1 diagnostic	0.029	0.026	0.021	0.030	0.018	0.019
CCSD(T)/cc-pVTZ[a] + ΔZPE[b]	0.0 (−433.52750)	14.0	25.3	35.0	37.0	38.6
UHF/MC-311G*[c] (ref 17)	0.0 (−433.04965)	12.4	46.7	44.6	55.3	37.7
MP3/MC-311G*[c] (ref 17)	0.0 (−433.40206)	8.7		33.0		
MP4/MC-311G*[c] (ref 17)	0.0 (−433.43070)	9.4	22.5	32.2	35.9	38.0
PMP3/MC-311G*[c] (ref 17)	0.0 (−433.41489)	15.0		39.4		

[a] At B3LYP/cc-pVTZ optimized geometry. [b] Zero-point vibrational energy differences were obtained from the B3LYP/cc-pVTZ harmonic frequencies. [c] At the UHF/6-31G* optimized geometry.

TABLE 11: Harmonic Frequencies (cm^{-1}) of the Different PCN and PNC Isomers and Infrared Intensities (km/mol) (in Parentheses)

theoretical level	harmonic freq (IR intensity)
	PCN($^3\Sigma^-$)
B3LYP/cc-pVTZ	333 (π, 3); 649 (σ, 24), 2037 (σ, 11)
UHF/6-31G*[a]	332 (π, 4.4); 681 (σ, 45.1); 1771 (σ, 119.6)
	PNC($^3\Sigma^-$)
B3LYP/cc-pVTZ	264 (π, 0.28); 693 (σ, 30); 1974 (σ, 125)
UHF/6-31G*[a]	275 (π, 0.1); 722 (σ, 81.3); 2210 (σ, 221.7)
	PCN($^1\Delta$)
B3LYP/cc-pVTZ	255 (π, 6); 420 (π, 0.28); 694 (σ, 16); 2034 (σ, 3)
	Cyclic (^{3}A″)
B3LYP/cc-pVTZ	213 i (a′, 6); 571 (a′, 46); 1938 (a′, 7)
CASSCF/cc-pVDZ	333 i (a′); 467 (a′, 53); 1892 (a′, 5)
UHF/6-31G*[a]	346 i (a′); 529 (a′); 2200 (a′)
	Cyclic (^{1}A′)
B3LYP/cc-pVTZ	624 (a′, 7); 814 (a′, 5); 1415 (a′, 16)
CASSCF/cc-pVDZ	601 (a′, 4); 775 (a′, 5); 1328 (a′, 10)
	PNC($^1\Delta$)
B3LYP/cc-pVTZ	212 (π, 2); 351 (π, 0.35); 738 (σ, 14); 1904 (σ, 73)
CASSCF/cc-pVDZ	254 (π, 0.41); 663 (σ, 52); 1936 (σ, 210)

[a] Reference 17.

TABLE 12: Geometrical Parameters (Å, deg) and Dipole Moments (debyes) for the PCN$^+$ and PNC$^+$ States

geometrical parameters	B3LYP/cc-pVTZ	UHF/6-31G*[a]
	PNC$^+$($^2\Pi$)	
r_{PN}	1.5888	1.579
r_{NC}	1.2213	1.203
dipole moment	2.90	2.81[a]
	PCN$^+$($^2\Pi$)	
r_{PC}	1.6901	1.675
r_{CN}	1.1783	1.193
dipole moment	3.67	3.85[a]
	Cyclic Cation (^{2}A′)	
r_{PC}	1.7937	1.950
r_{PN}	1.7364	1.817
θ_{CPN}	41.25	35.1
dipole moment	2.20	

[a] Dipole moments were obtained with the 6-31G* basis set taking the center of mass at the origin.

TABLE 13: Relative Energies (in kcal/mol) for the PCN$^+$ and PNC$^+$ States at Different Levels of Theory and Electronic Energies (hartrees) (in Parentheses) for the PCN$^+$($^2\Pi$) and PNC$^+$($^2\Pi$) Isomers

