Theoretical Study of C_nP, C_nP^+, C_nP^- ($n = 1-7$) Clusters

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Received: December 4, 1998

In this work, we report results of calculations, based on density functional theory (DFT/B3LYP/6-311G*), of the lowest state energies, electronic structures, dipole moments, and vibrational frequencies of C_nP, C_nP^+, and C_nP^- ($n = 1-7$) clusters. According to these calculations, the lowest-lying geometry of all these species is predicted to be a linear structure with phosphorus located at one end of the carbon chain. From various theoretical considerations, such as incremental binding energy diagrams and fragmentation patterns, we can deduce that anionic clusters, C_nP^-, with odd clustering atoms are much more stable than those with even clustering atoms, in good agreement with experimental results (odd−even parity). Similar predictions can be made for the neutrals, although the odd−even alternation in stability is much less marked in this case. Besides, cations C_nP^+ exhibit an even−odd parity effect completely opposite to that of C_nP^- and C_nP.

1. Introduction

Pure carbon clusters in their neutral, cationic, and anionic forms have been extensively studied by use of both experiment and theory.[1,2] Heteroatom-doped carbon clusters obtained from replacing a first-row element of the Mendeleev table, such as B, N, or O, have also attracted much attention in the past few years.[3−9]

Heteroatoms belonging to the second-row of the Mendeleev table such as silicon[10,11] or sulfur[12−14] have been also considered. Besides, only a few reports have been published on phosphorus carbide clusters.[15,16] We can note that phosporus is located between silicon and sulfur in the periodic table, making the cations, C_nP^+, isoelectronic to neutral C_nSi and the anions, C_nP^-, isoelectronic to neutral C_nS. Besides, phosporus is in the same column (V) of the Mendeleev table as nitrogen, and carbon clusters doped with one of these two elements (N or P) could, a priori, possess similar structural properties. For all these various reasons, it appears very interesting to simultaneously study the neutral, cationic, and anionic forms of phosphorus-doped carbon clusters in order to compare them with Si-doped, S-doped, and N-doped carbon clusters for which much information exists in the literature. Moreover, to obtain other important data, such as ionization energies or electronic affinities, the simultaneous knowledge of the neutral, cationic, and anionic species is needed. Our main conclusion is that the lowest-lying geometry of C_nP, C_nP^+, C_nP^- ($n = 1-7$) clusters is the linear chain with the P atom located at one end of the carbon chain. At the present time, experimental results on C_nP^+ are lacking, but some information is available on the anions.[15,16] Examination of the cohesive energy differences, or *incremental binding energies*, between the C_nP^- clusters with respect to their respective $n + 1$ and $n - 1$ congeners reveals that the n-odd anions are more stable than the n-even ones, in close agreement with experimental results. In contrast, this parity effect in cluster stability is reversed in the cations for which the n-even clusters are found to be more stable than the n-odd clusters.

2. Calculation Methods

All calculations have been carried out using the GAUSSIAN 94 package[17] running on the IBM RS6000 and the CRAY C94 and C98 of the National Computer Center Idris in Orsay (France). The B3LYP exchange-correlation functional has been used throughout employing a 6-311G* basis set. The B3LYP functional uses a combination of the hybrid three-parameter Becke exchange functional first proposed by Becke[18] together with the Lee−Yang−Parr nonlocal correlation functional.[19] From previous studies devoted to application of this method, it is thought that DFT/B3LYP/6-311G* calculations predict the low-lying structures of pure and heteroatom-doped medium-sized carbon clusters closer to the experimental values than MBPT(2)[20] and at moderate cost compared to any accurate ab initio method in use such as CCSD(T).[21] However, in some cases for which a clear discrepancy appears for the lowest-lying geometry with other published studies (C_4P^-, C_6P^-), calculations have been performed at several levels of theory [Møller−Plesset at second order (MP2); Becke-3LYP and coupled cluster theory with single−double−(triple) substitutions (CCSD(T))] and with two basis sets. The widely used 6-311G* basis set (see ref 22 for phosphorus) and the augmented Dunning correlation consistent valence triple-ζ,[23−25] which allows us to account in the best way for polarization and electronic correlation, are referred to as Aug-cc-pVTZ in the following. The various structures have been optimized with analytic gradient techniques. Dipole moments are calculated with the origin at the center of mass, and harmonic vibrational frequencies are obtained from analytic second-order derivatives. Open-shell calculations have been done in the unrestricted formalism. The expected values of $\langle S^2\rangle$ were also computed to check spin contamination.

