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Structural and electronic properties of $ZnC_n^{+/-}$ clusters

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ABSTRACT

The structures and molecular properties of open-chain and cyclic $ZnC_n^{+/-}$ (n = 1–8) clusters have been calculated by hybrid density functional theory. Equilibrium geometries, electronic energies, vibrational frequencies, dipole moments and rotational constants for individual species are provided. Some energetic aspects related to these clusters, such as their relative stabilities, are discussed in terms of the incremental binding energy, ionization energy and electron affinity. In addition, the competition between linear and cyclic structures is studied. In general, the incremental binding energy graphs show an even–odd parity effect with n-odd ZnC_n^+ clusters being more stable than the adjacent n-even ones, while in anionic clusters the opposite tendency is found. Ionization energies and electron affinities also exhibit a parity alternation trend with n-even clusters having higher values than the adjacent n-odd ones. It is found that $ZnC_n^{+/-}$ compounds prefer open-chain geometries over the cyclic ones with the only exception of ZnC_2^+.

1. Introduction

The study of small carbon clusters has engaged great interest in last decades [1]. This kind of molecules is being intensely studied mainly in connection with interstellar chemistry and gas-phase chemistry. In astrochemistry, carbon clusters have recently been proposed as possible carriers of diffuse interstellar bands [2,3]. On the other hand, pure carbon molecules are thought to be intermediates in the gas-phase chemistry taking place in chemical vapor deposition processes for production of thin diamond and silicon carbide films [4,5].

Addition of heteroatoms to pure carbon clusters provides a means to stabilize the carbon chain. Heteroatom-doped carbon clusters including a first- or second-row element have attracted great attention in the past years [6–30]. However, studies about carbon clusters doped with transition metal are scarcer [31–42]. The interaction between a transition metal and the carbon chain is important in understanding different cluster systems including endohedrofullerenes, catalytic growth of carbon nanotubes, and metallocarbohedrenes. Furthermore, understanding the nature of the chemical bond in heteroatom-doped carbon clusters is crucial in many fields, e.g., surface chemistry, catalysis, astrophysics and organometallic chemistry. From the theoretical point of view, molecules containing transition metals are one of the most interesting electronic systems. In part, this is because transition metals present various kinds of spin configurations.

Recently, we have carried out a theoretical study on the structure and stability of the neutral ZnC_n (n = 1–8) clusters [43]. The present work completes this previous study including now charged carbon–zinc clusters. We shall focus on the equilibrium geometries of the different ZnC_n^+ and ZnC_n^- (n = 1–8) isomers, as well as on their relative stabilities, addressing the competition between open-chain and cyclic compounds.

2. Theoretical methods

We have employed the same theoretical approach than in our previous study of neutral ZnC_n systems [43], since it is extensively tested in similar compounds. The B3LYP [44,45] exchange-correlation functional has been used throughout employing the 6-311G+(d) basis set. The B3LYP functional uses a combination of the hybrid three-parameter Becke exchange functional first proposed by Becke [46] together with the Lee–Yang–Parr [47] nonlocal correlation functional. The former is a linear combination of local density approximation, Becke's gradient correction [48], and the Hartree-Fock exchange energy based on Khon–Sham orbitals [49].

The 6-311+G(d) basis set specifies the standard Pople split-valence triple-ζ d-polarized basis set including an extra set of diffuse functions [50] for carbon atoms and the (15s11p6d1f)/[10s7p4d1f] basis set due to Watchters [51] and Hay [52], with the scaling factor of Raghavachari and Trucks [53] for zinc.

From previous studies, it is known that DFT/B3LYP/6-311+G(d) calculations predict structures of pure and heteroatom-doped carbon clusters in reasonable agreement with accurate ab initio methods such as CCSD(T) [54].

Harmonic vibrational frequencies were calculated for each optimized structure, using analytic gradient techniques. These

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frequencies were employed to estimate the zero-point vibrational energy (ZPVE) correction, and enable us to check the nature of stationary points. Other properties, such as dipole moments or rotational constants, were also computed.

All calculations were carried out using the Gaussian 98 [55] program package.

3. Results and discussion

The present study includes results for different ZnC_n^+ and ZnC_n^- ($n = 1–8$) isomers on the doublet and quartet potential energy surfaces. We have searched for different possible isomers, according to the experience with other heteroatom-doped carbon clusters [6–43]. Therefore, we have searched for linear species, non-linear, isomers with Zn in a middle position of the carbon chain, cyclic, bicyclic, fan, etc. However, we will only report results for two types of isomers which compete in stability: open-chain structures with the zinc atom located at one end of the carbon chain and cyclic structures where the zinc atom is bonded essentially to two carbon atoms of the C_n unit. Other possible open-chain structures with the zinc atom in a different position were also considered but are not shown here since they lie much higher in energy, according to the well-known fact that C–C bonds are much stronger than Zn–C ones. It should be pointed out that, in general, we have not found $ZnC_n^{+/-}$ *fan* structures, where the zinc atom is side-bonded to the entire C_n unit.

We will discuss separately the data for the two types of structures considered giving results for $\langle S^2 \rangle$ expectation values, dipole moments, and both absolute and relative energies. Other molecular data which might be helpful for experimentalists, such as harmonic vibrational frequencies and rotational constants are provided as Supplementary material (Tables S1–S4).

