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International Journal of Mass Spectrometry 189 (1999) 125–132

Geometrical structures of the phosphorus-doped carbon cluster cations C_nP^+ ($n = 1$–20)

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Received 20 January 1999; accepted 29 March 1999

Abstract

The C_nP^+ ($n = 1$–20) clusters have been investigated by the density functional theory. Equilibrium structures have been determined for linear and cyclic isomers. We have found that C_nP^+ are unambiguously linear up to $n = 9$ and, on the contrary, cyclic isomers are the most stable structures when $n \geq 13$. In the intermediate region, $10 \leq n \leq 12$, the cyclic and linear isomers of $C_{10}P^+$ are found to be almost isoenergetic, while a linear structure is favored for $C_{11}P^+$ and $C_{12}P^+$. (Int J Mass Spectrom 189 (1999) 125–132) © 1999 Elsevier Science B.V.

Keywords: Density functional theory (DFT); C_nP^+; Carbon clusters

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1. Introduction

Very large interest in pure carbon clusters has led to a variety of experimental [1–4] and theoretical predictions [5,6] of their structure and properties. From these united experimental and theoretical studies, it was inferred that in pure carbon clusters, C_n, linear and cyclic structures largely coexist when $n \leq 9$, but that the most stable geometric isomer appears to definitely change from linear to monocyclic ring at $n = 10$. In the past few years, a number of heteroatom-containing carbon clusters have also been studied fairly extensively by use of both experiment [7–12] and theoretical calculations [13–16]. These various investigations have shown that the addition of a foreign atom such as B, N, Si, P, or S to small and medium-sized pure carbon clusters can lead to drastic changes in both the geometry and electronic properties of these clusters. Previous density functional theory (DFT) studies have recently stressed out that the addition of a Si^+ cation to C_n leads to a similar irreversible change, i.e. from linear to cyclic form at $n = 10$, as for pure carbon clusters [16]. Besides, the introduction of a S^+ cation in a pure carbon structure completely modifies this behavior and the linear to cyclic transition is delayed up to $n = 18$, even though additionally, this change with size is not definitive, given that $C_{20}S^+$ is again found linear in its ground state [17]. A similar conclusion can be made for the neutral C_nS structures [18]. We report below DFT computations on C_nP^+ ($n = 1$–20) clusters in order to see how this change in structure appears when the heteroatom is phosphorus. The latter ele-

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PII S1387-3806(99)00062-7

ment being located between silicon and sulphur in the Periodic Table, we should observe an intermediate situation and we eventually conclude that this is truly the case. Unfortunately, there are no experimental data on C_nP cations to compare to our theoretical results. Besides there are published experimental results on the C_nP anions by Wang et al [9]. The latter authors conclude that C_nP^- are linear in their ground states with phosphorus located at the end of the carbon chain. We hope that the present calculations would stimulate similar experimental investigations on the corresponding cations.

2. Computational details

All DFT calculations were carried out using the library Gaussian 94 [19] on a HP 9000/770 workstation. B3LYP hybrid density functional was employed. The B3LYP consists of the Lee-Yang-Parr correlation functional [20] together with a hybrid exchange functional suggested by Becke [21]. Becke's three-parameter hybrid functional is a linear combination of the local density approximation, Becke's gradient correction [22] and the Hartree-Fock exchange energy based on Kohn-Sham orbitals [23]. The basis sets employed in this study are the Pople's 6-31G* and 6-311G* basis sets [24] for carbon and phosphorus. Other basis (6-31G^{++}** and B3LYP/Aug-cc-pVTZ) have also been used for small clusters ($n \leq 7$) but the results are very similar and consequently are not reported in the present article. As known, B3LYP density functional calculations are able to give accurate equilibrium geometries and harmonic frequencies for heteroatom-containing carbon clusters [14,25,26]. Standard Gaussian convergence criteria were used for these calculations.

3. Results and comments

Table 1 presents the calculated binding energies, vibrational frequencies, dipole moments, and rotational constants of the lowest-lying states of each linear and cyclic isomers of C_nP^+ ($n = 1$–6) clusters. Table 2 lists the structural parameters, total energies, relative stabilities, and dipole moments of the lowest-lying linear and cyclic C_nP^+ ($n = 7$–13) isomers. The corresponding geometries are graphically displayed in Fig. 1.