For the sake of space, we will present results only for the lowest-lying geometries, although explorations were also made for other states and geometries. Cyclic structures, branched structures, structures with the phosphorus not in the end position,

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10.1021/jp984615i CCC: $18.00

TABLE 1: Binding Energies, ⟨S^2⟩, Vibrational Frequencies, and Rotational Constants (B) for C_nP Structures Optimized with the B3LYP/6-311G* Method

isomer	point group	state	binding energies[a] (eV)	⟨S^2⟩	vibrational frequencies (cm^{-1})	ZPE (kcal mol^{-1})	dipole moment (D)	B (MHz)
CP	$C_{\infty v}$	$^2\Sigma^+$	5.2	0.78	1284(σ)	1.83	0.99	24020.7
C_2P	$C_{\infty v}$	$^2\Pi$	11.4	0.76	169(π), 276(π), 850(σ), 1715(σ)	4.30	3.20	6344.5
C_3P	$C_{\infty v}$	$^2\Pi$	17.9	0.76	120/186(π), 354/480(π), 704(σ), 1394(σ), 2004(σ)	7.49	3.70	2799.4
C_4P	$C_{\infty v}$	$^2\Pi$	24.3	0.78	114/128(π), 257/320(π), 471/581(π), 606(σ), 1215(σ), 1756(σ), 1998(σ)	10.65	4.40	1510.0
C_5P	$C_{\infty v}$	$^2\Pi$	30.7	0.78	86/93(π), 191/234(π), 391/449(π), 531(σ), 538/610(π), 1042(σ), 1552(σ), 1918(σ), 2111(σ)	13.93	4.90	912.8
C_6P	$C_{\infty v}$	$^2\Pi$	37.0	0.80	69/72(π), 170/187(π), 294/340(π), 465/548(π), 473(σ), 636/750(π), 932(σ), 1405(σ), 1702(σ), 1986(σ), 2072(σ)	17.30	5.44	597.4
C_7P	$C_{\infty v}$	$^2\Pi$	43.5	0.80	54/56(π), 136/150(π), 236/262(π), 401/441(π), 425(σ), 552/577(π), 778/820(π), 833(σ), 1255(σ), 1587(σ), 1916(σ), 2006(σ), 2160(σ)	20.94	6.03	413.2

[a] For C(^{3}P), $E = -37.855\,989$ au, and for P(^{4}S), $E = -341.280\,483$ au.

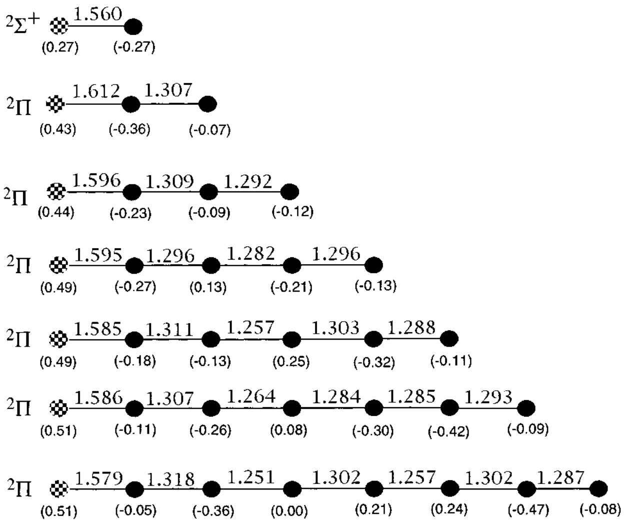


Figure 1. Equilibrium geometries of linear C_nP ($n = 1-7$) clusters at the B3LYP/6-311G* level of theory. Distances are in angstroms and angles in degrees. Mulliken charge distributions are given in parentheses.

optimized with DFT/B3LYP/6-311G* method, have also been considered, but these are all located higher above the corresponding linear ground state for the neutral, the cationic, and the anionic species, in each case with minimal energy separation of at least 15 kcal mol^{-1}.

3. Results and Discussion

3.1. C_nP Clusters. In Figure 1 are displayed the structures and Mulliken atomic charges for these clusters, and in Table 1 are collected other useful quantities such as the binding energies, ⟨S^2⟩, vibrational frequencies, ZPE, dipole moments, and rotational constants.

The lowest-lying geometry of C_nP ($n = 1-7$) clusters is found to be, in all cases, linear, in the $^2\Sigma^+$ electronic ground state for CP and $^2\Pi$ for all the other ($n = 2-7$) clusters. It can be noted that the ⟨S^2⟩ values are uniform and smaller than 5%. In any case, the linear quadruplet states and all other geometries (cyclic and branched structures) calculated for each species are all located higher in energy at 15 kcal mol^{-1} and more above the corresponding linear doublet ground state, preventing errors in the energetic ordering. Vibrational frequencies are also given even though it is well-known that in the case of dissymmetric occupancies of degenerate orbitals, the two components of π vibration are not equivalent. Nevertheless, considering the small difference value between the degenerate frequencies, we think that the order of magnitude is correct.