3.1. ZnC_n^+ clusters

In Table 1 we have collected the electronic energies, $\langle S^2 \rangle$ expectation values, dipole moments, and relative energies for the lowest-lying open-chain ZnC_n^+ species on the doublet and quartet potential surfaces. In addition, the optimized geometries for their most stable structures are shown in Fig. 1. All open-chain cationic clusters are true minima on the corresponding potential energy surface, since they have real harmonic vibrational frequencies (Table S1).

Table 1

Electronic energies, $\langle S^2 \rangle$ values, dipole moments, and relative energies (including ZPE correction) for open-chain ZnC_n^+ clusters at the B3LYP/6-311+G(d) level

Isomer	State	$-E$ (a.u.)	$\langle S^2 \rangle$	μ (D)	ΔE (kcal mol^{-1})
ZnC^+	$^2\Pi$	1816.925776	0.8084	0.59	0.00
	$^4\Sigma^-$	1816.900469	3.7557	1.00	16.09
ZnC_2^+	$^2\Sigma^+$	1855.036599	0.7803	4.00	0.00
	$^4\Sigma^-$	1854.974784	3.7561	1.12	38.37
ZnC_3^+	$^2A'$	1893.137904	0.7619	1.75	0.00
	$^4A''$	1893.089340	3.8187	1.41	30.84
ZnC_4^+	$^2A'$	1931.214211	0.8896	4.86	0.00
	$^4\Sigma^-$	1931.204951	3.7943	0.52	4.70
ZnC_5^+	$^2A'$	1969.336216	0.7571	1.72	0.00
	$^4\Sigma^-$	1969.278858	3.8442	4.39	36.75
ZnC_6^+	$^2A''$	2007.414421	1.1949	5.77	0.00
	$^4\Sigma^-$	2007.409042	3.8215	0.07	3.83
ZnC_7^+	$^2A'$	2045.528311	0.7563	1.68	0.00
	$^4\Sigma^-$	2045.476042	3.8724	4.59	34.30
ZnC_8^+	$^2A''$	2083.606872	1.3872	5.74	0.36
	$^4\Sigma^-$	2083.604945	3.8453	0.48	0.00

Our results for open-chain ZnC_n^+ isomers show that all clusters have doublet ground states. However, we must point out that for $n = 8$ the doublet and quartet states are almost isoenergetic (the relative energy is around 0.36 kcal/mol). Non-linear structures are found in all cases, with the only exception of $n = 2$. The electronic configurations for these cationic species can be derived from the electronic configurations of the corresponding neutral linear counterparts [43] by removing one electron from their frontier orbital (one valence π-electron in *n*-odd clusters and one valence σ-electron in *n*-even clusters). Consequently, the electronic configurations for ZnC_n^+ clusters, except for the two first members of the series, can be represented as

$$\{\text{core}\}1\sigma^2 \ldots 1\pi^4 1\delta^4 \ldots (n+3)\sigma^1 \quad n\text{-odd members } (n = 3, 5, 7)$$

$$\{\text{core}\}1\sigma^2 \ldots 1\pi^4 1\delta^4 \ldots \left(\frac{n+2}{2}\right)\pi^3 \quad n\text{-even members } (n{=}4, 6, 8)$$

The σ^1 configurations (for *n*-odd clusters) give $^2\Sigma^+$ electronic states in the linear geometry and $^2A'$ for non-linear species. On the other hand, the π^3 configuration (for *n*-even clusters) represents a $^2\Pi$ state in the linear geometry and $^2A''$ in the non-linear one (the corresponding component of $^2A'$ symmetry lies higher in energy except in the case of ZnC_4^+).

Carbon has a higher electronegativity (2.5) than zinc (1.6), and consequently the zinc atom bears a positive charge of approximately 1.0 e, whereas the carbon chain remains nearly uncharged.

As can be seen from Fig. 1, *n*-odd ZnC_n^+ clusters present higher values for the Zn–C bond distance (about 2.0 Å) than *n*-even ones. On the other hand, we observe an alternating short and long pattern in the C–C bond distances, $C_{odd}–C_{even}$ distances being shorter than the $C_{even}–C_{odd}$ ones. Furthermore, *n*-odd clusters with $n \geq 3$ show spin densities close to 1.0 for zinc. Consequently, the main valence structures contributing to the description of *n*-odd cationic clusters can be represented as

$$\bullet\overset{+}{\text{Zn}} \leftarrow \textbf{:}\text{C}(=\text{C}=\text{C})_{(n-1)/2}\textbf{:} \quad n \text{ odd } n = 3, 5, 7$$

On the other hand, *n*-even clusters present values for the Zn–C distance close to 1.9 Å. In these clusters the spin density is distributed among the odd carbon atoms, taking the highest value at C_1. Therefore, a qualitative view of the bonding can be depicted as

$$\overset{+}{\text{Zn}} - \overset{\bullet}{\text{C}}(=\text{C}=\text{C})_{(n-2)/2}{=}\text{C}\textbf{:} \quad n \text{ even } n = 2, 4, 6$$

To the best of our knowledge there are only available theoretical results for the first member of the series, ZnC^+. Gutsev et al. [56] studied the structure and properties of different monocarbides, as well as for their positively and negatively charged ions, employing different density functional theory methods. In their systematic study they also found a $^2\Pi$ ground state.