Results of calculations for $n \geq 14$ are not given in order to save space but are available upon request. B3LYP/6-311G* and B3LYP/6-31G* methods are respectively employed when $1 \leq n \leq 14$ and $14 \leq n \leq 20$.

3.1. Linear C_nP^+ isomers

Linear C_nP^+ ($n = 1$–20) clusters are found to be formed of a carbon chain with a terminal phosphorus atom bearing the positive charge. This outer position is always preferred by second-row atoms included in linear carbon chains as already encountered in other situations such as C_nSi^+ and C_nS^+ [16,17]. CP distances in n-odd clusters are ~1.62 Å for CP^+, ~1.63 Å for C_3P^+, regularly decrease from ~1.61 Å for C_5P^+ to ~1.58 Å for $C_{13}P^+$ and then stabilize around this value up to $n = 19$. CP distances in n-even clusters are slightly smaller and invariably of the order of 1.57 Å. With respect to the CP bond length found in CH_2PH (~1.67 Å), classified as a normal double CP bond [27], the CP distances in the linear C_nP^+ ($n = 1$–20) clusters are typical of strong CP double bonds. Given that the CC distances, with minimum value ~1.24 Å and maximum value ~1.33 Å, are also indicative of strong double CC bonds, linear C_nP^+ can be regarded as cumulene-like structure, with one lone pair at each extremities, i.e. $:C{=}C{=}...{=}C{=}P:^+$. We must however notice that a small bond alternation appears in n-even clusters, CC distances ~1.29–1.33 Å alternating with CC distances ~1.24–1.27 Å, confering to these molecules some polyacetylenic character not apparent in n-odd clusters.

The dipole moments increase monotonically with size from 0.35 D for CP^+ to 3.84 D for C_7P^+. As soon as $n \geq 8$, the dipole moment exhibits an

Table 1
Binding energies, vibrational frequencies, and rotational constants (A, B, C) for C_nP^+ (n = 1–6) structures optimized with B3LYP/6-311G* method

Isomer	Point group	State	Binding energies[a] (eV)	Vibrational frequencies (cm^{-1})	ZPE (kcal mol^{-1})	Dipole moment (debye)	A, B, C (MHz)
CP^+	$C_{\infty v}$	$^3\Pi$	4.7	1127(σ)	1.6	0.35	22 152.5
C_2P^+	$C_{\infty v}$	$^1\Sigma^+$	12.6	133(π)[d] 880(σ) 1831(σ)	4.2	2.37	6 421.0
	C_{2v}	$^1A_1$	12.0	197(*b*2) 942(*a*1) 1768(*a*1)	4.1	1.62	51 718.4 14 482.5 11 314.2
C_3P^+	C_{00v}	$^3\Sigma^+$	18.7	98(π)[d] 330(π)[d] 658(σ) 1255(σ) 1997(σ)	6.8	2.45	2 7.42.8
	C_{2v}	$^3B_1$	17.8	419(*b*1) 430(*b*2) 624(*a*1) 901(*a*1) 1131(*b*2) 1598(*a*1)	7.3	0.78	36 708.2 6 486.9 5 512.7
C_4P^+	$C_{\infty v}$	$^1\Sigma^+$	26.1	102(π)[d] 231(π)[d] 573(π)[d] 614(σ) 1269(σ) 1770(σ) 2211(σ)	11.0	2.94	1 519.7
	C_{2v}	$^1A_1$	22.6	277*i*(*b*2) 118(*b*1) 245(*a*1) 395(*a*2) 583(*b*2) 619(*a*1) 990(*a*1) 1621(*b*2) 1837(*a*1)	9.2	0.80	12 388.4 5 477.8 3 798.3
(P-C_4 rhombus)	C_{2v}	$^1A_1$	23.0	626*i*(*b*2) 2*i*(*b*2) 203(*b*1) 497(*b*1) 591(*a*1) 923(*a*1) 976(*b*2) 1326(*a*1) 1461(*a*1)	8.6	5.24	37 811.0 2 639.1 2 467.0
C_5P^+	$C_{\infty v}$	$^3\Sigma^+$	32.2	80(π)[d] 173(π)[d] 377(π)[d] 520(σ) 585(π)[d] 989(σ) 1495(σ) 1862(σ) 2118(σ)	13.5	3.18	907.7
	C_{2v}	$^1A_1$	31.0	320(*b*2) 339(*b*1) 437(*a*2) 475(*b*1) 508(*a*1) 595(*a*1) 622(*b*2) 727(*a*1) 1250(*a*1) 1594(*b*2) 1777(*a*1) 1800(*b*2)	14.9	0.52	7 444.7 3 968.0 2 588.5
C_6P^+	C_{00v}	$^1\Sigma^+$	39.3	67(π)[d] 155(π)[d] 276(π)[d] 476(σ) 542(π)[d] 778(π)[d] 954(σ) 1440(σ) 1758(σ) 2149(σ) 2229(σ)	18.1	3.39	600.2
	C_{2v}	$^1A_1$	38.2	128*i*(*b*2) 211(*b*1) 312(*a*1) 381(*a*2) 405(*b*2) 413(*a*2) 536(*b*1) 541(*a*1) 585(*b*2) 727(*a*1) 1238(*a*1) 1409(*b*2) 1753(*a*1) 1855(*a*1) 1930(*b*2)	17.4	0.76	54 440.4 2 611.6 1 764.5