The computed CP bond length is 1.56 Å for the CP molecule and 1.61 Å for C_2P, so then the CP distance presents a very small decrease when going from C_3P (~1.60 Å) to C_7P (~1.58 Å). This length appears very short with respect to that found in CH_3PH (~1.86 Å), assimilated to a normal CP single bond, and in CH_2PH (~1.67 Å), assimilated to a normal CP double bond.[26] The CP bond in C_nP can thus be assimilated to a moderately strong double bond. The dipole moment regularly increases from 0.99 D for CP to 6.03 D for C_7P. The CC bond lengths are ~1.28−1.31 Å, indicative of cumulene-type structures (i.e., all C=C double bonds). A small bond alternation in n-odd C_nP (C_5P, C_7P), CC distances of ~1.30−1.32 Å alternating with CC distances of ~1.25−1.26 Å, is noticeable, conferring to these molecules some polyacetylenic character. Analysis of the Mulliken charge distribution shows that P bears a positive charge, about $+0.37e$ for CP and about $+0.4e$ for C_2P, C_3P, and then stabilizes around $+ 0.5e$ for $4 \leq n \leq 7$. In return, the carbon chain is negatively charged. This is in agreement with the well-known experimental fact that carbon is more electronegative than phosporus.

The relative stability of C_nP clusters can be estimated by computing the consecutive binding energy differences between adjacent C_nP and $C_{n-1}P$ clusters. These energy differences, or *incremental binding energies*,[10,13,27] are labeled ΔE^I in Figure 2. From Figure 2 we can see that a small odd−even alternation in stability exists for C_nP. In fact, except for CP, all the other C_nP ($n = 2-7$) clusters are in the $^2\Pi$ electronic ground state, and the stability of both n-odd and n-even species should not differ much because none of them corresponds to a fully occupied HOMO. Nevertheless, C_nP clusters with odd n appear slightly more stable than those with even n because in the former case (odd n) the HOMO is a bonding π-type orbital and in the latter case (even n) the HOMO is a nonbonding π-type orbital located higher in energy than a bonding π-type orbital. This very small odd−even parity effect in cluster stability is similarly apparent in both the ionization energy and electron affinity curves (Figure 3) and also in the fragmentation patterns (Figure 4). Thus, from Figure 4, we can see that C extraction from a C_nP structure is a little more difficult to realize for n-odd clusters

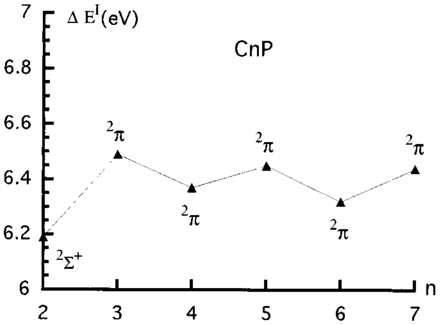


Figure 2. Incremental binding energies (eV) for the linear C_nP clusters vs the number of carbon atoms.

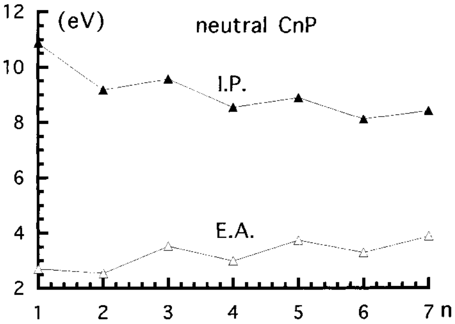


Figure 3. Ionization potentials (IP) and electronic affinities (EA) of C_nP clusters computed with the B3LYP/6-311G* method. Ionization potentials are calculated as total energy differences between the neutral and positively charged species, and electronic affinities are calculated as total energy differences between the neutral and negatively charged species.

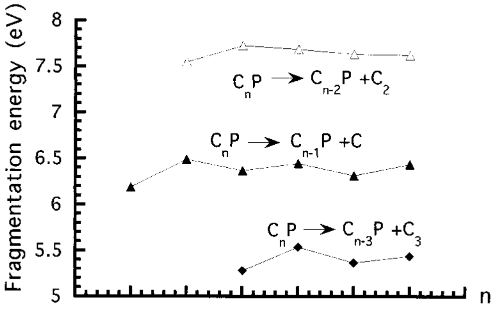


Figure 4. Fragmentation reaction energies (eV) for the C_nP clusters calculated with the B3LYP/6-311G* method.

than for n-even ones, even though the effect is not readily perceptible.

Besides, another feature, well marked in Figure 4, is that C_3 loss by C_nP clusters, with low dissociation energies of ~5.2−5.5 eV, is the dominant channel among the fragmentation pathways whereas C_2 loss, with high dissociation energies of ~7.5−7.7 eV, is much more difficult to realize.

3.2. C_nP^+ Clusters. In Figure 5 are displayed the structures and Mulliken atomic charges for C_nP^+. In Table 2 we report the corresponding binding energies, $\langle S^2\rangle$, vibrational frequencies, ZPE, and dipole moments. As for the neutrals, the lowest-lying isomers of the cations C_nP^+ are found to be the linears for $n = 1-7$. The $\langle S^2\rangle$ expectation value is generally calculated with a maximum deviation of 5%, indicating a rather low spin contamination for clusters whose ground state is $^3\Sigma^+$. Moreover, the energy differences between $^3\Sigma^+$ and the next $^1\Sigma^+$ are always found to be at least 13 kcal mol^{-1}, again preventing errors in the state ordering. In all cases, optimized cyclic and branched structures are likewise located well above the corresponding

