JCTC Journal of Chemical Theory and Computation

Structure and Stability of Small ZnC$_n$ Clusters

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Abstract: A theoretical study of the small ZnC$_n$ ($n = 1-8$) clusters has been carried out at the B3LYP/6-311+G(d) level. Different molecular properties for open-chain and cyclic species have been calculated. The computed properties include electronic energies, vibrational frequencies, dipole moments, and rotational constants for individual species. In addition, the relative stability of the different clusters is also discussed in terms of the incremental binding energy. In the case of open-chain clusters, the lowest-lying states correspond to triplet states with the exception of ZnC$_2$, whereas the electronic ground state is found to be a singlet state for cyclic clusters. The incremental binding energy graph shows a smooth even−odd parity effect in the incremental binding energy, n-even species being, in general, more stable than the adjacent odd-numbered ones. It was also found that the first members in the series, excepting ZnC$_2$, prefer open-chain structures, whereas when $n \geq 6$ cyclic ground states are favored.

1. Introduction

Carbon clusters have been the subject of study from both experimental and theoretical points of view for many decades.[1,2] These studies have involved small clusters (2−25 atoms) as well as larger clusters (up to 100 atoms), and also charged clusters have been considered. The interest in carbon clusters is mainly due to their applications in several fields. For instance, different molecules of this kind have been detected in astrophysical sources. In particular, carbon chains have been proposed as contributors to the formation of the long-chain cyanopolyynes, carbon dust, polycyclic aromatic hydrocarbons, and as possible carriers of diffuse interstellar bands.[3,4] Furthermore, carbon clusters are known to be present in the nucleation of carbon particles and formation of soot in hydrocarbon flames. Carbon clusters are also of interest in gas-phase chemistry, since they could act as intermediates in the chemical vapor depositions process for the production of thin diamond and silicon carbide films.[5,6] In addition to such practical implications, carbon clusters present interest in themselves because of the complexities in the properties and spectroscopy of these species.

The study of heteroatom-doped carbon clusters has also engaged great interest in recent years. In particular, the interaction between a transition metal and carbon is important in understanding several cluster materials including endohedrofullerenes, the catalytic growth of carbon nanotubes, and metallocarbohedrenes. Experimentally, anionic clusters can be produced from laser ionization and laser ablation.[7−11] An important conclusion obtained from observed records of time-of-flight mass spectra is that some clusters exhibit a dramatic even/odd alternation in signal intensity.

In order to explore these interesting experimental observations, several theoretical investigations have been conducted on XC$_n$ clusters in which the heteroatom is a first- or second-row element in the periodic table. On the other hand, the information about carbon clusters doped with transition metals is scarcer.

Recently, we have studied the MgC$_n$/MgC$_n^+$/MgC$_n^-$ [12,13] and CaC$_n$/CaC$_n^+$/CaC$_n^-$ [14,15] isovalent clusters. Furthermore, we have also carried out studies on the linear[16] and cyclic[17] carbon clusters doped with the first transition metal, scandium. In a recent paper,[18] the structure of VC$_n$ clusters has also been addressed. Linear and cyclic CrC$_n$ clusters have been studied by Zhai et al.[19] It would be interesting to provide information about carbon clusters doped with Zn, the isovalent element of Mg and Ca "bracketing" the first

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transition metal row, since, to the best of our knowledge, no data have ever been published for ZnC_n clusters.

In the present work, we have carried out a theoretical study of the ZnC_n ($n = 1-8$) open-chain and cyclic isomers, reporting their geometry structures and some spectroscopic data. It must be noted that the presence of 3d electrons increases the number of low-lying electronic states. Thus, information on these states can serve as helpful guidelines for the synthesis of related materials as well as for future theoretical studies of heteroatom-doped carbon clusters. In addition, we have also investigated the isomers' stabilities, incremental binding energy, and the competition between open-chain and cyclic isomers.

2. Computational Details

In our study, we have employed density functional theory (DFT). In particular, the popular hybrid B3LYP[20,21] exchange-correlation functional has been selected. This includes the Lee−Yang−Parr[22] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[23] The latter is a linear combination of local density approximation, Becke's gradient correction,[24] and the Hartree−Fock exchange energy based on Kohn−Sham orbitals.[25]

As in previous works, we have employed the triple split-valence d-polarized 6-311G+(d)[26] basis set including an extra set of diffuse functions.

This hybrid formalism has been previously proved in accord with more rigorous ab initio methods in the study of carbon clusters and medium-size heteroatom-doped carbon clusters.[27]

For each optimized structure, harmonic vibrational frequencies were computed using analytic gradient techniques. These frequencies were employed to estimate the zero-point vibrational energy 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 with the Gaussian 98[28] program package.