[a] For C(^3P) E = −37.855 989 a.u. and P^+(^3P) E = −340.898 061 a.u.

odd–even alternation with values slightly stronger for n-odd clusters (>4 D) than for n-even clusters (<4 D).

Linear C_nP^+ clusters possess $2n\pi$ electrons (see Table 3). For even n, the doubly degenerate π orbitals are all fully filled with four electrons resulting in a $^1\Sigma^+$ electronic ground state. Besides, for odd n, the highest occupied π orbital (HOMO) is half-filled with two electrons resulting in a $^3\Sigma^+$ electronic ground state (except for n = 1 for which a $^3\Pi$ state is found). According to the molecular orbital theory, the former situation (fully filled π orbitals) is energetically much more stable than the latter one (half-filled π orbitals). The incremental binding energy diagram displayed in Fig. 2 indeed reveals that C_nP^+ clusters with even clustering ($^1\Sigma^+$ ground state) have higher structural

Table 2
Structural parameters (distances in angstroms, angles in degrees), total energies (in hartree), relative stabilities ΔE (in kcal mol^{-1}) and dipole moments (in debye) of the different C_nP^+ ($7 \leq n \leq 13$) clusters obtained with a DFT/B3LYP/6-311G* method; the electronic ground state of each isomer is also given

Isomer	Point group	State	Structural parameters	ΔE^a	μ
C_7P^+				−607.559 715	
lin7[b]	$C_{\infty v}$	$^3\Sigma^+$	$d1 = 1.601$ $d2 = 1.293$ $d3 = 1.275$ $d4 = 1.273$ $d5 = 1.282$ $d6 = 1.274$ $d7 = 1.315$	0.0	3.84
cyc7	C_{2v}	$^1A_1$	$d0 = 1.468$ $d1 = 1.763$ $d2 = 1.338$ $d3 = 1.277$ $d4 = 1.302$ $\theta = 49.2$ $\theta1 = 183.7$ $\theta2 = 144.7$ $\theta3 = 118.2$ $\theta4 = 137.6$	35.3	0.58
C_8P^+				−645.670 678	
lin8	$C_{\infty v}$	$^1\Sigma^+$	$d1 = 1.568$ $d2 = 1.320$ $d3 = 1.246$ $d4 = 1.302$ $d5 = 1.253$ $d6 = 1.291$ $d7 = 1.268$ $d8 = 1.307$	0.0	3.77
cyc8	C_{2v}	$^3A_2$	$d1 = 1.760$ $d2 = 1.244$ $d3 = 1.340$ $d4 = 1.248$ $d5 = 1.339$ $\theta1 = 86.9$ $\theta2 = 161.7$ $\theta3 = 147.0$ $\theta4 = 142.5$ $\theta5 = 135.3$	45.7	0.37
C_9P^+				−683.752 121	
lin9	$C_{\infty v}$	$^3\Sigma^+$	$d1 = 1.593$ $d2 = 1.299$ $d3 = 1.269$ $d4 = 1.279$ $d5 = 1.277$ $d6 = 1.271$ $d7 = 1.281$ $d8 = 1.275$ $d9 = 1.310$	0.0	4.42
