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Small ScC$_n$ Cyclic Clusters: A Density Functional Study of Their Structure and Stability

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A theoretical study of the ScC$_n$, ScC$_n^+$, and ScC$_n^-$ ($n = 1-10$) cyclic clusters has been carried out employing the B3LYP density functional method. Predictions for several molecular properties that could help in their possible experimental characterization, such as equilibrium geometries, electronic structures, dipole moments, and vibrational frequencies, are reported. All ScC$_n$ cyclic clusters are predicted to have doublet ground states. For cationic clusters the ground state is alternate between singlets (n-even species) and triplets (n-odd members). In the case of anionic clusters the singlet−triplet separation is relatively small, with the singlets being favored in most cases. In general, even−odd parity effects are also observed for different properties, such as incremental binding energies, ionization energies, and electron affinities. For all neutral, cationic, and anionic clusters it is found that cyclic species are more stable than their open-chain counterparts. Therefore, cyclic structures are the most interesting possible targets for an experimental search of scandium-doped carbon clusters.

Introduction

Small heteroatom-doped carbon clusters containing second-row elements have received considerable attention in recent years, due to their relevance in both solid state chemistry and in gas-phase chemistry, particularly in astrochemistry. A number of systematic theoretical studies addressing their structure and stability, as well as of their cationic and anionic derivatives, have been carried out. In particular much of the interest has focused on carbide clusters containing nonmetallic elements, such as SC$_n$[1], SiC$_n$,[2−4] PC$_n$,[5] and ClC$_n$.[6] Nevertheless, quite recently metallic carbides, including AlC$_n$,[7,8] MgC$_n$,[9,10] CaC$_n$,[11,12] or NaC$_n$[13] clusters, have also been theoretically studied. It is also worth mentioning that a systematic analysis of the properties of second-row carbides has been carried out by Li and Tang.[14] Furthermore, the main factors governing the competition between linear and cyclic isomers for the second-row dicarbides have also been addressed in a recent theoretical work.[15]

This kind of study has been extended to other systems containing heavier atoms, such as PbC$_n$ linear clusters.[16] Quite recently a study of linear and cyclic CrC$_n$ ($n = 2-8$) has been published,[17] and there are also other theoretical studies of transition metal carbides in the recent literature, such as YC$_n$,[18] LaC$_n$,[18−20] NbC$_n$,[21] PdC$_n^+$,[22] and PtC$_n^+$.[23] In fact the study of binary carbon compounds containing transition metals is quite interesting. Early transition metals have been found to form stable gas-phase metal−carbon clusters ions, known as metallocarbohedrenes (*met-cars*), with an $M_8C_{12}^+$ stoichiometry.[24−28] *Networked* metallofullerenes[29] can also be obtained incorporating transition metals into a carbon cage. On the other hand, late transition metals are catalysts for the formation of carbon nanotubes,[30] and finally, endohedral metallofullerenes[31] can be obtained trapping rare-earth elements inside fullerene cages.

Therefore, theoretical investigations of small carbon clusters might be very useful to obtain information of metal−carbon interactions and may help to understand the growth mechanisms of the various metal−carbon nanomaterials, as well as to obtain insight into their physical and chemical properties in general. The main purpose of the present work is to provide information about the ScC$_n$ ($n = 2-10$) compounds and their cationic and anionic derivatives, which may help to understand the scandium−carbon chemistry. We must point out that there are some previous theoretical works for the first members of the series, namely, ScC,[32−34] ScC$_2$,[35−37] and ScC$_3$.[37,38] Since we have carried out a previous study of the open-chain ScC$_n$ isomers,[39] the present work will focus on the cyclic compounds. It should be emphasized that previous works on ScC$_2$[35−37] and ScC$_3$[37,38] predicted that the cyclic isomers should be the most stable ones. Therefore, in principle the cyclic compounds should be the most interesting for a possible experimental characterization. An analysis of the competition between open-chain and cyclic compounds will also be presented.

Computational Methods

We have employed a similar theoretical approach as in our previous studies on second-row heteroatom-doped carbon clusters.[6−13] All calculations have been made using the density functional theory (DFT), selecting the B3LYP exchange-correlation functional,[40,41] which has been widely applied to the study of many medium-sized heteroatom-doped carbon clusters, providing structures in good agreement with the experimental results.[42] This level of theory consists of the Lee−Yang−Parr[43] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[44] The latter is a linear combination of local density approximation, Becke's gradient correction,[45] and the Hartree−Fock exchange energy based on Kohn−Sham orbitals.[46]

We have used different basis sets in our calculations, but we will only present results with two of them considered representative enough. First, as in our previous works, we employed an all-electron basis set, namely, the triple split-valence d-polarized 6-311+G(d) basis set (the Wachters[47] and Hay[48] with the scaling factor of Ragavachari and Trucks[49] is used for scandium and the conventional 6-311G(d) basis set[50] for carbon atoms), which also includes diffuse functions. The use of effective core potentials (ECP) for the description of clusters