3. Results and Discussion

We have searched for different possible ZnC_n isomers, but we will only report the results for those which might be competitive in stability. For each ZnC_n species, we have considered different multiplicities: singlet, triplet, and quintet states. In particular, we include in the present study two different types of structures: open-chain structures with the zinc atom located at one end of the carbon chain and cyclic structures where zinc is bonded essentially to the two terminal 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 fact that C−C bonds are much stronger than Zn−C ones. For the same reason, other types of cyclic isomers, such as those in which a carbon atom or a zinc atom is in a bridge position outside a ring, were found to lie higher in energy, and they will not be included here. It should be pointed out that we have not found ZnC_n fan structures, that is, structures where the zinc atom

Table 1. Electronic Energies, $<S^2>$ Values, Dipole Moments, and Relative Energies (Including the ZPE Correction) for Open-Chain ZnC_n Clusters at the B3LYP/6-311+G(d) Level

isomer	state	$-E$ (a.u)	$<S^2>$	μ (D)	ΔE (kcal mol^{-1})
ZnC	$^1\Delta$	1817.193 612		3.27	33.96
	$^3\Sigma^-$	1817.247 618	2.1202	2.98	0.00
	$^5\Sigma^-$	1817.198 368	6.0045	1.87	31.09
ZnC$_2$	$^1\Sigma^+$	1855.363 605		7.48	0.00
	$^3\Pi$	1855.346 568	2.0052	4.14	11.53
	^{5}A′	1855.212 773	6.0224	2.54	93.06
ZnC$_3$	^{1}A′	1893.445 079		3.69	0.00
	$^3\Pi$	1893.437 249	2.0207	5.24	5.13
	$^5\Sigma^-$	1893.386 328	6.0688	1.50	32.34
ZnC$_4$	^{1}A′	1931.532 646		9.13	4.15
	$^3\Pi$	1931.539 267	2.0198	6.53	0.00
	$^5\Pi$	1931.442 319	6.0336	5.67	59.61
ZnC$_5$	^{1}A′	1969.626 375		5.15	0.00
	$^3\Pi$	1969.626 207	2.0339	7.16	0.36
	$^5\Sigma^-$	1969.575 183	6.1202	1.97	31.52
ZnC$_6$	^{1}A′	2007.712 418		10.77	6.28
	$^3\Pi$	2007.723 288	2.0307	8.28	0.00
	$^5\Pi$	2007.648 520	6.0552	7.64	45.28
ZnC$_7$	^{1}A′	2045.805 034		6.62	2.58
	$^3\Pi$	2045.810 183	2.0468	8.84	0.00
	$^5\Sigma^-$	2045.760 506	6.1670	2.46	30.79
ZnC$_8$	^{1}A′	2083.891 754		12.36	7.54
	$^3\Pi$	2083.905 250	2.0407	9.89	0.00
	$^5\Pi$	2083.844 736	6.0749	9.43	36.19

is side-bonded to the entire C_n unit; all of our attempts to obtain these structures led to cyclic conformations.

In order to analyze systematic trends, in the different properties considered, with the size of the clusters, we will present the results for each type of structure separately. Thus, we first present the results for the open-chain structures; second, cyclic isomers will be considered, and finally, we will discuss the competition between open-chain and cyclic isomers. On the other hand, in the next subsections, we will give some properties such as the electronic energies, dipole moments, and so forth, for the lowest-lying ZnC_n species on various potential surfaces; however, other molecular properties which might be helpful in an experimental search for these species, such as harmonic vibrational frequencies and rotational constants, are provided as Supporting Information (Tables S1 and S2).

3.1. ZnC_n Open-Chain Isomers. In Table 1, we show absolute electronic energies, $<S^2>$ expectation values, dipole moments, and relative energies at the B3LYP/6-311+G(d) level of theory, for the lowest-lying open-chain ZnC_n species on the singlet, triplet, and quintet potential surfaces. In addition, in Figure 1, the optimized geometries for the most stable open-chain structures at the B3LYP/6-311+G(d) level of theory are shown.

It can be readily seen from Table 1 that, except for the first member of the series ZnC, the $<S^2>$ values are uniform and deviate slightly from the pure spin value; consequently, it can be considered that the wave functions employed are