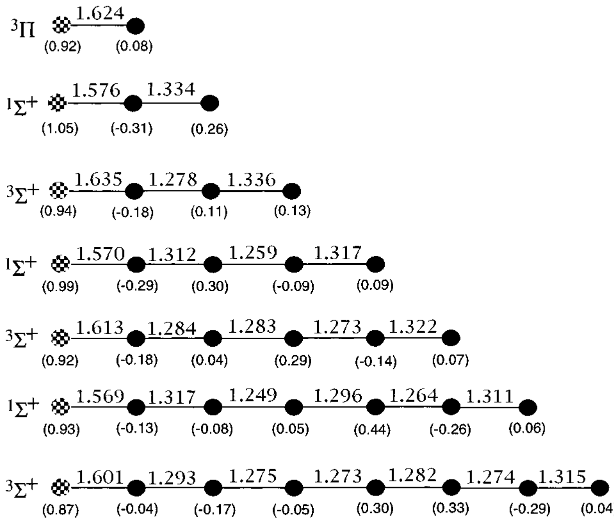


Figure 5. Equilibrium geometries of linear C_nP^+ ($n = 1-7$) clusters at the B3LYP/6-311G* level of theory. Distances are in angstroms and angles in degrees. Mulliken charge distributions are given in parentheses.

linear ground state with a relatively large energy separation of about 15, 21, and 30 kcal mol^{-1} for the lowest-lying cyclic isomers of C_2P^+, C_3P^+, C_5P^+, respectively. On the other hand, the lowest-lying cyclic structures of C_4P^+, C_6P^+, and C_7P^+ possess one or two large imaginary frequencies, indicating a saddle point on the corresponding energy surface. But in contrast with the neutrals, drastic even−odd alternation in the electronic ground state exists along the linear C_nP^+ series. Except for CP^+, the cationic clusters with odd n have a $^3\Sigma^+$ electronic ground state corresponding to a half-filled π-type orbital for the HOMO (electronic arrangement $\pi_+\alpha\pi_-\alpha$) and clusters with even n have a $^1\Sigma^+$ electronic ground state corresponding to fully occupied π-type orbitals. As is well-known,[5,10,28] the latter case (fully occupied π-type orbitals) corresponds to a situation energetically more favorable than the former one (half-filled π orbital). The electronic $^3\Pi$ ground state for CP^+ is obtained from the corresponding neutral by removal of a π electron from the HOMO (electron valence configuration of the neutral CP is $\{\text{core}\}\sigma^2\sigma^1\pi^4$). The computed CP distance in the cation CP^+ is ~1.62 Å, slightly longer than that of the neutral (evaluated to 1.56 Å). For $2 \le n \le 7$, this distance is ~1.57−1.58 Å in n-even clusters and slightly longer in n-odd clusters by 0.02−0.04 Å.

The atomic charge carried by the P atom is +0.9−1.0e; i.e., this atom appears fully cationic and, in return, the carbon chain is quasineutral (Figure 5). Dipole moments increase very regularly, as already found for the neutrals, but the interval of variation is much more reduced, from 0.35 D for C_2P^+ to 3.84 D for C_7P^+. The CC distances are typical of cumulene-type structures, that is, ~1.26−1.32 Å, although some polyacetylenic character appears in n-even clusters (C_4P^+, C_6P^+). C_nP^+ clusters can be obtained by removing the unpaired electron from phosporus in the corresponding C_nP neutrals, yielding the valence structure $^+$:P=C=C···C=C:.

C_nP^+, being isoelectronic to C_nSi, the lowest-lying geometry of C_nP^+, should be similar to C_nSi. That clusters with the same number of total valence electrons have a similar geometry may be suggested in order to deduce properties relative to some neutral species (C_nSi) (and difficult to investigate experimentally) by studying their charged isoelectronic partners (C_nP^+). Unfortunately, this simple rule is partially invalidated by the present analysis; e.g., C_3P^+ is found to be linear, but from ref 29 we know that C_3Si is cyclic.

TABLE 2: Binding Energies, $\langle S^2 \rangle$, Vibrational Frequencies, and Rotational Constants (B) for C_nP^+ Structures Optimized with the B3LYP/6-311G* Method