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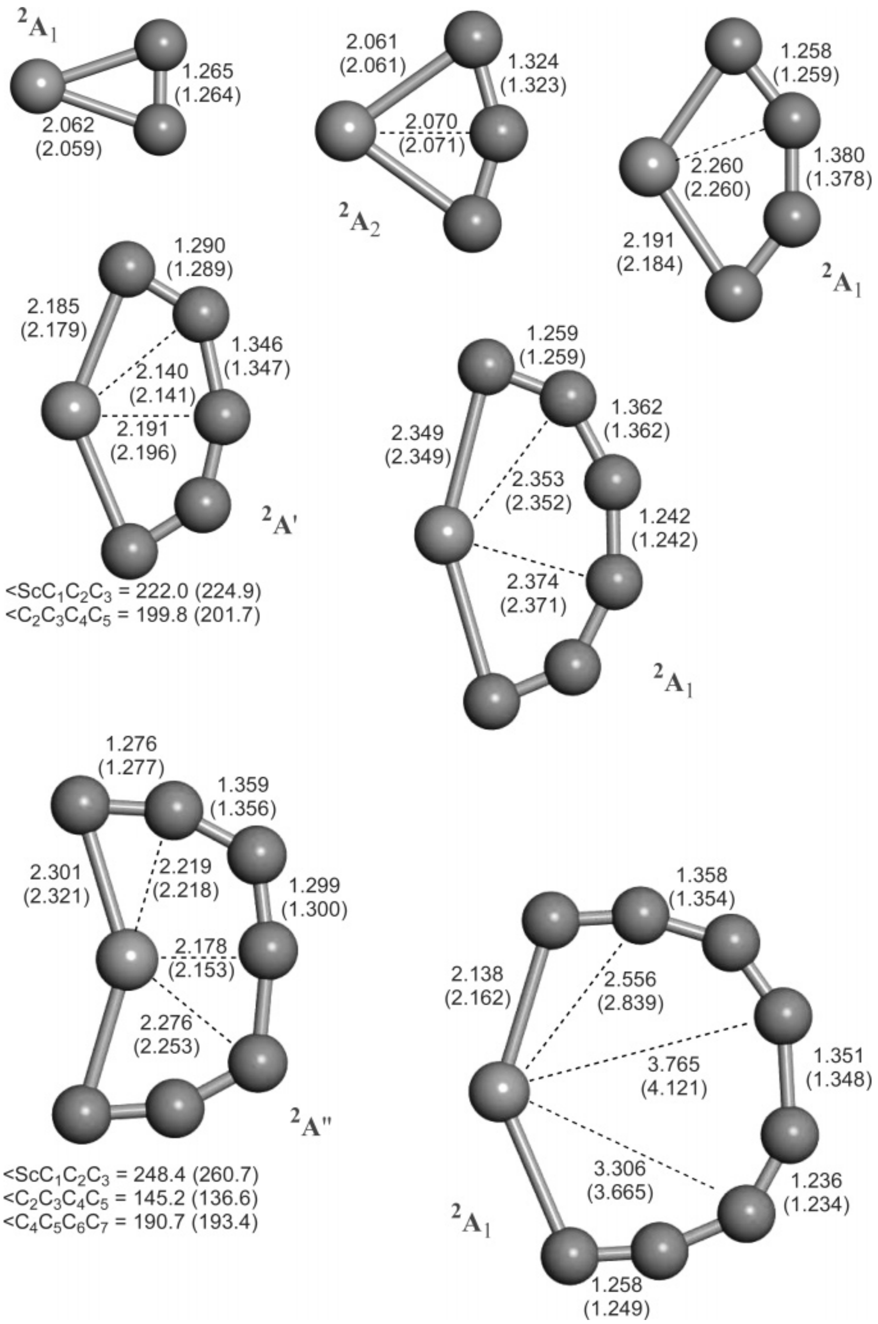

reduces significantly the computational time. Therefore, to check the performance of a basis set containing ECP in these systems we have employed a mixed basis set formed by the LanL2DZ (Los Alamos ECP plus DZ, LanL2DZ[51−53]) for scandium in conjunction with the 6-311+G(d) basis set for carbon atoms. This basis set will be denoted as LAN-6+(d).

Harmonic vibrational frequencies were computed for all structures. This allows us to estimate the zero-point vibrational energy (ZPVE) correction for each structure, as well as to assess the nature of the stationary points and therefore to characterize if they are true minima on the respective potential surface.

All calculations reported in this work were carried out with the Gaussian-98 program package.[54]

Results and Discussion

ScC$_n$ Cyclic Clusters. We have searched for different cyclic ScC$_n$ species on both the doublet and quartet surfaces. One of the main purposes of this work is to carry out a systematic study of some properties as a function of the size of the cluster, and consequently, we should compare isomers of the same type. Therefore, only ring (monocyclic) structures will be reported. Nevertheless, other possible cyclic isomers have also been considered. However, for the first members of the series they were found to lie higher in energy, and therefore it is expected that for small-size clusters, such as those studied in this work ($n = 2-10$) they will not be in general competitive. Furthermore, Zhai et al.[17] have found in their study of CrC$_n$ ($n = 2-8$) clusters that the linear (open-chain) and ring (monocyclic) isomers are in general the most competitive ones. However, to explore the competition of the main low-lying isomers, the results for different species will be presented in the case of the larger clusters, namely, those corresponding to $n = 9$ and $n = 10$. The relevant species are the monocyclic isomer where scandium is bonded only to the two contiguous carbon atoms (structure **1** in Figure 1), the ring isomer with scandium "embedded" in the carbon ring and bonded to several carbon