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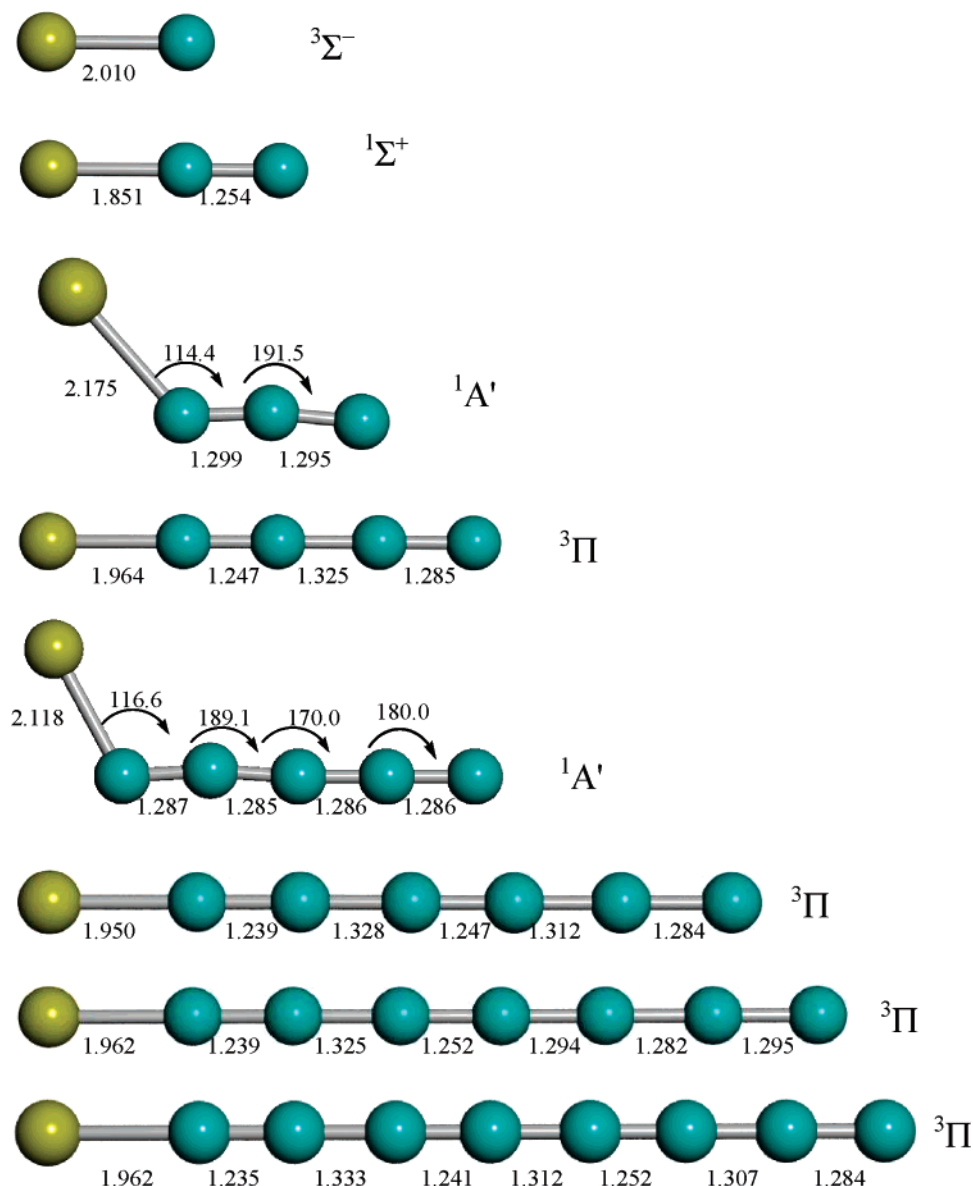*J. Chem. Theory Comput., Vol. 3, No. 2, 2007* **659**

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

nearly spin-pure, and in these species, spin contamination should not be a problem.

The reported lowest-lying open-chain structures all have real frequencies (Table S1), thus confirming that they are true minima on their respective potential surfaces.

As can be seen in Table 1, in most cases, the lowest-lying structure for ZnC$_n$ open-chain clusters was found to correspond to a triplet state, with the exception of ZnC$_2$, which presents a singlet state ($^1\Sigma^+$). In addition, in the cases of ZnC$_3$ and ZnC$_5$, singlet nonlinear structures are found to lie slightly below the triplet species. Nevertheless, the general trend, especially for larger clusters, is to favor triplet ground states.

The triplet lowest-energy states can be explained in terms of their valence electronic configuration. Linear zinc-doped carbon clusters, ZnC$_n$, present $4n + 12$ (n being the number of carbon atoms) valence electrons, which are distributed over the valence orbitals as follows:

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

for n-odd members

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

for n-even members

except for

ZnC: $\{\text{core}\}\ 1\sigma^2 1\pi^4 1\delta^4 2\sigma^2 3\sigma^2 2\pi^2(^3\Sigma^-)$

ZnC$_2$: $\{\text{core}\}\ 1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 4\sigma^2 2\pi^4(^1\Sigma^+)$

ZnC$_n$ clusters contain four valence δ electrons, $2n + 5$ valence σ electrons, and $2n + 3$ valence π electrons. A total

of $2n + 4$ valence σ electrons of the $2n + 5$ total ones fully occupy $n + 2$ σ orbitals, and the one valence σ electron remaining leads to a half-filled σ orbital, σ^1.

In n-even clusters, $2n$ is a four-multiple and the $2n + 3$ valence π electrons are distributed over π orbitals, leading to final π^3 distributions. On the other hand, in the n-odd ZnC$_n$ species, $2n + 2$ is a four-multiple and the $2n + 3$ π electrons lead to π^1 distributions. Both $\sigma^1\pi^1$ and $\sigma^1\pi^3$ configurations give $^3\Pi$ electronic states.

Before discussing our results, we are going to compare them with the previous theoretical results that have been reported for the ZnC system. The ground state of Zn is of ^{1}S symmetry with a $4s^2$ configuration; its first excited state is of ^{3}P symmetry with a $4s^14p^1$ configuration, and the experimental ^{3}P ← S energy gap is about 4.054 eV.[29] On the other hand, C presents a ground state of ^{3}P symmetry with a $2s^22p^2$ configuration, and the corresponding energy gaps are (^{5}S, ^{1}S, ^{1}D ← ^{3}P) 1.260, 2.084, and 4.179 eV, respectively. Therefore, the lowest ZnC dissociation channels in ascending energy order are (Zn + C) = (^{1}S + ^{3}P, ^{1}S + ^{1}D, ^{1}S + ^{1}S...).