cyc9	C_{2v}	$^1A_1$	$d0 = 1.496$ $d1 = 1.720$ $d2 = 1.327$ $d3 = 1.268$ $d4 = 1.300$ $d5 = 1.295$ $\theta = 51.6$ $\theta1 = 187.6$ $\theta2 = 161.3$ $\theta3 = 130.9$ $\theta4 = 124.4$ $\theta5 = 110.6$	7.6	2.65
$C_{10}P^+$				−721.859 343	
lin10	$C_{\infty v}$	$^1\Sigma^+$	$d1 = 1.567$ $d2 = 1.323$ $d3 = 1.244$ $d4 = 1.306$ $d5 = 1.249$ $d6 = 1.297$ $d7 = 1.256$ $d8 = 1.288$ $d9 = 1.271$ $d10 = 1.304$	0.1	4.04
cyc10	C_{2v}	$^1A_1$	$d0 = 1.469$ $d1 = 1.730$ $d2 = 1.344$ $d3 = 1.247$ $d4 = 1.319$ $d5 = 1.251$ $d6 = 1.321$ $\theta = 50.3$ $\theta1 = 197.1$ $\theta2 = 149.7$ $\theta3 = 155.9$ $\theta4 = 142.0$ $\theta5 = 140.1$	0.0	2.83
$C_{11}P^+$				−759.941 220	
lin11	$C_{\infty v}$	$^3\Sigma^+$	$d1 = 1.588$ $d2 = 1.304$ $d3 = 1.263$ $d4 = 1.285$ $d5 = 1.272$ $d6 = 1.276$ $d7 = 1.278$ $d8 = 1.271$ $d9 = 1.280$ $d10 = 1.277$ $d11 = 1.307$	0.0	4.92
cyc11	C_{2v}	$^1A_1$	$d0 = 1.442$ $d1 = 1.758$ $d2 = 1.333$ $d3 = 1.257$ $d4 = 1.298$ $d5 = 1.277$ $d6 = 1.289$ $\theta = 48.4$ $\theta1 = 194.2$ $\theta2 = 163.6$ $\theta3 = 155.4$ $\theta4 = 157.5$ $\theta5 = 132.3$ $\theta6 = 153.3$	2.0	0.56
$C_{12}P^+$				−798.045 423	
lin12	$C_{\infty v}$	$^1\Sigma^+$	$d1 = 1.567$ $d2 = 1.324$ $d3 = 1.242$ $d4 = 1.309$ $d5 = 1.247$ $d6 = 1.301$ $d7 = 1.253$ $d8 = 1.294$ $d9 = 1.259$ $d10 = 1.285$ $d11 = 1.273$ $d12 = 1.302$	0.0	4.22
cyc12	C_{2v}	$^1A_1$	$d0 = 1.389$ $d1 = 1.751$ $d2 = 1.376$ $d3 = 1.226$ $d4 = 1.351$ $d5 = 1.228$ $d6 = 1.353$ $d7 = 1.230$ $\theta = 46.7$ $\theta1 = 198.7$ $\theta2 = 161.8$ $\theta3 = 161.0$ $\theta4 = 150.6$ $\theta5 = 150.0$ $\theta6 = 144.5$	7.3	3.32
$C_{13}P^+$				−836.143 895	
lin13	$C_{\infty v}$	$^3\Sigma^+$	$d1 = 1.583$ $d2 = 1.309$ $d3 = 1.259$ $d4 = 1.290$ $d5 = 1.267$ $d6 = 1.281$ $d7 = 1.274$ $d8 = 1.274$ $d9 = 1.279$ $d10 = 1.271$ $d11 = 1.279$ $d12 = 1.278$ $d13 = 1.305$	9.9	5.33
cyc13	C_{2v}	$^1A_1$	$d0 = 1.458$ $d1 = 1.731$ $d2 = 1.332$ $d3 = 1.253$ $d4 = 1.301$ $d5 = 1.269$ $d6 = 1.292$ $d7 = 1.284$ $\theta = 49.8$ $\theta1 = 196.9$ $\theta2 = 167.8$ $\theta3 = 155.6$ $\theta4 = 165.5$ $\theta5 = 140.2$ $\theta6 = 163.3$ $\theta7 = 131.7$	0.0	3.01

[a] Total energies in Hartree.

[b] lin$n$ ≡ linear C_nP^+ isomer, cycn ≡ cyclic C_nP^+ isomer.