theoretical level	$^2\Pi$ PNC$^+$	$^2\Pi$ PCN$^+$	^{2}A′ cyclic cation
B3LYP/cc-pVTZ	0.0 (−433.818534)	1.8 (−433.815732)	16.1
CCSD(T)/cc-pVTZ[a]	0.0 (−433.157163)	0.8 (−433.155825)	13.9
T_1 diagnostic	0.027	0.032	0.024
CCSD(T)/cc-pVTZ[a] + ΔZPE[b]	0.0 (−433.150169)	1.1 (−433.148428)	13.6
CCSD(T)/cc-pVQZ[a]	0.0 (−433.191846)	1.4 (−433.189540)	
T_1 diagnostic	0.027	0.031	
CCSD(T)/cc-pVQZ[a] + ΔZPE[b]	0.0 (−433.184852)	1.7 (−433.182143)	
UHF/MC-311G*[c] (ref 17)	0.0 (−432.68807)	7.5 (−432.67616)	42.1
MP3/MC-311G*[c] (ref 17)	0.0 (−433.04040)	13.2 (−433.01939)	36.4
MP4/MC-311G* (ref 17)	0.0 (−433.06883)	11.7 (−433.05014)	33.8
PMP3/MC-311G*[c] (ref 17)	0.0 (−433.04266)	−0.7 (−433.4338)	32.6

[a] At B3LYP/cc-pVTZ optimized geometry. [b] Zero-point vibrational energy differences were obtained from the B3LYP/cc-pVTZ harmonic frequencies. [c] At the UHF/6-31G* optimized geometry.

TABLE 14: Harmonic Frequencies (cm^{-1}) of the Different PCN$^+$ and PNC$^+$ Structures and Infrared Intensities (km/mol) (in Parentheses)

theoretical level	harmonic freq (IR intensity)
	PNC$^+$ ($^2\Pi$)
B3LYP/cc-pVTZ	169 (π, 0.01); 247 (π, 1); 838 (σ, 28); 1816 (σ, 521)
UHF/6-31G*[a]	209 (π); 278 (π); 777 (σ); 1660 (σ)
	PCN$^+$($^2\Pi$)
B3LYP/cc-pVTZ	186 (π, 3); 291 (π, 1); 725 (σ, 55); 2045 (σ, 290)
UHF/6-31G*[a]	243 (π); 278 (π); 911 (σ); 2030 (σ)
	Cyclic Cation (^{2}A′)
B3LYP/cc-pVTZ	508 (a′, 39); 683 (a′, 19); 1654 (a′, 10)
CASSCF/cc-pVDZ	363 i (a′); 724 (a′, 39); 1598 (a′, 37)
UHF/6-31G*[a]	710 i (a′); 696 (a′); 2078 (a′)

[a] Reference 17.

double bonds, respectively. A typical P═C bond length is 1.665 Å;[44] the P═N bond in HP═NH is computed as 1.574 Å (cis) and 1.584 Å (trans) at the B3LYP/cc-pVTZ level.

The dipole moments are in good agreement with those of LB. For the linear PCN$^+$($^2\Pi$) isomer, we note an important deviation (−186 cm^{-1}) for the PC stretching mode at the B3LYP/cc-pVTZ and UHF/6-31G* levels (Table 14) which seems to be associated with the high degree of spin contamination in the UHF wave function, namely, $\langle S^2 \rangle = 1.260$.

TABLE 15: Direct and Corrected Total Atomization Energies (kcal/mol) for the Ground State of PCN

	PCN($^3\Sigma^-$)			
$\sum D_e$	CCSD(T)/cc-pVDZ// B3LYP/cc-pVDZ	CCSD(T)/cc-pVTZ// B3LYP/cc-pVTZ	CCSD(T)/cc-pVQZ// B3LYP/cc-pVTZ	CCSD(T)/cc-pV∞Z
direct	242.0	262.9	271.2	275.8[a]
corrected	271.9	274.5	276.1	

[a] Woon−Dunning extrapolation (ref 42).

A good correspondence between the calculated vibrational frequencies of linear PNC$^+$($^2\Pi$) is also observed (Table 14). We note here a deviation of 156 cm^{-1} for the CN stretching mode between the B3LYP/cc-pVTZ and UHF/6-31G* levels. It should be remarked here that spin contamination of the UHF wave function is almost negligible ($\langle S^2\rangle = 0.783$). Thus, it appears once again that inclusion of an adequate electron correlation treatment is necessary in order to obtain accurate stretching frequencies for multiple bonded systems.