Recently, a controversy has taken place about the ground state of diatomic carbides MC.[30−37] In these carbides, the $^3\Sigma^-$ state correlates to M(s^2;^{1}S) + C(^{3}P) and competes with a $^5\Sigma^-$ state correlating to M(s^{1}p^1;^{3}P) + C(^{3}P). The interplay between the atomic energy separation M(^{3}P) ← M(^{1}S) and the binding energy of the $^3\Sigma^-$ and $^5\Sigma^-$ states dictates ultimately the ground state of MC. However, in zinc carbide, this antagonism would probably be hindered by the ^{3}P ← ^{1}S energy separation (4.054 eV); thus, in principle, a $^3\Sigma^-$ ground state could be expected.

While there is an absence of experimental results on ZnC, some theoretical studies can be found in the literature involving zinc carbide. For instance, Boldyrev and Simons,[38] from a quadratic configuration interaction method, predicted a $^3\Sigma^-$ to be the ground state of ZnC with a $^5\Sigma^-$ state lying 23.9 kcal/mol higher in energy [QCISD(T)/6-311++G(2df,-2f) level of theory]. Kerkines et al.[34] tested a state-specific multireference Brillouin−Wigner coupled cluster (MRB-WCCSD) method against the single-reference CCSD method in the competing $^3\Sigma^-$ and$^5\Sigma^-$ states of zinc carbide. From their MRBWCCSD treatment, the $^5\Sigma^-$ ← $^3\Sigma^-$ gap was predicted to lie around 22−24 kcal/mol. Recently, Tsou-loucha et al.[39] carried out a study of the ground and excited states of zinc carbide using multireference methods in conjunction with quantitative basis sets. They predicted the $^5\Sigma^-$ state to lie 26.3 or 23.8 kcal/mol [with or without relativistic effects MRCI-(d10)+Q] above the ground $^3\Sigma^-$ state. Finally, Gutsev et al.[40] have performed a theoretical study of 3d-metal monocarbides using DFT and hybrid DFT methods.

We have studied the lowest-lying states in the singlet, triplet, and quintet ZnC potential surfaces, and our B3LYP calculations predicted a $^3\Sigma^-$ ground state with $^5\Sigma^-$ and $^1\Delta$ lying about 31 kcal/mol and 34 kcal/mol, respectively, higher in energy.

The valence electronic configuration for ZnC is

$$\{\text{core}\}\ 1\sigma^21\pi^41\delta^42\sigma^23\sigma^22\pi^2(^3\Sigma^-)$$
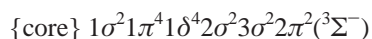
which could be represented by the following valence bond structure:

$$\text{Zn:} \rightarrow \overset{\bullet}{\underset{\bullet}{\text{C}}}:$$
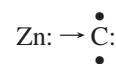
where Zn and C are held by a σ dative bond and the two π electrons remain practically located on C; see also, ref 39.

In ZnC, our computed Zn−C distance is 2.010 Å, in good agreement with previous data.[34−39]

In the case of ZnC$_2$, our calculations predicted a $^1\Sigma^+$ ground state with a $^3\Pi$ state lying 11.53 kcal/mol higher in energy. We found a relatively short Zn−C bond length, 1.851 Å, suggesting a moderately strong double bond, and a C−C distance of 1.254 Å. These geometrical parameters are compatible with a bonding picture resulting from a dative σ bond between Zn and the C$_2$ unit [resulting from donation of the 4s electrons to the C$_2$ lowest unoccupied molecular orbital $3\sigma_g$ orbital] enhanced by partial π bonding from d(Zn) $\rightarrow$ next-LUMO ($1\pi_g$) donation:

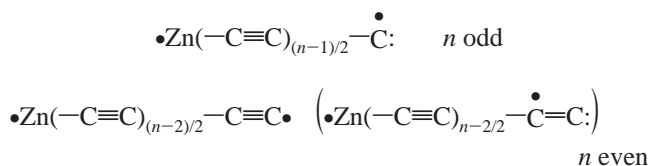$$\text{Zn}=\text{C}=\text{C:}$$
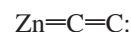
The $^3\Pi$ state is associated mainly with the following valence-bond scheme (supported by the spin densities):

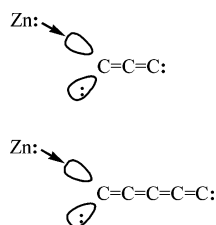$$\bullet\text{Zn}-\overset{\bullet}{\text{C}}=\text{C:}$$
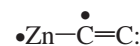
From Figure 1, it can be seen that the $^3\Pi$ states of ZnC$_n$ clusters ($n \geq 3$) present similar Zn−C distances ∼ 1.96 Å. The C−C bond lengths are all in the range 1.253−1.334 Å and can be assimilated to moderately strong double bonds. In addition, spin densities show an unpaired electron located at zinc and the second one distributed along the carbon chain (mainly at C$_1$). Consequently, the most important valence structure for these clusters is a cumulene type:

$$\bullet\text{Zn}-\overset{\bullet}{\text{C}}(=\text{C})_{n-2}=\text{C:}$$
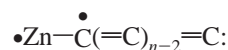
Nevertheless, an alternation in the C−C bond distances can be noted, C$_{odd}$−C$_{even}$ being shorter than C$_{even}$−C$_{odd}$. This suggests some degree of polyacetylenic character with alternating triple C−C bonds:

$$\bullet\text{Zn}(-\text{C}\equiv\text{C})_{(n-1)/2}-\overset{\bullet}{\text{C}}: \qquad n \text{ odd}$$

$$\bullet\text{Zn}(-\text{C}\equiv\text{C})_{(n-2)/2}-\text{C}\equiv\text{C}\bullet \quad \left(\bullet\text{Zn}(-\text{C}\equiv\text{C})_{n-2/2}-\overset{\bullet}{\text{C}}=\text{C:}\right)$$
$$n \text{ even}$$