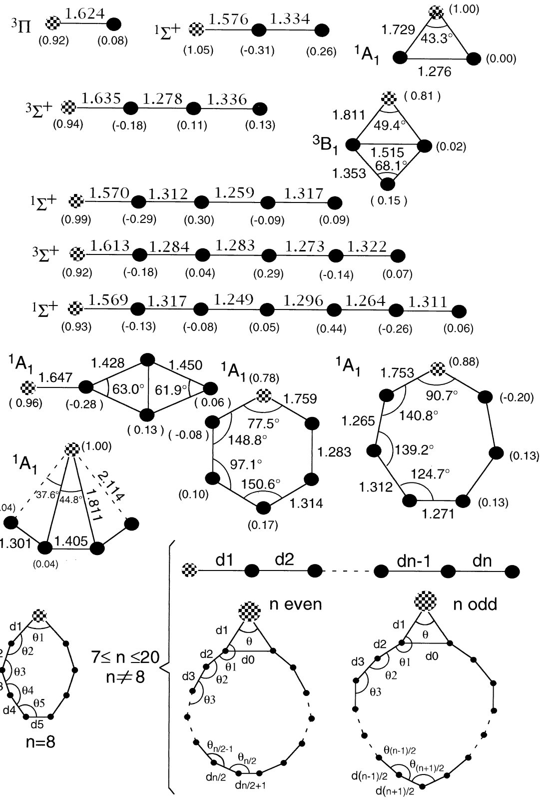

Fig. 1. B3LYP/6-311G* optimized geometries of the lowest-lying linear and cyclic structures of C_nP^+ cations. Bond lengths in angstroms and angles in degrees. Numbers in parentheses represent the Mulliken charge distributions.

stability than those with odd clustering ($^3\Sigma^+$ ground state). Interestingly enough, this parity effect is completely opposite to that found in linear C_nS. Linear C_nS clusters have $2n + 2\pi$ electrons and consequently, an odd–even effect in parity is existing in the latter compounds [18].

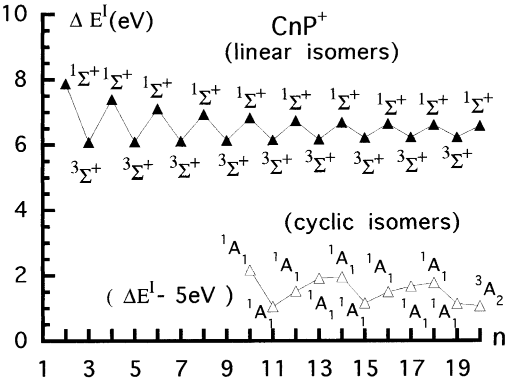

Fig. 2. Incremental binding energies (eV) for the linear and cyclic C_nP^+ clusters vs. the number of carbon atoms.

3.2. Cyclic isomers

The lowest-lying cyclic structure of C_2P^+ is a $^1A_1$ state located at about 15 kcal mol^{-1} above the linear ground state. By comparison the lowest-lying linear and cyclic isomers of the C_2Si^+ species were found to be nearly isoenergetic [28,29]. On the other hand, C_2P^+ is isoelectronic to C_2Si in its neutral form and it is known from previous work that the latter compound is cyclic in its ground state [30]. In this case, however, the extra charge beared by C_2P^+ destabilizes the structure by coulombic repulsion and then, even though C_2Si is cyclic, C_2P^+ is found to be ultimately linear in its ground state. The vibrational frequencies are all real indicating that the C_2P^+ cyclic isomer is a local minimum on the energy surface. The CP distances of about 1.73 Å are intermediate between a standard single CP bond, ~1.86 Å in CH_3PH, and a standard double CP bond length, ~1.76 Å in CH_2PH [27]. CP bonds in C_2P^+ may thus be ascribed as weak

Table 3
Valence orbital configuration for the linear C_nP^+ isomers

Geometries	Configuration
lin1	{core} $(\sigma)^2(\sigma)^2(\sigma)^1(\pi)^2(\pi)^1$
lin2	{core} $(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2$
lin3	{core} $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^1(\pi)^1$
lin4	{core} $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\pi)^2(\pi)^2\ (\sigma)^2$
lin5	{core} $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^1(\pi)^1$
lin6	{core} $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^2(\pi)^2$

double CP bonds. Besides the CC distance of 1.28 Å is representative of a strong double CC bond. The extra charge is entirely concentrated on the phosphorus atom ($+1.0e$) and the C_2 submolecule is neutral.