isomer	point group	state	binding energies[a] (eV)	$\langle S^2 \rangle$	vibrational frequencies (cm^{-1})	ZPE (kcal mol^{-1})	dipole moment (D)	B (MHz)
CP^+	$C_{\infty v}$	$^3\Pi$	4.7	2.03	1127(σ)	1.61	0.35	22152.5
C_2P^+	$C_{\infty v}$	$^1\Sigma^+$	12.6	0.00	133(π)^d, 880(σ), 1831(σ)	4.25	2.37	6421.0
C_3P^+	$C_{\infty v}$	$^3\Sigma^+$	18.7	2.05	98(π)^d, 330(π)^d, 658(σ), 1255(σ), 1997(σ)	6.81	2.45	2742.8
C_4P^+	$C_{\infty v}$	$^1\Sigma^+$	26.1	0.00	102(π)^d, 231(π)^d, 573(π)^d, 614(σ), 1269(σ), 1770(σ), 2211(σ)	10.97	2.94	1519.7
C_5P^+	$C_{\infty v}$	$^3\Sigma^+$	32.2	2.09	80(π)^d, 173($^\pi$)^d, 377(π)^d, 520(σ), 585(π)^d, 989(σ), 1495(σ), 1862(σ), 2118(σ)	13.46	3.18	907.7
C_6P^+	$C_{\infty v}$	$^1\Sigma^+$	39.3	0.00	67(π)^d, 155($^\pi$)^d, 276(π)^d, 476(σ), 542(π)^d, 778(π)^d, 954(σ), 1440(σ), 1758(σ), 2149(σ), 2229(σ)	18.07	3.39	600.2
C_7P^+	$C_{\infty v}$	$^3\Sigma^+$	45.4	2.13	53(π)^d, 126($^\pi$)^d, 223(π)^d, 391(π)^d, 424(σ), 555(π)^d, 813(σ), 830(π)^d, 1226(σ), 1542(σ), 1855(σ), 2006(σ), 2151(σ)	20.55	3.84	412.9

[a] For C(^{3}P), $E = -37.855\,989$ au, and for P$^+$(^{3} P), $E = -340.898\,061$ au.

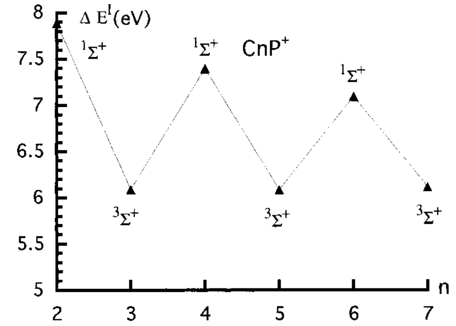


Figure 6. Incremental binding energies (eV) for the linear C_nP^+ clusters vs the number of carbon atoms.

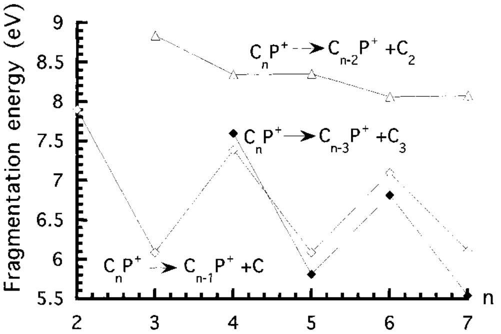


Figure 7. Fragmentation reaction energies (eV) for the C_nP^+ clusters calculated with the B3LYP/6-311G* method.

The incremental binding energy diagram for the cations (Figure 6) shows that n-even structures are drastically more stable than n-odd ones, as already ascertained above from electronic structure considerations. Similar conclusions can be drawn from the fragmentation patterns by considering the reactions $C_nP^+ \rightarrow C_{n-m}P^+ + C_m$ with $m = 1, 2, 3$ (Figure 7). C or C_3 loss leads to a parity inversion of the number of carbon atoms, the original (parent) clusters with an even (respectively, odd) number of carbon atoms giving fragment (daughter) clusters with an odd (respectively, even) number of carbon atoms. In contrast, no parity effect is perceptible on the curve corresponding to the C_2 loss channel.

3.3. C_nP^- Clusters. In Figure 8 are displayed the low-lying geometries for C_nP^- and in Table 3 the corresponding vibrational frequencies and other useful quantities for the experimentalists (dipole moments and rotational constants) calculated at the B3LYP/6-311 G* level of theory.

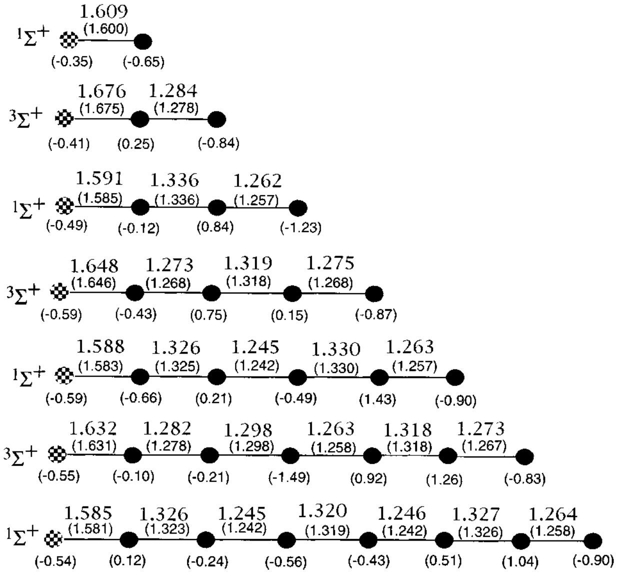


Figure 8. Equilibrium geometries of linear C_nP^- ($n = 1-7$) clusters at the B3LYP/6-311G* and B3LYP/Aug-cc-pVTZ levels of theory (the latter in parentheses). Distances are in angstroms and angles in degrees. B3LYP/Aug-cc-pVTZ Mulliken charge distributions are given in parentheses.