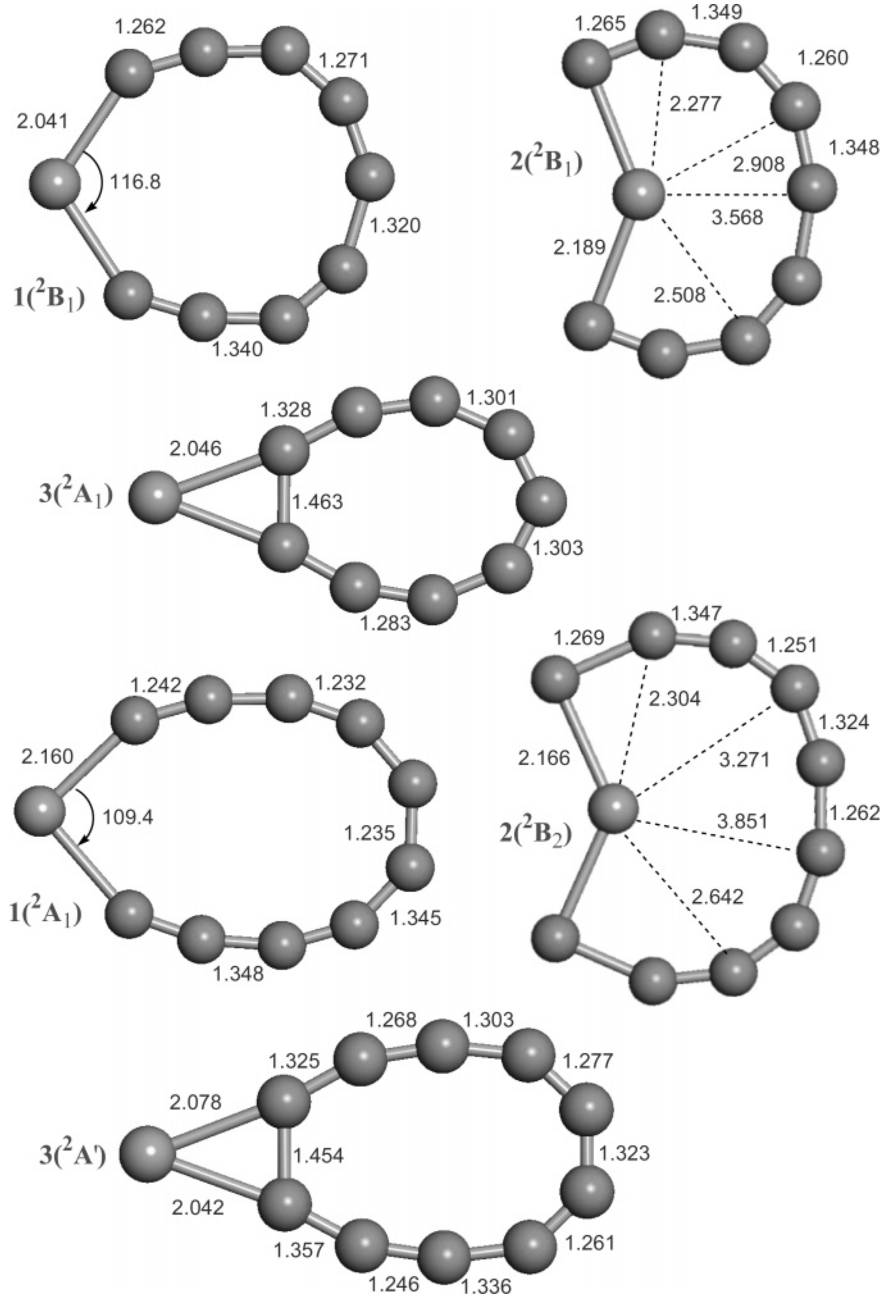

Figure 1. Equilibrium geometries of ScC_n monocyclic clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

atoms (structure **2**), and the isomer with scandium bridging across a C−C bond (structure **3**). It is interesting to point out that we have considered another possible isomer in which scandium is bonded to a single atom in the carbon ring, as suggested by Clemmer et al.[55] in their experimental study on LaC_n^+. In the case of ScC_n (as well as in the cationic and anionic derivatives) such isomer lies much higher in energy than the predicted most stable one, and furthermore, it has three imaginary frequencies, one of them corresponding to the degenerate rearrangement of the bridged structure **3**. Consequently, this isomer is not relevant in the case of ScC_n clusters.

In Table 1 we have collected the electronic energies, $<S^2>$ expectation values, dipole moments, binding (atomization) energies, and relative energies at the B3LYP/6-311+G(d) and B3LYP/LAN-6+G(d) levels of theory for the lowest-lying cyclic ScC_n species on the doublet and quartet potential surfaces. Other properties that might help in an experimental search of these species, such as the harmonic vibrational frequencies and rotational constants, are provided as Supporting Information (Table S1). In addition, in Figure 1 the optimized geometries for the predicted lowest-lying structures are shown.