It should be noted that ZnC$_3$ and ZnC$_5$ present ^{1}A′ states slightly lower in energy than the $^3\Pi$ ones (5.13 kcal/mol lower in energy for ZnC$_3$ and 0.36 kcal/mol for ZnC$_5$). In these cases, we observe longer Zn−C distances (2.175 Å for ZnC$_3$ and 2.118 Å for ZnC$_5$) than in the other clusters, and similar C−C bond lengths. In these species, deviation from linearity is important, since the ∠ZnCC angle takes values of 114° and 116° respectively for ZnC$_3$ and ZnC$_5$. The geometrical parameters as well as the molecular orbitals suggest a bonding picture resulting from a dative σ bond between Zn and an empty orbital of the terminal carbon of the C$_n$ unit

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Zn:
C=C=C:

Zn:
C=C=C=C=C:

The Mulliken population analysis indicates that the zinc atom bears a positive charge (between +0.45 and +0.78); thus, the Zn$-$C bond shows a certain degree of ionic character. As a consequence of the ionic character of the Zn$-$C bond, relatively high dipole moments are found.

The dipole moments, shown in Table 1, regularly increase with the number of carbon atoms running from 2.98 for ZnC to 9.89 D for ZnC$_8$. It can be remarked that the high magnitude of the dipole moments might help in the possible experimental detection of these species.

By comparing zinc-doped carbon clusters to their magnesium and calcium isovalent systems, we observed that ZnC$_n$ compounds exhibit a rather similar behavior. MgC$_n$[12] clusters present $^3\Pi$ ground states (except MgC, $^3\Sigma^-$, and MgC$_2$,$^1\Sigma^+$), whereas CaC$_n$[14] n-even clusters have singlet ground states (even though the singlet$-$triplet difference is rather small).

3.2. ZnC$_n$ Cyclic Isomers. The electronic energies, $<S^2>$ expectation values, dipole moments, and relative energies at the B3LYP/6-311+G(d) level of theory, for the lowest-lying cyclic ZnC$_n$ species on the singlet, triplet, and quintet potential surfaces, are given in Table 2. In Figure 2, the optimized geometries for the predicted most stable cyclic species are shown.

As we have mentioned before, no fan structures have been found after an exhaustive search on the respective potential surfaces. Our attempts to obtain fan species collapsed into the corresponding cyclic structures. The only species which resembles a fan isomer is that corresponding to ZnC$_4$ in Figure 2. This is the most stable species on the ZnC$_4$ potential surface, and the Zn$-$C distances suggest the possibility of interaction of the metal with the entire carbon chain (typical of a fan structure). A topological analysis of the charge density[41] shows that this is a truly monocyclic species with formal peripheral Zn$-$C bonds and no transannular Zn$-$C bonding. Nevertheless, the geometrical parameters (Zn$-$C bonds 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.

All cyclic ZnC$_n$ structures have singlet lowest-lying states. Quintet states are clearly much less stable. On the other hand, triplet states are not so high in energy, especially for n-odd species. In fact, in the case of ZnC$_3$, singlet and triplet states are very close in energy, the triplet one lying slightly higher in energy. Therefore, in such a case, no definitive conclusion about the lowest-lying cyclic state can be drawn, and higher-level calculations should be required.

The Zn$-$C distances are larger for the cyclic structures than for their open-chain counterparts for the first members

Table 2. Electronic Energies, $<S^2>$ Values, Dipole Moments, and Relative Energies (including the ZPE Correction) for Cyclic ZnC$_n$ Clusters at the B3LYP/6-311+G(d) Level

isomer	state	$-E$ (a.u)	$<S^2>$	μ (D)	ΔE (kcal mol^{-1})
ZnC$_2$	$^1A_1$	1855.372 935		6.35	0.00
	$^3A_2$	1855.357 356	2.0125	1.91	13.04
	$^5A_1$	1855.212 791	6.0097	0.76	99.42
ZnC$_3$	$^1A_1$	1893.428 832		1.75	0.00
	$^3A_2$	1893.428 559	2.0197	2.20	0.07
	$^5A_1$	1893.339 773	6.0540	2.97	55.51
ZnC$_4$	$^1A_1$	1931.509 083		3.75	0.00
	$^3A_2$	1931.494 300	2.0093	2.43	8.11
	$^5A_1$	1931.404 511	6.0292	1.85	63.56
ZnC$_5$	$^1A_1$	1969.604 686		2.24	0.00
	$^3B_1$	1969.588 413	2.1125	2.10	10.17
	$^5A_2$	1969.528 952	6.0613	1.19	47.38
ZnC$_6$	$^1A_1$	2007.733 103		1.13	0.00
	$^3A''$	2007.681 770	2.0410	2.77	30.95
	$^5A_2$	2007.620 343	6.0781	0.01	69.12
ZnC$_7$	$^1A_1$	2045.812 691		1.70	0.00
	$^3B_1$	2045.800 458	2.1338	1.09	7.11
	$^5B_1$	2045.711 463	6.1253	3.18	62.13
ZnC$_8$	$^1A_1$	2083.914 092		0.76	0.00
	$^3A''$	2083.868 988	2.0379	1.79	26.89
	$^5A_1$	2083.834 998	6.0941	1.82	48.08