Our DFT calculations conclude that C_nP^- ($n = 1-7$) adopt linear structures for the lowest-lying geometry. As was previously found in the case of the C_nP^+ species, the spin contamination is low, smaller than 5%, which will not severely affect results. For open-shell C_nP^- clusters, the energy differences between $^3\Sigma^+$ and the next $^1\Sigma^+$ are likewise significant, about 13 kcal mol^{-1} or more (see Table 4), again preventing errors in the state ordering. A noteworthy feature is that these singlet−triplet energetic separations calculated at the B3LYP/6-311G* level are in excellent agreement with the results of CCSD(T) quality (see Tables 4 and 5b).

Electronic ground states alternate between $^1\Sigma^+$ for n-odd C_nP^- clusters and $^3\Sigma^+$ for n-even ones. This implies that n-odd clusters, with a fully occupied π orbital (HOMO in the π^4 electronic arrangement), are more stable than n-even clusters, which possess a half-filled HOMO in the $\pi_+\alpha\pi_-\alpha$ electronic arrangement, as can be seen from the incremental binding energy diagram (Figure 9) and the fragmentation patterns (Figure 10). This result is in good agreement with the odd−even alternation in the time-of-flight mass spectra observed by Huang et al.[15] In

TABLE 3: Binding Energies, $\langle S^2 \rangle$, Vibrational Frequencies, and Rotational Constants (B) for C_nP^- Structures Optimized with the B3LYP/6-311G* Method

isomer	point group	state	binding energies[a] (eV)	$\langle S^2 \rangle$	vibrational frequencies (cm^{-1})	ZPE (kcal mol^{-1})	dipole moment (D)	B (MHz)
CP^-	$C_{\infty v}$	$^1\Sigma^+$	7.0	0.00	$1190(\sigma)$	1.70	2.42	22560.3
C_2P^-	$C_{\infty v}$	$^3\Sigma^+$	13.1	2.02	$305(\pi)^d$, $759(^{\sigma})$, $1725(\sigma)$	4.42	3.37	6120.1
C_3P^-	$C_{\infty v}$	$^1\Sigma^+$	20.6	0.00	$209(\pi)^d$, $511(^{\pi})^d$, $701(\sigma)$, $1504(\sigma)$, $2047(\sigma)$	8.14	4.45	2795.7
C_4P^-	$C_{\infty v}$	$^3\Sigma^+$	26.4	2.05	$139(\pi)^d$, $336(^{\pi})^d$, $521(\pi)^d$, $568(\sigma)$, $1132(\sigma)$, $1817(\sigma)$, $1932(\sigma)$	10.64	5.05	1479.6
C_5P^-	$C_{\infty v}$	$^1\Sigma^+$	33.6	0.00	$100(\pi)^d$, $256(^{\pi})^d$, $470(\pi)^d$, $525(\sigma)$, $622(\pi)^d$, $1048(\sigma)$, $1598(\sigma)$, $2028(\sigma)$, $2177(\sigma)$	14.68	6.37	907.7
C_6P^-	$C_{\infty v}$	$^3\Sigma^+$	39.5	2.09	$76(\pi)^d$, $200(^{\pi})^d$, $350(\pi)^d$, $457(\sigma)$, $504(\pi)^d$, $702(\pi)^d$, $880(\sigma)$, $1341(\sigma)$, $1731(\sigma)$, $1963(\sigma)$, $2039(\sigma)$	17.26	6.57	589.6
C_7P^-	$C_{\infty v}$	$^1\Sigma^+$	46.5	0.00	$60(\pi)^d$, $159(^{\pi})^d$, $281(\pi)^d$, $421(\sigma)$, $457(\pi)^d$, $596(\pi)^d$, $828(\sigma)$, $845(\pi)^d$, $1248(\sigma)$, $1642(\sigma)$, $1979(\sigma)$, $2162(\sigma)$, $2197(\sigma)$	21.83	8.30	410.8

[a] For C(^{3}P), $E = -37.855\,989$ au, and for P$^-$(^{3}P), $E = -341.312\,362$ au.

TABLE 4: Low-Lying Singlet and Triplet States of C_nP^- ($n = 1-7$)[a]

C_nP^- anions	electronic states	E(MP2/ 6-311G*)	E(B3LYP/ 6-311G*)	E(B3LYP/ Aug-cc-p VTZ)	E[CCSD(T)/ 6-311G*// B3LYP/ 6-311G*]
CP^-	$^1\Sigma^+$	0.0	0.0	0.0	0.0
	$^3\Pi$	89.0	69.6	68.2	73.9
C_2P^-	$^1\Sigma^+$	14.3	19.3	19.1	18.4
	$^3\Sigma^+$	0.0	0.0	0.0	0.0
C_3P^-	$^1\Sigma^+$	0.0	0.0	0.0	0.0
	$^3\Sigma^+$	210.7	58.5	49.0	65.4
C_4P^-	$^1A'$	0.0	*b*	*b*	*b*
	$^1\Sigma^+$	0.1	15.6	15.6	13.7
	$^3\Sigma^+$	2.7	0.0	0.0	0.0
C_5P^-	$^1A'$	0.0	*b*	*b*	*b*
	$^1\Sigma^+$	0.4	0.0	0.0	0.0
	$^3\Sigma^+$	184.5	46.5	39.6	55.3
C_6P^-	$^1A'$	0.0	*b*	*b*	*b*
	$^1\Sigma^+$	0.4	13.5	13.6	10.0
	$^3\Sigma^+$	20.9	0.0	0.0	0.0
C_7P^-	$^1A'$	0.0	*b*	*b*	*b*
	$^1\Sigma^+$	0.2	0.0	0.0	0.0
	$^3\Sigma^+$	73.5	34.1	33.6	50.8