As can be seen in Table 1 (as well as in the subsequent tables for the corresponding cations and anions, see below), the S^2 expectation values for all species are very close to the spin pure values, and therefore spin contamination has an almost negligible effect. All reported structures are true minima on their respective potential surface, since all their vibrational frequencies are real. The only exception is doublet ScC_7, which exhibits a small imaginary frequency (60i cm^{-1}) with the LAN-6+(d) basis set. With the 6-311+(d) basis set we were able to obtain a $^2A''$ state with all its frequencies real, but at the B3LYP/LAN-6+(d) level only the C_{2v}-symmetric ($^2A_2$ electronic state) could be obtained. Even though the imaginary frequency is rather small, the deviation from planarity is important (see the dihedral angles in Figure 1). In general it is observed that there is a rather good agreement in the Sc−C and C−C distances obtained with both

TABLE 1: Electronic Energies, $<S^2>$ Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Cyclic ScC$_n$ Clusters with the B3LYP/6-311+G(d) (First Line) and B3LYP/LAN-6+(d) (Second Line) Methods

isomer	state	$-E$ (au)	$<S^2>$	BE (eV)	μ (D)	ΔE (kcal mol^{-1})
ScC$_2$	$^2A_1$	836.776155	0.7521	11.83	6.42	0.00
		122.520288	0.7529	1192	6.83	0.00
	$^4B_2$	836.710097	3.7628		3.60	40.87
		122.455954	3.7630		3.95	39.75
ScC$_3$	$^2A_2$	874.841272	0.7584	17.35	8.46	0.00
		160.588283	0.7578	17.53	8.42	0.00
	$^4B_1$	874.827155	3.7999		4.64	8.59
		160.571028	3.8012		5.15	10.53
ScC$_4$	$^2A_1$	912.970882	0.7516	24.60	4.47	0.00
		198.714872	0.7517	24.69	4.97	0.00
	$^4A_2$	912.888063	3.7726		4.18	50.86
		198.633301	3.7724		4.67	50.42
ScC$_5$	$^2A'$	951.046077	0.7714	30.42	5.05	0.00
		236.788908	0.7717	30.47	5.08	0.00
	$^4B_1$	951.014466	3.8505		3.27	19.05
		236.758021	3.8299		3.65	18.54
ScC$_6$	$^2A_1$	989.140956	0.7513	36.74	1.20	0.00
		274.883963	0.7512	36.80	1.38	0.00
	$^4A_2$	989.068679	3.7838		1.32	43.62
		274.812849	3.7831		1.49	43.01
ScC$_7$	$^2A''$	1027.222128	0.7773	42.74	2.87	0.00
	$^2A_2$	312.960531	0.7765	42.69	1.73	0.00
	$^4B_1$	1027.189443	3.8528		0.83	19.97
		312.932524	3.8509		0.70	17.11
ScC$_8$	$^2A_1$	1065.308697	0.7528	48.84	1.66	0.00
		351.053452	0.7517	48.93	2.79	0.00
	^4A	1065.254337	3.8071		1.84	33.31
		350.992754	3.8148		3.81	36.73
ScC$_9$	**1**($^2B_1$)	1103.389966				6.27
	2($^2B_1$)	1103.399732	0.7734	55.07	0.21	0.00
		389.139241	0.7729	55.04	0.20	0.00
	2($^4B_1$)	1103.373026	3.8821		3.53	15.98
		389.118492	3.8825		4.24	12.41
	3($^2A_1$)	1103.373026				24.30
ScC$_{10}$	**1**($^2A_1$)	1141.490668				1.15
	2($^2B_2$)	1141.490727	0.7704	61.34	1.83	0.00
		427.235228	0.7808	61.39	2.11	0.00
	2($^4A'$)	1141.445858	3.8101		1.25	27.61
		427.190541	3.8082		1.13	27.17
	3($^2A'$)	1141.481360				8.09

basis sets. Furthermore, other properties computed at both levels, such as dipole moments, vibrational frequencies, and even relative stabilities, are very close. Therefore, it seems that the inclusion of effective core potentials in the basis set does not deteriorate the predictions at the B3LYP level for ScC$_n$ compounds.

All cyclic ScC$_n$ clusters have doublet ground states, according to the predictions at the B3LYP level shown in Table 1. The doublet−quartet energy difference is found to be higher for the *n*-even clusters than for the *n*-odd ones. In any case the energy differences between the doublet ground states and the corresponding lowest-lying quartets seem large enough in all cases as to be confident in this prediction. We may compare our results for the first members of the series with other values in the literature. In particular, a very recent CASPT2 study[37] of ScC$_2$ and ScC$_3$ obtained the same doublet ground states, whereas the lowest-lying quartets were found to lie 43.14 kcal/mol ($^4B_2$ electronic state) for ScC$_2$ and 7.48 kcal/mol ($^4B_1$) for ScC$_3$ higher in energy than the corresponding ground states, in reasonable agreement with our predicted values at the B3LYP level (40.87 and 8.59 kcal/mol, respectively). The geometrical parameters provided by the CASPT2 calculations are also in reasonable agreement with the B3LYP values, with the exception of the C−C bond distance in ground-state ScC$_2$. For ScC$_2$ the CASPT2 level[37] gives Sc−C = 2.085 and C−C = 1.294 Å, whereas for ScC$_3$ the geometrical parameters are Sc−C1 = 2.105, Sc−C2 = 2.117, C−C = 1.324 Å. Our B3LYP geometrical parameters for ScC$_2$ and ScC$_3$ are nearly coincident with other DFT calculations.[36,38]

It can be seen in Figure 1 that all C−C bond distances are in the range of 1.24−1.38 Å, following in general the same pattern observed in the case of open-chain isomers,[39] with a clear alternation of C−C bond distances (C$_{\text{odd}}$ − C$_{\text{even}}$ distances considerably shorter than C$_{\text{even}}$ − C$_{\text{odd}}$ ones). For the first members of the series, from ScC$_2$−ScC$_6$, it can be observed that the structures seem to result from a π-type interaction of scandium with the entire carbon chain. This is reflected in the very similar Sc−C distances for all carbon atoms. This tendency of scandium to interact with the whole carbon unit is also reflected in the last members of the series, ScC$_7$−ScC$_{10}$, where the scandium atom is almost "embedded" in a C$_n$ chain in the lowest-lying isomers. The only exception is ScC$_8$, which mainly exhibits an interaction of the scandium atom with the terminal carbon atoms of the chain.