of the series ($n = 2-5$), whereas they are very similar to the linear isomers for the larger species ($n = 6-8$). In all cases, the C$-$C distances show clear alternations, with C$_{odd}-$C$_{even}$ distances shorter than C$_{even}-$C$_{odd}$ ones. As expected, dipole moments are always lower than those found in the open-chain isomers. The general trend is to decrease as the number of carbon atoms increases, although there are some oscillations in this behavior.

3.3. Relative Stabilities of ZnC$_n$ Clusters. In order to compare the relative stability of the clusters with different sizes, we will use the concept of incremental binding energies.[42,43] The incremental binding energy can be defined as the change in energy accompanying the following process:

$$\text{ZnC}_n \rightarrow \text{ZnC}_{n-1} + \text{C}$$

and it can be computed as the consecutive binding energy differences between adjacent ZnC$_n$ and ZnC$_{n-1}$ clusters.

The results for the incremental binding energy, as a function of the number of carbon atoms, for the different open-chain and cyclic ZnC$_n$ clusters are shown in Figure 3. It can be observed that there is an even$-$odd alternation for the open-chain isomers, with n-even species being comparatively more stable than n-odd ones. However, this alternation is not very pronounced, and in fact, the incremental binding energy varies smoothly along the series. This parity effect can be attributed to the number of available $\pi-$ valence electrons, mainly the electron number in π-type highest occupied molecular orbital (HOMO).[44] As we pointed out before, open-chain ZnC$_n$ clusters ($^3\Pi$) present $\sigma^1\pi^1$ configurations (n-odd clusters) and $\sigma^1\pi^3$ configurations (n-even clusters). In this sense, n-even species are comparatively more stable because of the presence of three electrons in
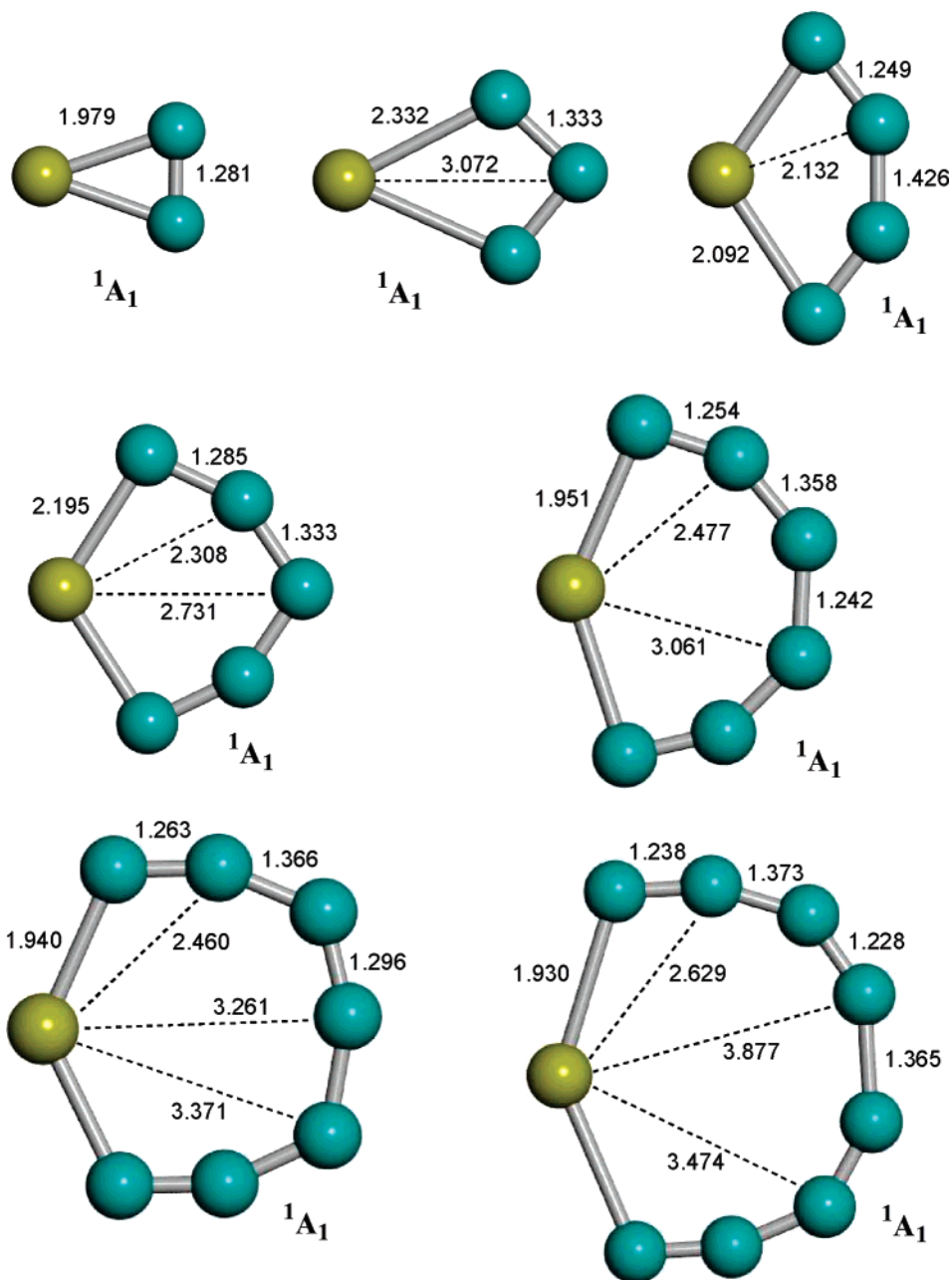
Figure 2. Equilibrium geometries of ZnC_n cyclic clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.
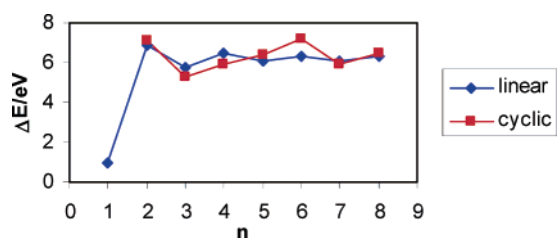