[a] Energies are given in kcal mol^{-1}. [b] The $^1A'$ state is virtually identical to the $^1\Sigma^+$ state.

the same way, it appears from Figure 3 that the calculated electronic affinities for the neutrals indicate that n-even C_nP^- can lose more easily an electron than those with odd n. This feature is also consistent with experiments that n-odd C_nP^- are more abundant in the recorded mass spectra.[15] A simple explanation for this is that the energy required to remove an electron from a closed-shell (and particularly stable) configuration (n-odd C_nP^-) is much higher than the energy needed for removal of an electron from an open-shell configuration (n-even C_nP^-).

The CP distance in CP^- is ~1.61 Å, typical of a strong double bond. For n-odd clusters this distance is ~1.59−1.60 Å. CP distances in n-even clusters are slightly longer (~1.68 Å for C_2P^-, ~1.65 Å for C_4P^-, and ~1.63 Å for C_6P^-). CC distances for n-even clusters are ~1.26−1.32 Å, typical of cumulenic structures. By contrast, there exists a weak alternation in the CC distances for the n-odd species, conferring to the latter ones some acetylenic character. For example, evaluated from phosphorus, these distances are 1.33, 1.24, 1.33, 1.25, 1.33, and 1.26 Å in C_7P^-. The dipole moments increase monotonically with size from 2.42 D for CP^- to 8.30 D for C_7P^-. These dipole moments are higher than those found in the neutrals and cations, by ~1−2 D compared to the neutrals and by ~2−3 D compared to the cations.

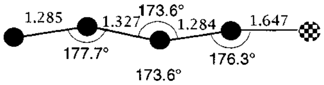
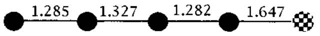
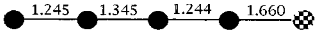
In fact, in the case of C_nP^- anions, the inclusion in the basis set of a very large number of diffuse and polarization functions could well be necessary in order to obtain reliable geometries for the low-lying states. Calculations have thus been performed in order to examine the influence of the flexibility of the basis set upon the structural parameter determination. For this purpose, we have employed the augmented correlation-consistent polarized valence triple-ζ (Aug-cc-pVTZ) basis set of Dunning and co-workers.[24−26] Finally, however, the calculated results presented in Figure 8 for both 6-311 G* and Aug-cc-pVTZ basis sets clearly show that the additional diffuse functions included in the Aug-cc-pVTZ do not appear really significant in the geometry optimization of C_nP^- [this statement is all the more important because we are concerned with the geometry determination of medium-sized, and subsequently large-sized, clusters for which the use of a very large basis set, such as Aug-cc-pVTZ, becomes largely prohibitive, in terms of CPU time, beyond $n = 7$]. As a matter of fact, by changing the basis set from 6-311 G* to Aug-cc-pVTZ, the CP distances in n-even (respectively, n-odd) clusters are systematically shortened by only ~10^{-3} Å (respectively, ~5×10^{-3} Å). In the same way, the CC distances are slightly reduced by similar values equal to or smaller than ~5×10^{-3} Å.

Aug-cc-pVTZ Mulliken charge distributions are given in Figure 8. We can see that the negative charge seems mostly concentrated at the two extremities of the chain, in agreement with the fact that the highest occupied orbital (HOMO) of these clusters is partially localized on the terminal atoms. There nevertheless exist strong oscillations of the charge along the carbon chain. Thus, except for C_4P^-, the penultimate carbon bears a positive charge larger than $+1e$ for C_5P^- ($+1.43e$), C_6P^- ($+1.27e$), and C_7P^- (+1.04e).