For the two last members of the series, ScC$_9$ and ScC$_{10}$, isomer **1** lies rather close to the predicted lowest-lying isomer (**2**), with energy separations of only 6.27 and 1.15 kcal/mol, respectively. Isomer **3**, corresponding to a bicyclic structure with scandium in a bridged position, lies somewhat higher in energy, namely 24.30 and 8.09 kcal/mol, respectively, for the ScC$_9$ and ScC$_{10}$ species. Therefore, the energetic results show that small scandium-doped carbon clusters have monocyclic ground states. The largest members of the studied species seem to prefer conformations where the scandium atom is almost "embedded" into the carbon ring.

The dipole moments of the smaller cyclic ScC$_n$ clusters are quite large, as a consequence of the high ionic character of the Sc−C bond, with the scandium atom bearing in most cases a relatively high positive charge. Nevertheless, as expected, dipole moments of cyclic clusters are much lower than those of the corresponding open-chain species. It is also clearly observed that in general the dipole moment decreases with the number of carbon atoms.

The relative stability of cyclic ScC$_n$ compounds will be discussed, following the suggestion by Pascoli and Lavendy,[5] in terms of the incremental binding energies.[56] In our case the incremental binding energy are defined as the change in energy accompanying the following process:

$$ScC_n \rightarrow ScC_{n-1} + C$$

In practice incremental binding energies can be computed as the consecutive binding energy differences between adjacent ScC$_n$ and ScC$_{n-1}$ clusters. In Figure 2 the incremental binding energies for the different cyclic ScC$_n$ clusters are represented versus the number of carbon atoms. It seems that up to $n = 7$ there is a clear even−odd alternation, *n*-even clusters being more stable than *n*-odd ones. This is the same behavior found for cyclic CaC$_n$ clusters.[12] Nevertheless, it can be seen in Figure 2 that from $n = 7$ the incremental binding energies monotonically increase with the number of carbon atoms, although in a very smooth way. In fact incremental binding energies are quite similar for the last clusters in the series, taking values around 6.01−6.24 eV.

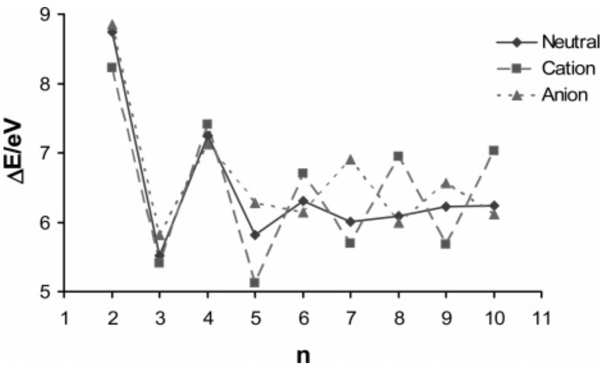

Figure 2. Incremental binding energies (eV) for the ScC$_n$, ScC$_n^+$, and ScC$_n^-$ monocyclic clusters vs the number of carbon atoms.

TABLE 2: Electronic Energies, <S^2> Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Cyclic ScC$_n^+$ Clusters with the B3LYP/6-311+G(d) (First Line) and B3LYP/LAN-6+(d) (Second Line) Methods

isomer	state	−E (au)	<S^2>	BE (eV)	μ (D)	ΔE (kcal mol^{-1})
ScC$_2^+$	$^1A_1$	836.521155		11.46	7.47	0.00
		122.264683		11.80	7.28	0.00
	$^3A_2$	836.475347	2.0187		6.96	28.18
		122.221677	2.0187		6.93	26.37
ScC$_3^+$	$^1A_1$	874.575599			9.75	3.47
		160.323034			9.52	1.24
	$^3B_1$	874.581595	2.0528	16.86	6.65	0.00
		160.325414	2.0520	17.22	6.52	0.00
ScC$_4^+$	$^1A_1$	912.71018		24.28	5.40	0.00
		198.459044		24.56	5.26	0.00
	$^3B_2$	912.645677	2.0206		5.50	44.17
		198.388171	2.0225		5.43	43.24
ScC$_5^+$	$^1A_1$	950.766561		29.39	3.89	0.00
		236.506748		29.65	3.84	0.00
	$^3A'$	950.759112	2.0784		4.41	4.59
		236.498254	2.0765		4.38	5.33
ScC$_6^+$	$^1A_1$	988.876220		36.10	1.35	0.00
	$^1A'$	274.611692		36.24	1.36	0.00
	$^3A''$	988.815609	2.0413		4.17	36.61
		274.554723	2.0426		4.22	34.45
ScC$_7^+$	$^1A'$	1026.939744			7.59	4.28
		312.683836			7.46	4.48
	$^3B_1$	1026.946150	2.1252	41.80	6.24	0.00
		312.690698	2.1229	42.17	6.11	0.00
ScC$_8^+$	$^1A_1$	1065.064994		48.74	5.15	0.00
		350.808644		49.09	4.90	0.00
	$^3A''$	1065.011895	2.0222		5.72	32.01
		350.760366	2.0214		5.73	29.10
ScC$_9^+$	**1**($^1A_1$)	1103.130440			8.40	2.66
		388.875479			8.26	2.95
	1($^3B_1$)	1103.133327	2.1492	54.42	7.40	0.00
		388.878786	2.1531	54.81	7.44	0.00
	2(^1A)	1103.123514				7.05
	3($^1A_1$)	1103.133209			12.777	2.54
ScC$_{10}^+$	**1**($^1A_1$)	1141.256226		61.44	9.62	0.00
		427.004306		61.90	9.53	0.00
	1($^3B_2$)	1141.211923	2.0131		7.91	26.21
		426.960528	2.0128		7.86	25.91
	2($^1A_1$)	1141.231176				15.53
	3($^1A'$)	1141.248287			13.652	5.71