Figure 3. Incremental binding energies (eV) for ZnC_n open-chain and cyclic clusters at the B3LYP/6-311+G(d) level of theory vs the number of carbon atoms.

the HOMO, instead of just one electron as in the case of *n*-odd clusters. However, in both cases, the π-type HOMO is not fully filled and a similar stability for the different open-chain species can be expected. Consequently, the incremental binding energy varies smoothly for these systems.

Incremental binding energies for cyclic isomers do not exhibit a strict parity alternation effect. There seems to be a preference for *n*-even clusters, as in the case of open-chain isomers, but this trend breaks for ZnC_4.

The energy differences between cyclic and open-chain species are shown in Figure 4 as a function of the number of carbon atoms. The general trend is that open-chain isomers are preferred for small clusters, up to $n = 5$, with the exception of the first member of the series ZnC_2. On the other hand, cyclic isomers are preferred for larger clusters, although in these cases, the energy difference between both structures is rather small.

We may compare these results with those obtained for other carbon clusters doped with transition metals.[16−18] It seems that early transition metals, such as Sc or V, clearly favor cyclic (or fan) isomers. In those cases, the open-chain
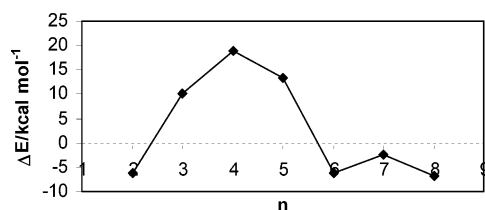
Structure and Stability of Small ZnC$_n$ Clusters

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Figure 4. Relative energies, including the ZPE correction (kcal/mol), of the cyclic ZnC$_n$ isomers with respect to the corresponding open-chain structures vs the number of carbon atoms.

isomers are relatively unstable, with energy differences between open-chain and cyclic isomers within the range 15−35 kcal mol^{-1} for ScC$_n$[17] clusters and 10−22 kcal mol^{-1} for VC$_n$[18] species. On the other hand, for late transition metals (Zn being a prototypical case), the open-chain isomers are comparatively more stable, and in fact, the smaller clusters have open-chain ground states. This behavior is probably related to two concomitant effects. In first place, charge donation from the metal to the carbon unit (which is expected to play an important role in the stabilization of transition metal carbides[45]) 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, back-donation from the carbon unit (which is expected to contribute to some extent to the stabilization of these species and is also in principle more favorable in C$_{2v}$ than in C$_{\infty v}$ symmetry) should be hindered to a large extent for late transition metals, because of the large occupancy of the metal 3d orbitals (which are fully occupied for Zn).

4. Conclusions

A theoretical study on the open-chain and cyclic ZnC$_n$ clusters ($n = 1−8$) has been carried out by using hybrid density theory with the 6-311G+(d) basis set.

According to our calculations, open-chain ZnC$_n$ clusters usually present triplet ground states. ZnC$_2$ has a singlet ground state, whereas for ZnC$_3$ and ZnC$_5$, the nonlinear singlet lies slightly below the linear triplet structure. All cyclic species studied in this study have singlet ground states.

The relative stability of the different clusters has been estimated employing the concept of incremental binding energies. For open-chain ZnC$_n$ clusters, a slight alternation stability effect is observed with n-even clusters being more stable than n-odd ones. These odd−even alternation trends have been interpreted according to the different electronic configuration. In the case of cyclic isomers, even though there is no strict parity effect, it seems that n-even species are also favored.

Our study suggests that, for late transition metals, such as Zn, open-chain isomers are comparatively more stable than in the case of early transition metals, which clearly favor cyclic ground states. For small ZnC$_n$, the open-chain isomer is the most stable one.

Predictions for some molecular properties such as rotational constants, dipole moments, and vibrational frequencies, which could be useful for an eventual experimental charac-

terization, have been also provided (see the Supporting Information).

Supporting Information Available: Rotational constants and vibrational frequencies for open-chain and cyclic species (Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.