The first cyclic C_3P^+ in the energetic ordering is a rhombic $^3B_1$ structure. It possesses moderately strong single CP bonds with length equal to about 1.81 Å and typical double CC bonds with length of the order of 1.35 Å. As for C_2P^+ the phosphorus bears the positive charge. The transannular CC bond corresponds to a normal single CC bond with length of 1.51 Å (1.54 Å in ethane). This triplet cyclic isomer, located at about 21 kcal mol^{-1} above the linear ground state, is a high-energy local minimum on the energy surface, i.e. its frequencies are all real. The first singlet cyclic ($^1A_1$) lies at 33 kcal mol^{-1} above the linear and exhibits a $b1$ imaginary frequency indicating that it is not a true minimum on the energy surface. By comparison, we recall that for C_3Si, in both neutral and ionized forms, the cyclic arrangement of nuclei was predicted to be more stable than the linear one [31,32,33].

Assuming, at the initial computational stage, a closed pentagonal form for C_4P^+, we obtain a quite unexpected optimized structure composed of a bent carbon chain capped by a phosphorus atom (Fig. 1). The phosphorus atom bears the totality of the extra charge and the carbon atom chain is neutral. The CC distances, ~1.30 and 1.40 Å, respectively, correspond to moderately strong and weak double CC bonds. Besides CP bond lengths are very long, ~1.84 and 2.11 Å, and can, respectively, be ascribed as normal and very weak single CP bonds. In any way, this structure, located well higher in energy (82 kcal mol^{-1}) above the linear ground state, possesses an imaginary frequency and, consequently, is not a local minimum on the energy surface. (There indeed exists another isomer slightly more stable than this structure and the lowest-lying planar C_4P^+ is eventually a P-capped bicyclic C_4 rhombus located at about 73 kcal mol^{-1} above the linear ground state. But, again, the latter structure is a saddle point on the energy surface with one imaginary frequency.)

The next cyclic isomers in the C_nP^+ series corresponding to the cations C_5P^+, C_6P^+, C_7P^+, and C_8P^+ likewise possess one or two imaginary frequencies and each of them represents a saddle point on the related energy surface. All these species are located well above their related linear ground state. The energy differences are of the order of 29, 25, 35, and 46 kcal mol^{-1}, respectively, for C_5P^+, C_6P^+, C_7P^+, and C_8P^+. Besides the lowest-lying cyclic isomers for the C_nP^+ ($n \geq 9$) cations have all their frequencies real and each of these structures thus corresponds to a local minimum on the energy surface. Cyclic C_9P^+ is still located above the linear ground state but, this time, the energy separation is relatively small ~8 kcal mol^{-1} (Fig. 3). For C_9P^+ and larger clusters, the phosphorus atom systematically takes an exohedral position with regard to the carbon monocyclic ring-like substructure. The CP bonds with lengths ~1.72–1.76 Å, can be assimilated to double CP bonds. Along the C_n ring, double CC bonds ~1.30–1.34 Å alternate with strong double bonds ~1.24–1.28 Å. The C_n substructure in cyclic C_nP^+ ($n = 9$–20) can thus be depicted as a quasi-cumulenic-bonded ring with some superimposed polyacetylenic character. However, the phosphorus-bridged CC bond, ~1.43–1.52 Å, is somewhat elongated from a normal double bond, also this substructure is markedly distorted compared with a purely cumulenic or polyacetylenic entity.

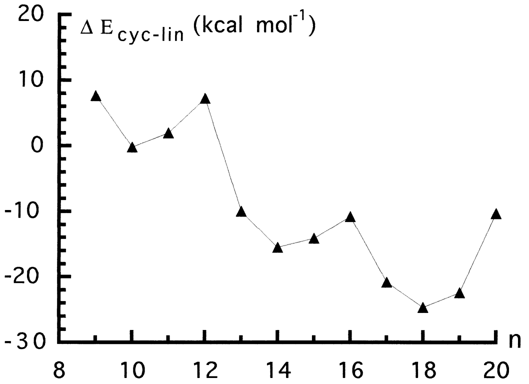

Fig. 3. Energy separation between the lowest energy cyclic and linear structures for the C_nP^+ clusters as a function of n. A negative value indicates that the linear isomer is less stable than the corresponding cyclic one.