Data for the cyclic ZnC_n^+ clusters are given in Table 2, whereas the corresponding geometries for the lowest-lying species are shown in Fig. 2.

All cyclic ZnC_n^+ species have doublet ground states, whereas the quartet states are clearly higher in energy. From Fig. 2, it can be observed an alternation in C–C bond distances, $C_{odd}–C_{even}$ distances being shorter than the $C_{even}–C_{odd}$ ones. It must be remarked at this point that the first member in the series, ZnC_2^+, is not a truly cyclic structure. We have recently shown [57] that this apparently cyclic ZnC_2^+ species is best described as a T-shaped isomer, since only an $M–C_2$ bond critical point was found from a topological analysis of the electronic charge density [58].

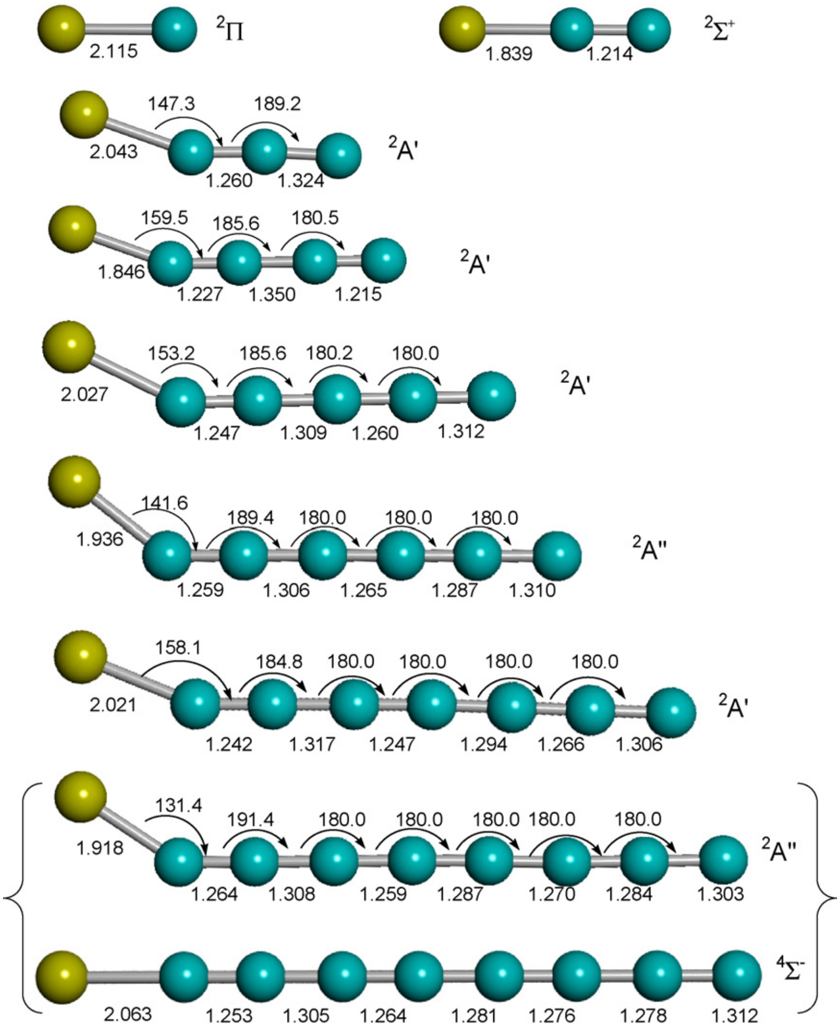

Fig. 1. Equilibrium geometries of open-chain ZnC_n^+ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

3.2. ZnC_n^- clusters

In Fig. 3 the optimized geometries for the more stable open-chain ZnC_n^- clusters are given, whereas in Table 3 we show different properties for these anionic species in the doublet and quartet potential energy surfaces.

Table 2
Electronic energies, $\langle S^2\rangle$ values, dipole moments, and relative energies (including ZPE correction) for cyclic ZnC_n^+ clusters at the B3LYP/6-311+G(d) level

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	μ (D)	ΔE (kcal mol^{-1})
ZnC_2^+	$^2A_1$	1855.043435	0.7709	3.27	0.00
	$^4B_1$	1854.976358	3.7622	1.01	41.15
ZnC_3^+	$^2A_1$	1893.114310	0.7603	1.45	0.00
	$^4B_2$	1893.094423	3.7583	1.69	12.66
ZnC_4^+	$^2B_2$	1931.173422	0.8278	1.65	0.00
	$^4B_1$	1931.154505	3.7951	0.02	11.27
ZnC_5^+	$^2A_1$	1969.284407	0.8116	0.83	0.00
	$^4A_2$	1969.246035	3.8485	1.21	24.56
ZnC_6^+	$^2A'$	2007.401771	0.7908	0.55	0.00
	$^4A_2$	2007.361506	3.8589	1.41	24.86
ZnC_7^+	$^2B_2$	2045.510115	0.8151	0.39	0.00
	$^4B_1$	2045.459249	3.8700	0.86	31.34
ZnC_8^+	$^2A'$	2083.604992	0.7794	0.34	0.00
	$^4B_1$	2083.570381	3.8424	0.32	21.07

Except the first member of the series, anionic clusters present doublet ground states. All of them are true minima on their respective doublet potential energy surfaces (see Table S3).