All the vibrational frequencies are real for the cyclic CPN$^+$ cation (^{2}A′) at the B3LYP/cc-pVTZ level, indicating that this structure is a true energy minimum. This result is contradictory to that of LB who found a transition state with an imaginary frequency of 710 i cm^{-1} (UHF/6-31G*) associated to the migration of the P atom from C to N. A transition state is also found by us at the CASSCF/cc-pVDZ level with an imaginary frequency of 363 i cm^{-1}. A great difference of 424 cm^{-1} is seen for the a′ mode at the B3LYP/cc-pVTZ and UHF/6-31G* levels, indicating some problems with the last theoretical level.

Relative energies for the cations are given in Table 13. It has already been mentioned by LB, on the basis of their spin-projected PMP2 and PMP3 relative energies, that the two linear isomers are nearly isoenergetic. They conclude that “it is difficult to definitively establish which one is the ground state, and higher level calculations should be necessary to draw a final conclusion”. At the CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ level we found that PNC$^+$($^2\Pi$) is the ground state, followed by PCN$^+$($^2\Pi$) at 0.84 kcal/mol and by cyclic CPN$^+$(^{1}A′) at 13.9 kcal/mol. When the basis set is expanded to cc-pVQZ in the CCSD(T) treatment, the energy separation becomes now 1.4 kcal/mol. We note in passing that the coupled cluster T_1 diagnostic values are well below the critical value of 0.08 for CCSD(T). We also mention that at the CASSCF/cc-pVDZ and CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ levels PCN$^+$($^2\Pi$) is the ground state followed by PNC$^+$($^2\Pi$) at 3.7 and 1.72 kcal/mol, respectively.

3.6. Thermochemistry. The direct and corrected total atomization energies (kcal/mol) for PCN in its $^3\Sigma^-$ ground state are given in Table 15.

For PCN($^3\Sigma^-$) at the CCSD(T)/cc-pVDZ level from a B3LYP/cc-pVDZ reference geometry, a direct total atomization energy $\sum D_e = 242.0$ kcal/mol has been obtained. With the correction formula, mentioned in section 3.3, a corrected total atomization energy of 271.9 kcal/mol is found. At the CCSD(T)/cc-pVTZ level, the following values are obtained: $\sum D_e$(direct) = 262.9 and $\sum D_e$(corrected) = 274.5 kcal/mol. At the CCSD(T)/cc-pVQZ: $\sum D_e$(direct) = 271.2 and $\sum D_e$(corrected) = 276.1 kcal/mol.

The Woon−Dunning extrapolation procedure[42] yields a value of 275.8 kcal/mol for the direct atomization energy (CCSD(T)/cc-pV∞Z level). This value is in excellent agreement with the corrected CCSD(T)/cc-pVQZ value of 276.1 kcal/mol. We therefore propose 276.0 ± 1 kcal/mol as our best estimate for the total atomization energy of PCN in its $^3\Sigma^-$ ground state. The adiabatic ionization potentials (eV) for the two lowest PCN($^3\Sigma^-$) and PNC($^3\Sigma^-$) states are collected in Table 16. At the highest level in our calculations, CCSD(T)/cc-pVQZ, we find adiabatic ionization potentials IP of 10.38 eV for PCN($^3\Sigma^-$) and 9.72 for PNC($^3\Sigma^-$). If we apply the Woon−Dunning extrapolation, we find the following extrapolated IP’s: 10.39 eV for PCN($^3\Sigma^-$) and 9.73 eV for PNC($^3\Sigma^-$). These values are in excellent agreement with the CCSD(T)/cc-pVQZ+ΔZPE values. We propose therefore 10.39 and 9.73 eV as our best estimate for the adiabatic ionization potentials of linear PCN($^3\Sigma^-$) and PNC($^3\Sigma^-$), respectively.

TABLE 16: Adiabatic Ionization Potentials (eV) for the Two Lowest PCN and PNC States

	C_2P($^2\Pi$)			
state	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ cc-pV∞Z[a] + ΔZPE[b]
PCN($^3\Sigma^-$)	10.10	10.32	10.38	10.39
PNC($^3\Sigma^-$)	9.46	9.67	9.72	9.73

[a] Woon−Dunning extrapolation (ref 42). [b] Zero-point energy differences were obtained from the B3LYP/cc-pVTZ harmonic frequencies.

4. Conclusions

In the present work an ab initio molecular orbital study of the $C_2P^{(+)}$ and CNP$^{(+)}$ species has been carried out. The following theoretical levels were selected: CCSD(T), DFT (with the B3LYP exchange-correlation functional), and CASSCF in conjunction with Dunning’s correlation consistent basis set family.