ScC$_n^+$ Cyclic Clusters. A summary of the molecular properties for the lowest-lying singlet and triplet states of ScC$_n^+$ cyclic clusters is provided in Table 2 (and Table S2 of the Supporting Information), whereas the geometrical parameters for the ground states are shown in Figure S1 of the Supporting Information. All structures are true minima on the corresponding potential energy surface since all their vibrational frequencies are real.

It can be seen in Table 2 that n-even ScC$_n^+$ cyclic clusters have singlet ground states, whereas for n-odd compounds the lowest-lying cationic species corresponds to a triplet electronic state. There is only one exception, ScC$_5^+$, which has a singlet ground state. Nevertheless, it must be emphasized that the singlet−triplet energy difference is quite large for all n-even cyclic clusters (around 28−44 kcal/mol in all cases), whereas for n-odd clusters this energy separation is very small (around 3−4.5 kcal/mol). Furthermore, it should not be discarded that at higher correlated levels of theory, which could favor closed-shell electronic states, the singlet−triplet separation could be narrowed even more. Therefore, singlet states could also be possible experimental targets.

Comparing the geometries of the cationic clusters with their neutral counterparts, it can be observed that in general Sc−C distances are slightly shortened for n-even clusters, whereas they are lengthened for n-odd ones. Nevertheless the most important difference is that for the lowest-lying isomer of the largest cationic species the scandium atom interacts mainly with the terminal carbon atoms (structure **1** in Figure S1) and not with the entire carbon chain as observed for the neutrals. Consequently, the geometry of the largest cationic and neutral clusters is quite different, with the scandium atom not being “embedded” by the ring. In fact, in the case of the cations even the bicyclic bridged structures **3** are more stable than the corresponding species **2** with scandium almost embedded in the carbon ring. Bridged structures are comparatively more stable for the cations than for neutral and anionic species (see below). On the other hand, the C−C distances follow the same patterns observed for the neutral ScC$_n$ clusters, with values close to typical cumulenic structures and some acetylenic character, which is reflected in the alternation of C−C distances.

The incremental binding energies for the different ScC$_n^+$ clusters are represented in Figure 2. A clear even−odd alternation is observed, with the n-even cations being comparatively much more stable than the n-odd ones. This alternation does not seem to be attenuated for the larger members of the series as in the case of their neutral counterparts, since for example the difference in incremental binding energies between ScC$_9^+$ and ScC$_{10}^+$ is of the same magnitude as the difference between the $n = 7$ and $n = 8$ members. It seems clear from inspection of Figure 2 that upon ionization n-even clusters are favored.

ScC$_n^-$ Cyclic Clusters. The main properties of the anionic cyclic clusters are given in Table 3 (as well as in the Supporting Information, Table S3), whereas the optimized geometries for the lowest-lying species are shown in Figure S2 in the Supporting Information. All anionic species reported in this work are true minima on their respective potential surface.

The energy difference between the singlet and triplet states is in most cases rather small. In fact, for ScC$_3^-$, ScC$_4^-$, and ScC$_6^-$ the lowest-lying state corresponds to a triplet according to the B3LYP results. In these cases it is possible that the singlet structures could also be accessible to experimental observations. Nevertheless it seems that for larger clusters singlet states are favored and even the singlet−triplet separation is usually more than 10 kcal/mol.

Concerning the geometrical parameters, it can be seen in Figure S2 that in general there are not drastic differences in the bond lengths between neutral and anionic species. As a general trend the Sc−C distances are shortened for n-odd anionic clusters when compared with those of their respective neutrals, whereas for n-even clusters the opposite behavior is found, with