The $C_{10}P^+$ cluster is the first one in the C_nP^+ series where the cyclic isomer is predicted to be more stable than the corresponding linear, even though the energy difference between the linear and the cyclic structure is quite small indeed $\sim$0.1 kcal mol^{-1} (Fig. 3). The $C_{11}P^+$ and $C_{12}P^+$ clusters are again linear in their ground state by 2 and 7 kcal mol^{-1}, respectively. Eventually for $n \geq 13$, the cyclic structure is favored over the corresponding linear one. In the cyclic isomer series ($n \geq 13$), the stability is dependent on "magic numbers," i.e. the stability is maximum for $n = 10, 14, 18$ as shown on the incremental energy diagram depicted in Fig. 2. A comparison with the neighbouring heteroatom-containing species, that is C_nSi^+ and C_nS^+, is most interesting. The C_nSi^+ clusters become definitely cyclic at $n = 10$ [16] while C_nS^+ clusters are predicted to be linear in their ground state up to $n = 17$ [17]. For C_nP^+, with P located between Si and S, an intermediate situation occurs where the structure shifts from linear to cyclic ring, for the first time, at $n = 10$, but with an insignificant linear-cyclic energy separation and the clear transition to cyclic ground state is delayed at $n = 13$.

In fact, as soon as $n \geq 10$, each of the cyclic isomers relative to the cations studied C_nSi^+, C_nP^+, and C_nS^+ may be regarded as a pure carbon monocyclic ring, C_n, with an heteroatom X (Si, P, S) bearing a large fraction of the extra charge and bound to the outside of the C_n ring. It is worthy to note that the pure carbon monocycle still imposes the "$4n + 2$ rule" in the stability of C_nSi^+, C_nP^+, and C_nS^+ cyclic species, the latter ones exhibiting magic peaks at $n = 10, 14, 18$ in the incremental energy diagrams as soon as $n \geq 10$ [16,17]. The heteroatom X bridges over a CC bond of the C_n submolecule and forms with the two carbon atoms of this bond a C_2X^+ entity. As a matter of fact, the cyclic C_nX^+ isomers ($n \geq 10$) can still be viewed as a bicyclic structure with a transannular CC bond. The stability of the C_2X^+ moiety can thus play a role in the overall stability of these clusters. First, the linear and cyclic C_2Si^+ isomers are predicted to be almost isoenergetic [28,29] and we know that the C_nSi^+ clusters become cyclic at $n = 10$ [16]. In contrast with this situation encountered in C_nSi^+ clusters, the cyclic isomer of C_2P^+ is less stable than the corresponding linear one by 15 kcal mol^{-1}. It is thus a little more difficult to close up a C_nP^+ cluster (transition to cyclic form shifted at $n = 13$) than to close up a C_nSi^+ cluster (transition to cyclic form located at $n = 10$), most likely because the relative stability of the C_2P^+ moiety in cyclic C_nP^+ is much lower than the corresponding one valued for the C_2Si^+ submolecule in cyclic C_nSi^+. Besides, C_2S^+ is linear in its ground state and the first cyclic isomer of this cluster, representing a local minimum in the energy surface, is located well above the linear at about 35 kcal mol^{-1} [17]. Once again, this certainly explains, in part, why it is so difficult to close up a C_nS^+ cluster (transition to cyclic form shifted at $n > 17$) in spite of the very large stability of the monocyclic C_n substructure when $n \geq 10$.

4. Conclusion

Density functional computations using B3LYP functional have been carried out on linear and cyclic C_nP^+ ($n = 1$–20) clusters for which correlation effects are known to be important. The calculations find a linear arrangement of nuclei, with the phosphorus atom attached at one end of the carbon chain, as ground state when $n \leq 9$. $C_{10}P^+$ is predicted to be cyclic in its ground state but present a very weak barrier to linearity. Again $C_{11}P^+$ and $C_{12}P^+$ are found to be linear and the C_nP^+ cations become definitely cyclic only when $n \geq 13$. In all cyclic structures with $n \geq 9$, the phosphorus atom occupies an exohedral position with regard to the carbon monocyclic ring. Incremental energy diagrams clearly show that along the linear series n-even clusters are more stable than the adjacent n-odd ones. On the other hand, cyclic structures follow a fourfold periodicity in stability as soon as $n \geq 10$.

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