Table 3
Electronic energies, $\langle S^2\rangle$ values, dipole moments, and relative energies (including ZPE correction) for open-chain ZnC_n^- clusters at the B3LYP/6-311+G(d) level

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	μ (D)	ΔE (kcal mol^{-1})
ZnC^-	$^2\Pi$	1817.265088	0.8410	4.91	22.69
	$^4\Sigma^-$	1817.300886	3.7611	2.76	0.00
ZnC_2^-	$^2\Sigma^+$	1855.469923	0.7544	7.79	0.00
	$^4A''$	1855.347543	3.7666	2.38	76.01
ZnC_3^-	$^2A''$	1893.530932	0.7933	6.07	0.00
	$^4\Sigma^-$	1893.515940	3.784	9.69	10.26
ZnC_4^-	$^2\Sigma^+$	1931.663270	0.7551	13.07	0.00
	$^4\Sigma^-$	1931.570862	3.7601	8.17	57.11
ZnC_5^-	$^2A''$	1969.732601	0.8413	8.32	0.00
	$^4\Sigma^-$	1969.721922	3.8084	13.46	7.67
ZnC_6^-	$^2\Sigma^+$	2007.854313	0.7558	16.80	0.00
	$^4A'$	2007.776611	3.7638	15.73	47.37
ZnC_7^-	$^2A''$	2045.924787	0.9975	10.93	0.00
	$^4\Sigma$	2045.918599	3.8341	16.80	5.41
ZnC_8^-	$^2\Sigma^+$	2084.042127	0.7563	20.21	0.00
	$^4A'$	2083.976016	3.7695	15.96	39.75

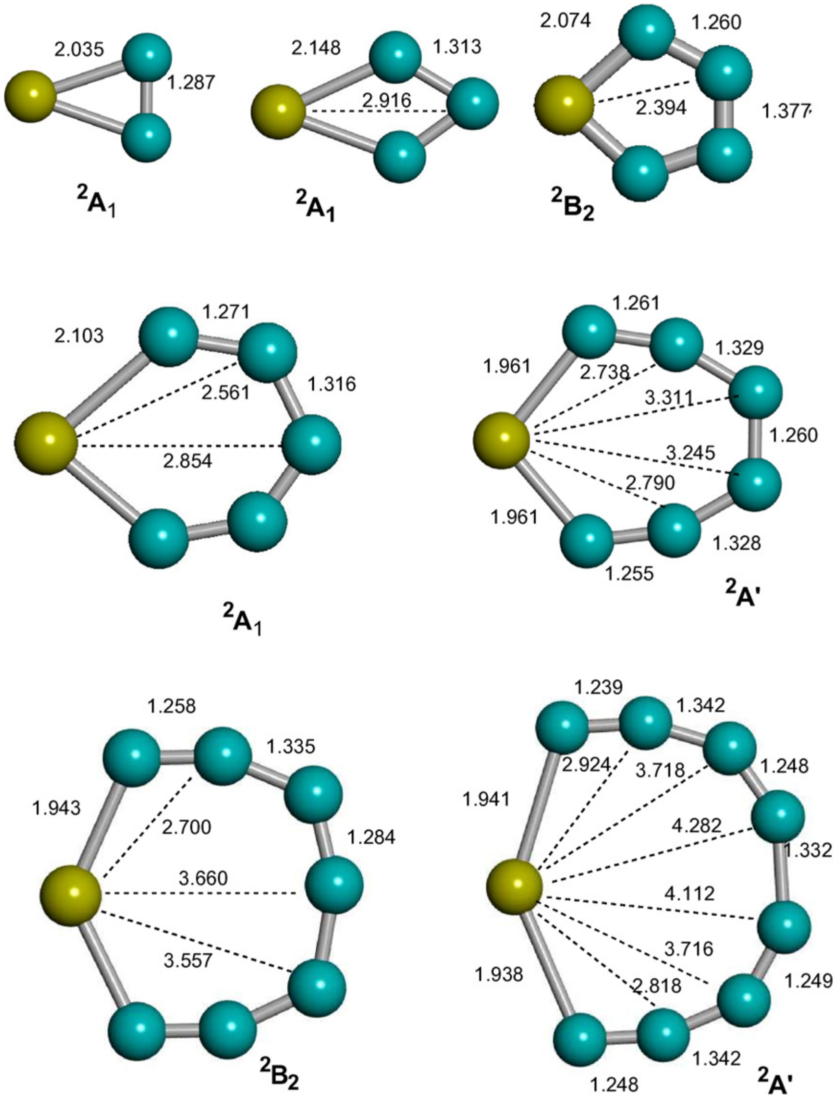

Fig. 2. Equilibrium geometries of cyclic ZnC_n^+ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

In n-odd anionic clusters the extra electron is incorporated to the $((n+3)/2)\pi$-orbital of their neutral counterparts, whereas in the n-even ones, the extra electron goes to the $((n+2)/2)\pi$-orbital. Consequently, the electronic configurations for ZnC_n^- clusters can be represented as

$$\{\mathrm{core}\}1\sigma^2 \ldots 1\pi^4 1\delta^4 \ldots (n+3)\sigma^2 \left(\frac{n+3}{2}\right)\pi^1$$

n-odd members ($n = 3, 5, 7$)

$$\{\mathrm{core}\}1\sigma^2 \ldots 1\pi^4 1\delta^4 \ldots (n+3)\sigma^1 \left(\frac{n+2}{2}\right)\pi^4$$

n-even members ($n = 4, 6, 8$)

The π^1 electronic configurations (in n-odd clusters) give $^2\Pi$ electronic states in linear geometry and $^2A''$ states in non-linear geometry, whereas the σ^1 configurations (in n-even members) result in $^2\Sigma^+$ electronic states.