Our results concerning the $C_2P^{(+)}$ system are largely the same as those of Largo and collaborators (LBLU). Significant differences are the following:

1. The scaled MP2/6-31G* frequencies of LBLU for CCP($^2\Pi$) are in poor agreement with our B3LYP/cc-pVTZ values. The high spin contamination which affects the $^2\Pi$ wave function in the LBLU study is probably the main reason for the deviation.
2. For the b_2 mode of the cyclic C_2P($^4A_2$) isomer, a realistic value of 451 cm^{-1} has been obtained (compared to 4113 cm^{-1} (scaled) at the MP2/6-31G* level by LBLU).
3. Contrary to the results of LBLU at MP2/6-31G*, two imaginary frequencies have been found for linear CPC($^2\Pi_g$) at both the B3LYP/cc-pVTZ and CASSCF-pVDZ levels of theory.
4. Large deviations are seen between the relative energies of the C_2P^+ states at the PMP4/MC-311G* (LBLU) and CCSD(T)/cc-pVTZ (ours) theoretical levels.
5. At the B3LYP/cc-pVTZ and CASSCF/cc-pVDZ theoretical levels two imaginary frequencies have been found for CPC$^+$($^1\Sigma^+{}_g$) in contrast to the MP2/6-31G* level (LBLU) where all the frequencies are real. Therefore, CPC$^+$($^1\Sigma^+{}_g$) should be considered as a saddle point of order two.
6. Our value for the adiabatic ionization potential of the CCP($^2\Pi$) state (9.05 eV) differs by +0.7 eV from that proposed by LBLU.

Our main results for the CNP$^{(+)}$ system can be summarized as follows:

1. For neutral PCN and PNC, the following sequence of states has been computed at the CCSD(T)/cc-pVTZ//B3LYP/

cc-pVTZ level: linear PCN($^3\Sigma^-$); linear PNC($^3\Sigma^-$) 14.2 kcal/mol, linear PCN($^1\Delta$) 25.2 kcal/mol, cyclic CPN(^{3}A$''$) 36.2 kcal/mol, cyclic CPN(^{1}A$''$) 37.7 kcal/mol, and linear PNC($^1\Delta$) 38.8 kcal/mol.

2. The ground state of the single ionized species is linear PNC$^+$($^2\Pi$) followed by linear PCN$^+$($^2\Pi$). The energy difference is very small: 0.8 (CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ) to 1.4 kcal/mol (CCSD(T)/cc-pVQZ//B3LYP/cc-pVTZ). Cyclic CPN$^+$(^{2}A$'$) lies much higher in energy (13.9 kcal/mol) and was found to be a local energy minimum at the doublet surface (B3LYP/cc−pVTZ level).

3. The IR spectrum at the B3PYP/cc-pVTZ level of the linear PCN($^3\Sigma^-$) isomer is dominated by the PC stretching mode, whereas at the UHF/6-31G* level (Largo and Barrientos (LB)), the CN stretching mode is predicted to be the most intense.

4. The IR spectra of both linear PNC$^+$($^2\Pi$) and PCN$^+$($^2\Pi$) are dominated by the CN stretching mode.

5. All the vibrational frequencies are real for the cyclic CPN$^+$ cation (^{2}A$'$) at the B3LYP/cc-pVTZ level, indicating that this structure is a true energy minimum. This result is contradictory to that of LB who found a transition state at the UHF/6-31G* level.

6. A total atomization energy of 276.0 ± 1 kcal/mol has been calculated for PCN($^3\Sigma^-$).

7. Adiabatic ionization potentials (eV) are: linear PCN($^3\Sigma^-$) 10.39, and linear PNC($^3\Sigma^-$) 9.73.

Acknowledgment. J.E.Y. acknowledges a graduate fellowship from the Bijzonder Onderzoeksfonds of the LUC. J.M. is an NFWO/FNRS (National Science Foundation of Belgium) Senior Research Associate (Onderzoeksleider). This work constitutes part of the research results of project IUAP 48 (Characterization of Materials) sponsored by the Office for Science Policy Programming of the Prime Minister's Cabinet.

References and Notes

(1) Ridgeway, S. T.; Wallace, L.; Smith, G. R. *Astrophys. J.* **1976**, *207*, 1002.

(2) Turner, B. E.; Bally, J. *Astrophys. J* **1987**, *321*, L75.

(3) Ziurys, L. M. *Astrophys. J.* **1987**, 321, L81.