TABLE 3: Electronic Energies, $<S^2>$ Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Cyclic ScC_n^- Clusters with the B3LYP/6-311+G(d) (First Line) and B3LYP/LAN-6+(d) (Second Line) Methods

isomer	state	$-E$ (au)	$<S^2>$	BE (eV)	μ (D)	ΔE (kcal mol^{-1})
ScC_2^-	$^1A'$	836.826075		13.36	1.74	0.00
		122.569128		13.24	2.57	0.00
	$^3A_2$	836.820792	2.0027		2.90	3.32
		122.567613	2.0028		2.90	0.90
ScC_3^-	$^1A_1$	874.882660			0.32	11.72
		160.626705			0.47	12.66
	$^3A_2$	874.901699	2.0083	19.16	2.40	0.00
		160.647211	2.0079	19.12	2.41	0.00
ScC_4^-	$^1A_1$	913.016928			0.01	5.47
		198.758769			0.97	7.07
	$^3A_1$	913.025819	2.0119	26.29	1.18	0.00
		198.770269	2.0120	26.21	1.42	0.00
ScC_5^-	$^1A'$	951.119536		32.57	6.45	0.00
		236.865243		32.53	6.38	0.00
	$^3B_1$	951.112268	2.0205		0.92	3.60
		236.855276	2.0209		1.30	5.29
ScC_6^-	$^1A_1$	989.198153			1.08	4.53
		274.941386			1.01	5.02
	$^3B_2$	989.205785	2.0159	38.71	0.33	0.00
		274.949934	2.0154	38.63	0.01	0.00
ScC_7^-	^1A	1027.322745		45.61	2.14	0.00
		313.064929		45.48	2.32	0.00
	$^3A_2$	1027.297866	2.0276		1.84	14.48
		313.041823	2.0273		1.73	13.37
ScC_8^-	$^1A'$	1065.403990		51.60	2.00	0.00
		351.145399		51.45	2.00	0.00
	$^3A_1$	1065.389903	2.0219		3.24	8.34
		351.133894	2.0217		3.18	6.74
ScC_9^-	**1**($^1A_1$)	1103.460328				29.35
	2($^1A_1$)	1103.507803		58.16	0.58	0.00
		389.249719		58.02	0.70	0.00
	2($^3B_1$)	1103.487735	2.0317		1.10	11.80
		389.231529	2.0318		0.93	10.58
	3($^1A_1$)	1103.430471			2.248	49.70
ScC_{10}^-	**1**($^1A_1$)	1141.542194				33.34
	2($^1A_1$)	1141.594708		64.28	1.60	0.00
		427.339340		64.21	1.68	0.00
	2($^3B_2$)	1141.574423	2.0183		1.49	11.99
		427.319269	2.0194		1.57	11.67
	3($^1A'$)	1141.549412			2.367	29.70

Sc−C distances being slightly longer for the anions. It is also worth mentioning that the ground state of the first member of the series, ScC_2^-, is found to be of C_s symmetry, whereas both the triplet and quintet states are C_{2v}-symmetric. Furthermore, this compound looks like an angular structure rather than a true cycle, since the −ScCC angle is about 93.7°. Nevertheless, perhaps the most interesting feature of the ScC_n^- geometries is that, as for the neutrals, the scandium atom seems to interact preferentially with the entire carbon chain, as evidenced by the Sc−C distances. Again for the larger clusters (from $n = 7$) the scandium atom, as a consequence of this interaction, has a certain tendency to be "embedded" in the carbon ring. In the cases of ScC_9^- and ScC_{10}^- we report in Table 3 the results for the other isomers (structures **1** and **3**). There is a clear preference for structure **2**, with scandium embedded in the carbon ring, since both isomers **1** and **3** lie more than 29 kcal/mol higher in energy.

The incremental binding energies for the anionic clusters are shown in Figure 2 There is not a general pattern for the entire set of cluster. The smaller clusters show an even−odd alternation, *n*-even clusters being much more stable than the *n*-odd ones, but this trend is reversed from ScC_6^-, and the *n*-odd anionic clusters are more stable for the last members of the family. Nevertheless, the difference in stability between *n*-odd and *n*-even compounds is attenuated as the size of the cluster is increased.

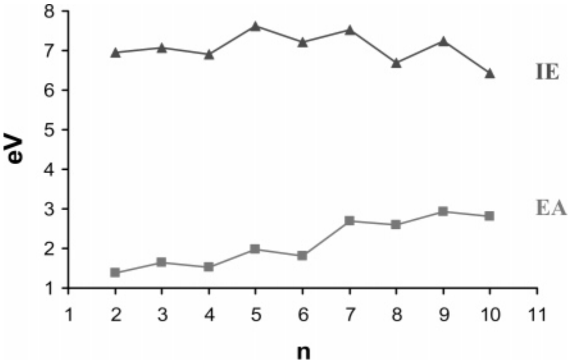

Figure 3. Ionization energies (IE) and electron affinities (EA), in eV, of ScC_n monocyclic clusters vs the number of carbon atoms.

Ionization Energies and Electron Affinities. We have computed the ionization energies (IE) and electron affinities (EA) employing the energies of the cationic, anionic, and neutral ScC_n clusters. The IEs and EAs as functions of the number of carbon atoms are shown in Figure 3. Since these magnitudes were computed as the energy difference between the charged and neutral species (including zero-point vibrational energies) at their respective optimized geometries, the values correspond to adiabatic IE and EA.