As it was pointed out in ZnC_n^+ systems, n-odd anionic clusters present higher values for the Zn–C bond distance (about 2.1 Å) than the n-even ones (about 1.9 Å). On the other hand, for n-odd ZnC_n^- clusters all C–C bond lengths are rather close, within the range 1.27–1.31 Å, typical of cumulenic structures. Therefore, the dominant valence structure contributing to their description could be summarized as

$$\mathbf{:}\mathrm{Zn} \leftarrow \mathbf{:}\underset{\bullet}{\bar{\mathrm{C}}}(=\mathrm{C})_{n-2}{=}\mathrm{C}\mathbf{:} \quad n\text{-odd}, \quad n = 3, 5, 7$$

In n-even species an alternation in the C–C distances is observed with C_{odd}–C_{even} distances being shorter than C_{even}–C_{odd} ones. Consequently, in these clusters a certain degree of polyacetylenic character should be considered and the main valence structures contributing to their description can be represented as

$$^{\bullet}\mathrm{Zn}{-}(\mathrm{C}{\equiv}\mathrm{C}{-})_{(n-2)/2}\mathrm{C}{\equiv}\bar{\mathrm{C}}\mathbf{:} \quad n\text{-even}, \quad n = 4, 6, 8$$

The structures and molecular properties corresponding to cyclic anionic clusters are given in Fig. 4 and Table 4, respectively. Again, doublet states are favored over quartet states.

As we have mentioned before, no fan structures were found after a search on the potential energy surface. The only species which resembles a fan isomer is that corresponding to ZnC_4^-. In this structure the Zn–C distances suggest the possibility of interaction of the metal with the entire carbon chain (typical of fan structures).

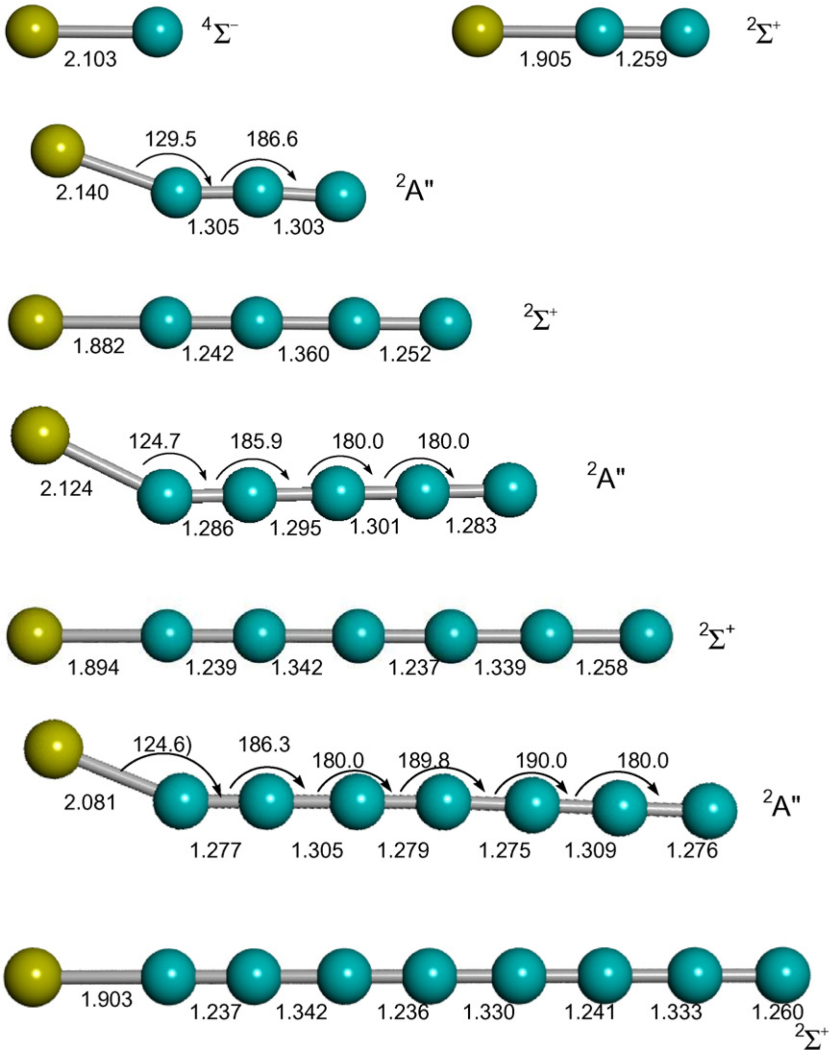

Fig. 3. Equilibrium geometries of open-chain ZnC_n^- clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

A topological analysis of the electronic charge density [58] shows that this is a truly monocyclic species with formal peripheral Zn–C bonds and no transannular Zn–C bonding. Nevertheless the geometrical parameters, short Zn–C bond distances and CCC angles around 140°, might suggest that the metal interacts with the whole quasi-linear carbon unit. All other species are clearly monocyclic structures, where the metal essentially interacts with the terminal carbon atoms of the C_n unit. The ZnC_3^- cluster constitutes a singular case, because it can be seen as a bicyclic species with a transannular C–C bond length of 1.555 Å.