(4) Guelin, M.; Cernicharo, J.; Paubert, G.; Turner, B. E. *Astron. Astrophys.* **1990**, *230*, L9.

(5) Thorne, L. R.; Anicich, V. G.; Huntress, W. T., Jr. *Chem. Phys. Lett.* **1983**, *98*, 162.

(6) Thorne, L. R.; Anicich, V. G.; Prasad, S. S.; Huntress, W. T., Jr. *Astrophys. J.* **1984**, *280*, 139.

(7) Smith, D.; McIntosh, B. J.; Adams, N. G. *J. Chem. Phys.* **1989**, *90*, 6213.

(8) Maclagan, R. G. A. R. *Chem. Phys. Lett.* **1989**, *163*, 349.

(9) Maclagan, R. G. A. R. *J. Phys. Chem.* **1990**, *94*, 3373.

(10) Largo, A.; Flores, J. R.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1991**, *95*, 170.

(11) Redondo, P.; Largo, A.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1991**, *95*, 4318.

(12) Largo, A.; Redondo, P.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1991**, *95*, 5443.

(13) Largo, A.; Flores, J. R.; Barrientos, C.; Ugalde, J. M. *J. Phys. Chem.* **1991**, *95*, 6553.

(14) Lopez, X.; Ugalde, J. M.; Barrientos, C.; Largo, A.; Redondo, P. *J. Phys. Chem.* **1993**, *97*, 1521.

(15) Turner, B. E.; Tsuji, T.; Bally, J.; Guelin, M.; Cernicharo, J. *Astrophys. J.* **1990**, *365*, 569.

(16) Millar, T. J. *Astron. Astrophys.* **1991**, *242*, 241.

(17) Largo, A.; Barrientos, C. *J. Phys. Chem.* **1991**, *95*, 9864.

(18) Largo, A.; Barrientos, C.; López, X.; Ugalde, J. M. *J. Phys. Chem.* **1994**, *98*, 3985.

(19) Martin, J. M. L.; El-Yazal, J.; François, J. P. *Mol. Phys.* **1995**, *86*, 1437.

(20) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(21) Devlin, F. J.; Finley, J. W.; Stephens, P. J.; Frisch, M. J. *J. Phys. Chem.* **1995**, *99*, 16883.

(22) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(23) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94* Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(26) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1988**, *58*, 1200.

(27) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(28) MOLPRO (1996) is a suite of programs written by Werner, H. J.; Knowles, P. J.; with contributions by Almlöf, J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R. M.; Reisch, E.-A.; Stone, A. J.; Taylor, P. R.; Lindh, R.

(29) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(30) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(31) SIRIUS is a multiconfigurational SCF program written by Jensen, H. J. Aa; Ågren, H.; and Olsen, J. ABACUS is multiconfigurational SCF energy derivatives program written by Helgaker, T.; Jensen, H. J. Aa; Jørgensen, P.; Olsen, J.; Taylor, P. R.

(32) Lee, T. J.; Taylor, P. R. *Int. J. Quantum. Chem. Symp.* **1989**, *23*, 199.

(33) Martin, J. M. L.; Lee, T. J.; Scuseria, G. E.; Taylor, P. R. *J. Chem. Phys.* **1992**, *97*, 6549.

(34) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(35) De Frees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

(36) Martin, J. M. L.; Lee, T. J. *J. Chem. Phys.* **1993**, *98*, 7951.

(37) Lee, T. J.; Scuseria, G. E. Achieving Chemical Accuracy with Coupled-Cluster Theory. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995; p 47.

(38) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem.* **1996**, *100*, 6047.

(39) Lee, T. J.; Fox, D. J.; Schaefer, H. F., III; Pitzer, R. M. *J. Chem. Phys.* **1984**, *81*, 356.

(40) Martin, J. M. L. *J. Chem. Phys.* **1992**, *97*, 5012.

(41) Peterson, K. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *99*, 3898 and references therein.

(42) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 1914.

(43) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(44) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 7015.

(45) Cowley, A. H.; Mitchell, D. J.; Whangbo, M. H.; Wolfe, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 5224.

(46) Barthelat, M.; Mathis, R.; Mathis, F. *J. Mol. Struct.* **1981**, *85*, 351.

(47) Simandiras, E. D.; Rice, J. E.; Lee, T. J.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3187.

(48) Thomas, J. R.; DeLeeuw, B. J.; Vacek, G.; Schaefer, H. F., III *J. Chem. Phys.* **1993**, *98*, 1336.