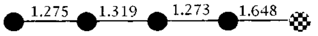
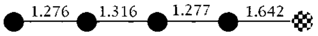
C_nP^- clusters have also been investigated by Zhan and Iwata[16] by employing the MP2/6-31G(d) [END$^+$] method. The basis used by them is an usual 6-31G(d) basis set augmented with additional diffuse sp functions only on the two end atoms. These authors find bent structures for the ground state of C_4P^- and C_6P^-, in contrast to the present work where these two clusters are found to be strictly linear. To understand the origin of this conflict, we have optimized the geometry of C_4P^- at the MP2/6-311G* level, and energies have been calculated at both MP2/

TABLE 5: Optimized Geometries for the Low-Lying Singlet and Triplet States of C_4P^-

(a) Calculated at the MP2/6-311G* Level[a]

	MP2/ 6-311G*	E(MP2/ 6-311G*)	E(CCSD(T)/ 6-311G*)
$^1A'$		0.0	11.6
$^1\Sigma^+$		0.1	11.8
$3\Sigma^+$		2.7	0.0

(b) Calculated with B3LYP/6-311G* Method[b]

	B3LYP/ 6-311G*	E(B3LYP/ 6-311G*)	E(B3LYP/ Aug-cc-pVTZ)	E[CCSD(T)/ 6-311G*]
$^3\Sigma^+$		0.0	0.0	0.0
$^1\Sigma^+$		15.6	15.6	13.7

[a] Energies, given in kcal mol^{-1}, are calculated at MP2/6-311G*//MP2/6-311G* and CCSD(T)/6-311G*//MP2/6-311G* levels. [b] Energies, given in kcal mol^{-1}, are calculated at B3LYP/6-311G*//B3LYP/6-311G*, B3LYP/Aug-cc-pVTZ//B3LYP/Aug-cc-pVTZ, and CCSD(T)/6-311G*//B3LYP/6-311G* levels.

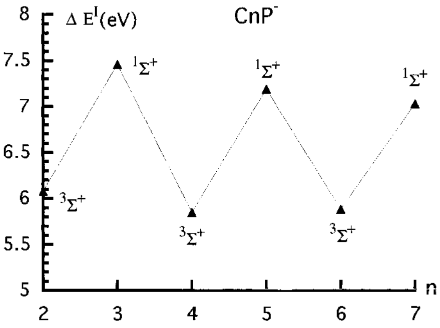


Figure 9. Incremental binding energies (eV) for the linear C_nP^- clusters vs the number of carbon atoms.

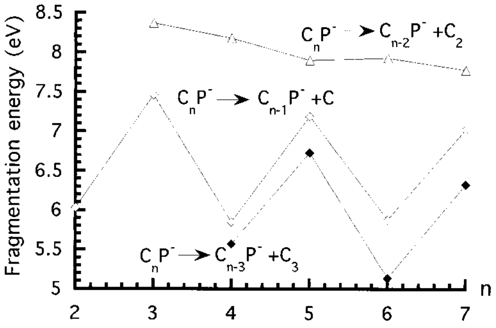


Figure 10. Fragmentation reaction energies (eV) for the C_nP^- clusters calculated with the B3LYP/6-311G* method.

6-311G* and CCSD(T)/6-311G* levels (Table 4a). Calculations at the MP2/6-311G*//MP2/6-311G* level effectively give results in very close agreement with those previously reported by Zhan and Iwata,[16] in particular that C_4P^- is slightly bent in its ground state (Table 5a). But the optimized geometry obtained at this level of theory may be qualitatively incorrect for C_nP^-. As a matter of fact, computations performed at the CCSD(T)/6-311G*// MP2/6-311G* level indeed predict that this bent structure lies at 14.0 kcal mol^{-1} above the true linear ground state ($^3\Sigma^+$). The latter statement is also confirmed by other computations made at various levels of theory, i.e., B3LYP/6-311G*// B3LYP/6-311G*, B3LYP/Aug-cc-pVTZ//B3LYP/Aug-cc-pVTZ, and CCSD(T)/6-311G*//B3LYP/6-311G*, from all of which we derive quite comparable relative energies, in clear contrast to relative energies obtained at the MP2 level (Tables 4 and 5a). In any case, starting from the bent MP2 geometry given by Zhan and Iwata, DFT B3LYP/6-311G* calculations directly converge to a linear structure.

We can thus conclude that electron correlation is insufficiently taken into account at the MP2/6-31G* or MP2/6-31G(d)[END$^+$] level of energy computations such as those reported in ref 16 for C_nP^- and that much higher levels of theory definitely predict C_4P^- to be linear. A very similar conclusion can be made, in particular for C_6P^-, but also for the other to suppress C_nP^- ($n = 2-7$) clusters (Table 4).

Eventually, C_nP^- being isoelectronic to C_nS, it would be most interesting to note that both of them adopt linear geometries and are presenting the same alternation of $^1\Sigma$ for odd n and $^3\Sigma$ for even n in their electronic ground states, leading to a similar odd−even parity effect in cluster stability.

4. Conclusion

C_nP, C_nP^+, and C_nP^- have been simultaneously studied by a DFT method. The lowest-lying geometry is found to be linear with the P atom located at the very end of the carbon chain. An odd−even parity effect exists for both the neutral and anionic species, but this effect is strong in the anionic series while it is much less pronounced in the neutral series. Besides, the cations present a reversed, even−odd, alternation in stability. The simple rule that a similar number of valence electrons implies a similar geometry for two isoelectronic clusters is invalidated for C_3P^+ (linear) and C_3Si (cyclic). Finally, the analysis of the fragmentation energy diagrams shows that C_nP in neutral, cationic, or anionic form can easily lose a C_3 fragment but that C_2 loss is relatively difficult to realize.

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