All the structures in their lowest-lying states are true minima on their respective doublet potential energy surface, with the exceptions of ZnC_3^- ($^2A_1$) and ZnC_4^- ($^2A_1$), both having one imaginary frequency. For the ZnC_3^- system we found a true minimum corresponding to a ring of three members with the zinc atom outside the ring (it is 5.31 kcal/mol lower in energy than the corresponding four-member ring). In the case of the ZnC_4^- species all our attempts to find non-symmetric minima failed, leading to the open-chain isomers.

Table 4
Electronic energies, $\langle S^2\rangle$ values, dipole moments, and relative energies (including ZPE correction) for cyclic ZnC_n^- clusters at the B3LYP/6-311+G(d) level

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	μ (D)	ΔE (kcal mol^{-1})
ZnC_2^-	$^2A_1$	1855.468397	0.7550	5.19	0.00
	$^4B_2$	1855.354702	3.7586	1.63	71.08
ZnC_3^-	$^2A_1$	1893.503772	0.7552	2.46	0.00
	$^4B_1$	1893.484306	3.7836	4.68	12.59
ZnC_4^-	$^2A_1$	1931.630265	0.7521	4.02	0.00
	$^4B_2$	1931.514250	3.7616	2.31	70.71
ZnC_5^-	$^2A'$	1969.698215	0.7708	2.80	0.00
	$^4B_1$	1969.670451	3.8039	1.63	17.38
ZnC_6^-	$^2B_2$	2007.812103	0.7701	4.27	0.00
	$^4A''$	2007.750985	3.7805	1.54	37.15
ZnC_7^-	$^2A_2$	2045.908129	0.7786	3.45	0.00
	$^4B_1$	2045.857749	3.8731	1.29	30.21
ZnC_8^-	$^2A_1$	2083.996023	0.7624	2.77	0.00
	$^4B_2$	2083.947830	3.7932	2.53	29.42

3.3. Stabilities of $ZnC_n^{+/-}$ clusters

In order to discuss the relative stability of the clusters, we will use the concept of incremental binding energies [18,59] that has proved in our previous works in transition metal-doped carbon clusters [38–43] to be useful when comparing clusters with different sizes. The incremental binding energy is defined as the change

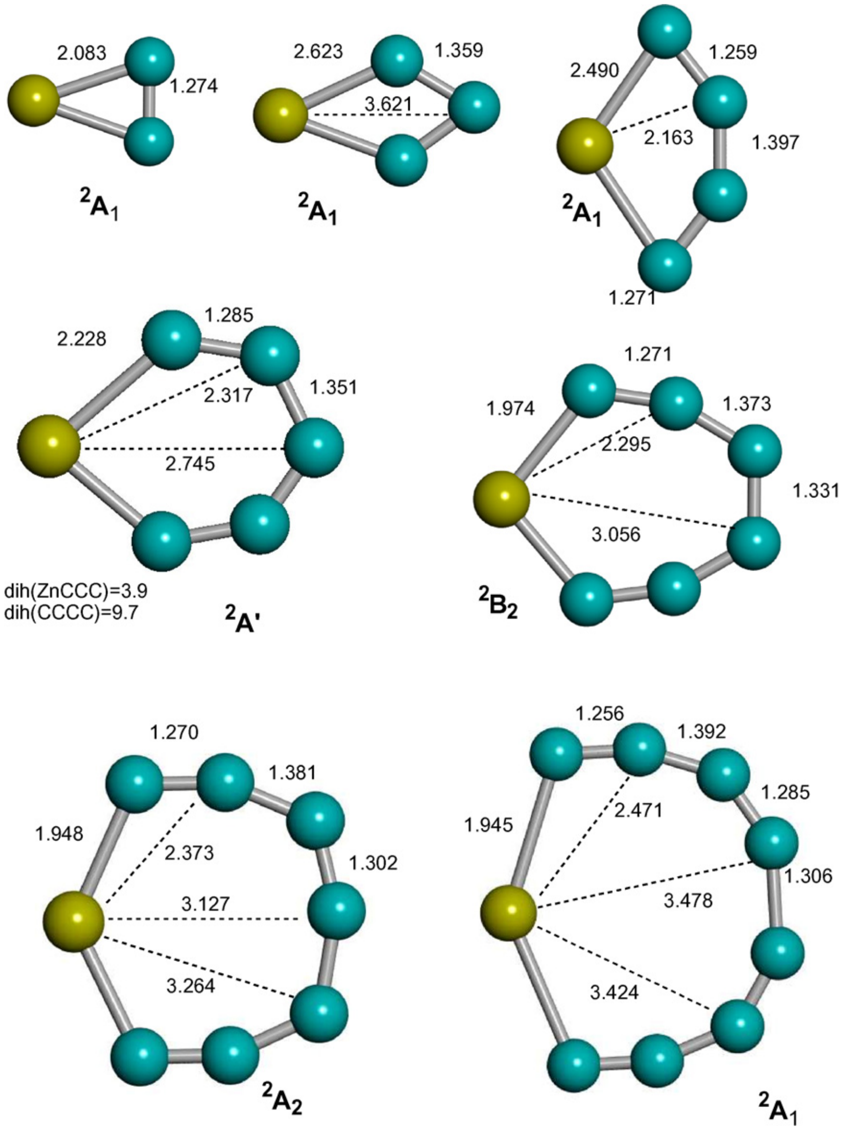

Fig. 4. Equilibrium geometries of cyclic ZnC_n^- clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