(2) Van Orden, A.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313.

(3) Fulara, J.; Lessen, D.; Freivogel, P.; Maier, J. P. *Nature* **1993**, *366*, 439.

(4) Freivogel, P.; Fulara, J.; Maier, J. P. *Astrophys. J.* **1994**, *431*, L151.

(5) Allendorf, M. D. J. *Electrochem. Soc.* **1993**, *140*, 747.

(6) Koinuma, H.; Horiuchi, T.; Inomata, K.; Ha, H.-K.; Nakajina, K.; Chaudhary, K. A. *Pure Appl. Chem.* **1996**, *68*, 1151.

(7) Consalvo, D.; Mele, A.; Stranges, D.; Giardini-Guidoni, A.; Teghil, R. *Int. J. Mass. Spectrom. Ion Processes* **1989**, *91*, 319.

(8) Leleyter, M.; Joyes, P. *Surf. Sci.* **1985**, *156*, 800.

(9) Orth, R. G.; Jonkmann, H. T.; Michl, J. *Int. J. Mass Spectrom. Ion Processes* **1982**, *43*, 41.

(10) Becker, S.; Dietze, H. J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *82*, 287.

(11) Huang, R. B.; Wang, C. R.; Liu, Z. Y.; Zheng, L. S.; Qi, F.; Sheng, L. S.; Yu, S. Q.; Zhang, Y. W. Z. *Phys. D: At., Mol. Clusters* **1995**, *33*, 49.

(12) Redondo, P.; Barrientos, C.; Cimas, A.; Largo, A. *J. Phys. Chem. A* **2003**, *107*, 4676.

(13) Redondo, P.; Barrientos, C.; Cimas, A.; Largo, A. *J. Phys. Chem. A* **2003**, *107*, 6317.

(14) Largo, A.; Redondo, P.; Barrientos, C. *J. Phys. Chem. A* **2004**, *108*, 6421.

(15) Redondo, P.; Barrientos; Largo, A. *J. Phys. Chem. A* **2004**, *108*, 11132.

(16) Redondo, P.; Barrientos, C.; Largo, A. *J. Phys. Chem. A* **2005**, *109*, 8594.

(17) Redondo, P.; Barrientos, C.; Largo, A. *J. Phys. Chem. A* **2006**, *110*, 4057.

(18) Redondo, P.; Barrientos, C.; Largo, A. *J. Chem. Theory Comput.* **2006**, *2*, 885.

(19) Zhai, H. J.; Wang, L. S.; Jena, P.; Gutsev, G. L.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **2004**, *120*, 8996.

(20) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524.

(21) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547.

(22) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

(23) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053.

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

(25) Kohn, W.; Sham, L. J. *Phys. Rev. A: At., Mol., Opt. Phys.* **1965**, *140*, 1133.

(26) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

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

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millan, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelly, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc: Pittsburgh, PA, 1998.

(29) Moore, C. E. *Atomic Energy Levels*; NSRDS-NBS Circular No. 35; U.S. GPO: Washington, DC, 1971.

(30) Castro, M. A.; Canuto, S.; Müller-Plathe, F. *Phys. Rev. A: At., Mol., Opt. Phys.* **1992**, *46*, 4415.

(31) Da Silva, C. O.; Teixeira, F. E. C.; Azevedo, J. A. T.; Da Silva, E. C.; Nascimento, M. A. C. *Int J. Quantum Chem.* **1996**, *60*, 433.

(32) Serrano, A.; Canuto, S. *Chem. Phys. Lett.* **1997**, *269*, 193.

(33) Takada, H. H.; Pelegrini, M.; Roberto-Neto, O.; Machado, F. B. C. *Chem. Phys. Lett.* **2002**, *363*, 283.

(34) Kerkines, I. S. K.; Pittner, J.; Čarsky, P.; Mavridis, A.; Hubač, I. *J. Chem. Phys.* **2002**, *117*, 9733.

(35) Papakondylis, A.; Mavridis, A. *J. Phys. Chem. A* **2003**, *107*, 7650.

(36) Halfen, D. T.; Apponi, A. J.; Ziurys, L. M. *Astrophys. J.* **2002**, *577*, L67.

(37) Pelegrini, M.; Roberto-Neto, O.; Ornellas, F. R.; Machado, F. B. C. *Chem. Phys. Lett.* **2004**, *383*, 143.

(38) Boldyrev, A. I.; Simons, J. *Mol. Phys.* **1997**, 92, 365.

(39) Tsouloucha, A.; Kerkines, I. S. K.; Mavridis, A. *J. Phys. Chem. A* **2003**, *107*, 6062.

(40) Gutsev, G. L.; Andrews, L.; Bauschlicher, C. W. *Theor. Chem. Acc.* **2003**, *109*, 298.

(41) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, United Kingdom, 1990.

(42) Pascoli, G.; Lavendy, H. *J. Phys. Chem. A* **1999**, *103*, 3518.

(43) Raghavachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191.

(44) Boldyrev, A. I.; Simons, J. *J. Phys. Chem. A* **1997**, 101, 2215.

(45) Rayón, V. M.; Redondo, P.; Barrientos, C.; Largo, A. *Chem.—Eur. J.* **2006**, *12*, 6963.

CT6001797