A clear even−odd alternation in the IEs is observed in Figure 3, *n*-odd clusters having higher IE than *n*-even ones. This behavior should be in principle related to the stability of ScC_n^+ cyclic clusters. We have already seen in Figure 2 that the cationic species exhibit a clear parity effect, with *n*-even compounds being much more stable than *n*-odd ones. This alternation in stability is more pronounced than in the neutral clusters, and therefore influences the behavior of IEs, with *n*-even clusters having smaller IEs. In general, when comparing among *n*-even clusters or *n*-odd ones, there seems to be a tendency for IEs to take lower values as the number of carbon atoms increases. It is also interesting to note that the estimated IEs for ScC_2 and ScC_4, 6.95 and 6.90 eV, respectively, are within the error bars of the experimental determinations, namely, 7.6±1 eV (ScC_2) and 6.7±1 eV (ScC_4).[57]

There is also an even−odd alternation in the EAs of ScC_n clusters, *n*-odd clusters having larger EAs. In this case the EAs are increased with the number of carbon atoms in both *n*-even and *n*-odd series of ScC_n clusters. For the first members of the series there are some reference values in the literature. The EA of ScC_2 has been estimated as 1.65 eV from experimental measures[58] and 1.52 eV from CASPT2 calculations.[37] The EA of ScC_3 obtained from experiments is 1.64 eV,[59] whereas theoretical estimates result in a value of 1.67 eV.[37] At the B3LYP/6-311+G(d) level we obtain EAs of 1.37 eV for ScC_2 and 1.65 eV for ScC_3. Whereas the EA for ScC_2, with an angular structure for the anion at the B3LYP level very different than its neutral counterpart, deviates substantially from both the experimental and theoretical determinations, in the case of ScC_3 a very good agreement is obtained.

Linear−Cyclic Stability. The energy differences between cyclic and open-chain isomers for ScC_n clusters and their cationic and anionic derivatives are shown in Figure 4. A positive value indicates that the cyclic isomer is more stable than the open-chain isomer.

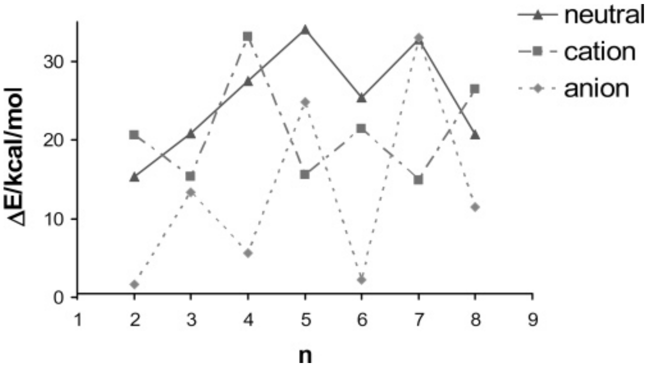

Figure 4. Energy separation between the monocyclic and open-chain structures for the ScC$_n$ clusters as a function of *n*. A positive value indicates that the monocyclic isomer is more stable than the corresponding open-chain one.

The general behavior of the ScC$_n^+$ cluster is very similar to their isoelectronic analogues CaC$_n$. Clearly, cyclic arrangements are favored, especially for *n*-even clusters. It is also clear that for the cations there is an even−odd alternation, *n*-even cyclic structures being comparatively more stable than *n*-odd ones. The possible explanation for this alternation resides in the number of π electrons, as in the case of pure carbon monocyclic clusters.[55]

On the other hand, for both ScC$_n$ and ScC$_n^-$ clusters the opposite behavior is found, with *n*-odd cyclic structures being comparatively more stable than *n*-even ones (for the neutral clusters this even−odd alternation is not observed for the first members of the series).

Nevertheless, the most important conclusion obtained from inspection of Figure 4 is that all neutral, cationic, and anionic clusters are predicted to prefer cyclic arrangements. Therefore, it seems that cyclic species should be the most obvious targets for an eventual experimental search. Only for *n*-even anions the linear species seem to be competitive, with energy separations below 10 kcal/mol (for $n = 2$, SC$_2^-$ and SCC$^-$ are almost isoenergetic, with an energy difference of just 1.7 kcal/mol at the B3LYP/6-311+G(d) level).

Conclusions

Density functional theory calculations have been carried out for ScC$_n$, ScC$_n^+$, and ScC$_n^-$ ($n = 2-10$) cyclic clusters by the employment of the B3LYP method with the 6-311G(d) and LAN-6+(d) basis sets. Predictions for the geometrical parameters and other molecular properties that could be useful for an eventual experimental characterization have been provided.

According to our calculations, all cyclic ScC$_n$ clusters have doublet ground states. In the case of the cationic clusters, *n*-even ScC$_n^+$ compounds have singlet ground states, whereas *n*-odd ones have triplet ground states. For the anionic clusters the energy difference between the singlet and triplet states is in most cases rather small. In fact, for ScC$_3^-$, ScC$_4^-$, and ScC$_6^-$ the lowest-lying state corresponds to a triplet according to the B3LYP results. For the rest of anionic compounds the ground state is found to be a singlet.

One of the most interesting features of the geometrical parameters, especially for the neutral and the anionic clusters, is that there is a certain tendency for scandium to interact with the entire carbon chain, rather than just with the carbon atoms at the end of the chain. In fact, for the largest members of the neutral and anionic series the scandium atom is almost "embedded" in a C$_n$ carbon chain.

The relative stabilities of the different clusters have been discussed employing the concept of incremental binding energies. Ionization energies and electron affinities have also been computed, and both properties exhibit a clear parity alternation trend, with *n*-odd clusters having larger IEs and EAs than *n*-even ones. The competition between linear and cyclic isomers has been also analyzed. All species are found to prefer a cyclic arrangement. Therefore, cyclic structures are the most interesting possible targets for an experimental search of scandium-doped carbon clusters.

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Supporting Information Available: Vibrational frequencies and rotational constants for ScC$_n$, ScC$_n^+$, and ScC$_n^-$ clusters (Tables S1−S3); optimized geometries for cationic and anionic clusters (Figures S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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