in energy associated to the processes:

$$ZnC_n^+ \rightarrow ZnC_{n-1}^+ + C$$

$$ZnC_n^- \rightarrow ZnC_{n-1}^- + C$$

It is computed as the binding energy differences between adjacent clusters. Therefore, incremental binding energies for linear ZnC_n^+ clusters are computed from the values given in Table 1 taking in each case the lowest-lying state. The same procedure employing the values in Tables 2–4 provides incremental binding energies for cyclic ZnC_n^+, linear ZnC_n^- and cyclic ZnC_n^- clusters, respectively.

The results for the incremental binding energy, as a function of the number of carbon atoms for the different clusters, are displayed in Fig. 5. Fig. 5a contains data for ZnC_n^+ clusters and Fig. 5b includes results for ZnC_n^- clusters. From Fig. 5a we observe an odd–even alternation in stability for open-chain cationic species, except for the first member, with n-odd members being more stable than the adjacent n-even species. For cyclic ZnC_n^+ clusters the incremental binding energies do not show parity effects. In these structures the stability increases for clusters with $n \geq 5$.

In the case of linear and cyclic anionic clusters, Fig. 5b shows that in both cases n-even clusters are in general more stable than the corresponding $n-1$ and $n+1$ clusters.

This parity effects can be attributed to the number of available π– valence electrons, mainly the number of electrons in π-type highest occupied molecular orbital (HOMO) [60]. As we pointed out before, linear ZnC_n^+ clusters have σ^1 configurations, for n-odd members, and π^3 configurations, for n-even ones. Therefore, in the last case the π-type HOMO is not fully filled. Since the situation of fully filled π-orbitals (n-odd clusters) is energetically more favorable than the unfilled π-orbitals (n-even clusters) an odd–even alternation in the stability of ZnC_n^+ clusters takes place with the n-odd members being more stable than the adjacent n-odd ones.

In the anionic clusters the opposite tendency is found. Linear ZnC_n^- clusters present π^1 configurations, for n-odd systems, and σ^1 configurations, for n-even members, and consequently n-even ZnC_n^- clusters will be more stable than n-odd ones.

The relative energies of the different $ZnC_n^{+/-}$ clusters are presented in Fig. 6. We have taken as reference the energy of the linear isomers. From this figure it can be inferred that the linear conformation (open-chain) is the preferred arrangement in both cationic

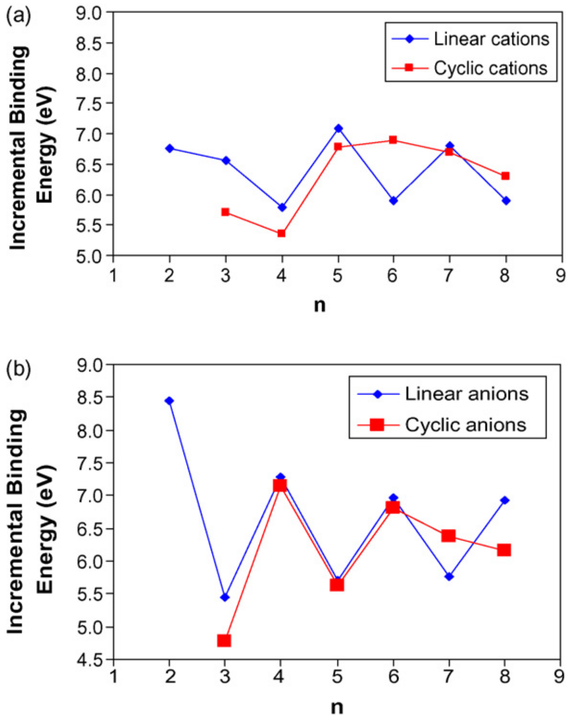

Fig. 5. Incremental binding energies (eV) at the B3LYP/6-311+G(d) level of theory for the different isomers vs. the number of carbon atoms. (a) ZnC_n^+ clusters and (b) ZnC_n^- clusters.

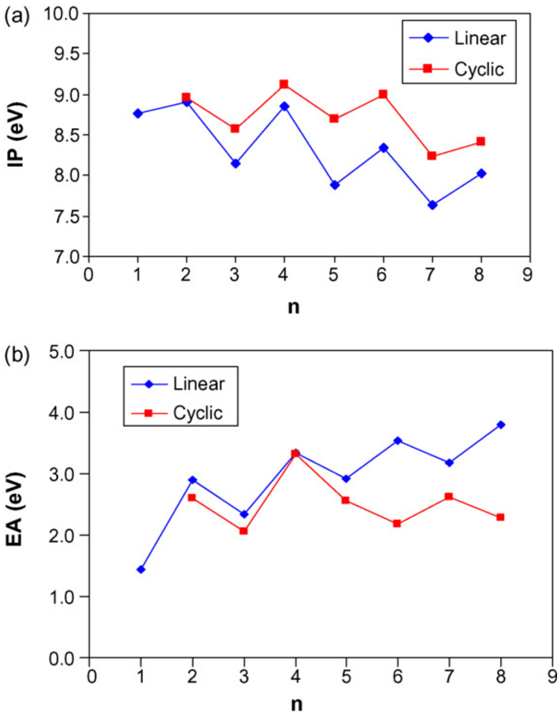

Fig. 7. Ionization potentials (IP) and electron affinities (EA), in eV, of ZnC_n clusters at the B3LYP/6-311+G(d) level of theory vs. the number of carbon atoms. (a) Ionization potentials and (b) electron affinities.

and anionic clusters, with the only exception of ZnC_2^+. In this case the cyclic structure is nearly 5 kcal/mol lower in energy than the linear one. It must be noted that cyclic ZnC_2^+ is in fact a T-shaped species and in our previous work [57] we found very small barrier for interconversion between both isomers. Therefore, it seems a case of polytopic system [61].

It may be interesting to compare these results with those obtained for other carbon clusters doped with transition metals [38,42,62]. Early transition metals, such as Sc, Ti or V, clearly favor cyclic (or fan) arrangements. For those systems the open-chain isomers are relatively unstable, with energy differences large enough to be sure of the geometrical preference. On the other hand, for late transition metals, Zn being a prototypical case, both the open-chain ZnC_n^+ and ZnC_n^- isomers are comparatively more stable than the corresponding cyclic ones. We have already discussed [43] that this behavior could be related to two concomitant effects. In first place, the charge donation from the metal to the carbon unit, which is expected to play an important role in the stabilization of transition metal carbides [63], is more favorable along C_{2v} symmetry than for linear arrangements and should favor cyclic isomers. However, the energy of the metal 4s (and 3d) orbital lowers along the transition series, and consequently this interaction is less favorable for late transition metals. In second place, the back-donation from the carbon unit, which is expected to contribute to some extent to the stabilization of these species, is also in principle more favorable in C_{2v} than in $C_{\infty v}$ symmetry, and should be hindered to a large extent for late transition metals, due to the large occupancy of the metal 3d orbitals (which are fully occupied for Zn).

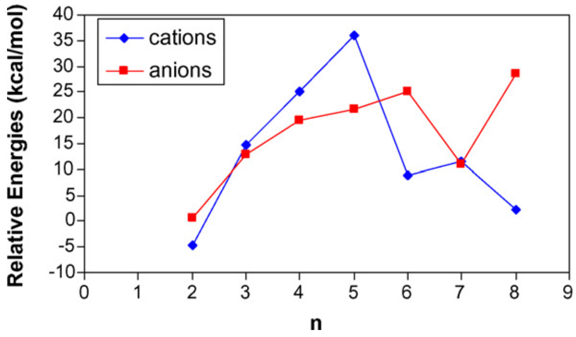

Fig. 6. Relative energies (kcal/mol) at the B3LYP/6-311+G(d) level of theory of the cyclic isomers with respect to the corresponding open-chain structures vs. the number of carbon atoms.

3.4. Ionization potentials and electron affinities

In Fig. 7 we present the ionization potentials (IP) and electron affinities (EA) for the ZnC_n species as a function of the number of carbon atoms in the cluster. Fig. 7a includes the ionization potentials, whereas in Fig. 7b we have collected the results for the electron affinities.

Ionization potentials and electron affinities were computed in the adiabatic form, as the difference between the total energies of the neutral and charged species at their respective optimized geometries including the zero-point vibrational corrections.

In general, it can be noted an even–odd alternation in both IPs and EAs, n-even clusters having higher IPs and EAs than the adjacent n-odd ones. From Fig. 7 it can also be observed that there is a tendency to lower IPs and higher EAs as the size of the cluster increases. These trends allow extrapolations for clusters with higher number of carbon atoms.

Finally it should be remarked that both IPs and EAs graphs for ZnC_n compounds present a similar even–odd alternation than their isovalent clusters MgC_n [83] and CaC_n [85]. The main difference is the magnitude of the IPs in the different clusters, $IPs(CaC_n) < IPs(MgC_n) < IPs(ZnC_n)$. This is directly related to the different magnitude of the IPs of the heteroatoms, IP(Ca) < IP(Mg) < IP(Zn), since cationic clusters are obtained from their neutral counterparts by removing an electron mainly located at the heteroatom.

4. Conclusions

A theoretical study of linear and cyclic $ZnC_n^{+/-}$ clusters (n = 1–8) has been carried out using density functional theory with the 6-311+G(d) basis sets.

According to our calculations, $ZnC_n^{+/-}$ clusters usually present doublet ground states.

The relative stability of the different clusters has been estimated employing the concept of incremental binding energies. For cationic species, it can be observed an even–odd alternation in the clusters stability; n-odd cationic clusters are more stable than the adjacent n-even ones, whereas in anionic clusters the opposite behavior is found.

Both ionization potentials and electron affinities exhibit a parity alternation effect, with n-even clusters having larger IPs and EAs than n-odd ones.

From our study it can be concluded that the open-chain conformations are the preferred arrangements in both ZnC_n^+ and ZnC_n^- clusters, with the only exception of ZnC_2^+.

Geometrical parameters and some molecular properties such as vibrational energies, dipole moments and rotational constants, that could be useful for an eventual experimental characterization, are provided.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2008.03.006.

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