Small Carbon Clusters Doped with Early Transition Metals: A Theoretical Study of ScC_n, ScC_n^+, and ScC_n^- ($n = 1-8$) Open-Chain Clusters

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A theoretical study of the ScC_n, ScC_n^+, and ScC_n^- ($n = 1-8$) open-chain clusters has been carried out. Predictions for their electronic energies, rotational constants, dipole moments and vibrational frequencies have been made using the B3LYP method with different basis set including effective core potentials, ECPs. For the ScC_n open-chain clusters the lowest-lying states correspond to quartet states for n-odd members, whereas for n-even species the ground state is found to be a doublet. In the cationic and anionic species, the electronic ground state is found to be a singlet for even n and a triplet for odd n. An even−odd parity effect (n-even clusters being more stable than n-odd ones) is observed in neutral and charged clusters. Ionization energies and electron affinities also exhibit a clear parity alternation trend, with n-even clusters having higher values than n-odd ones.

Introduction

The study of the structure and properties of transition-metal carbides is one of the most interesting subjects of study in the last years. Carbon interacts with transition metals in different ways. Early transition metals have been found to form stable gas-phase metal−carbon clusters ions, known as metallocarbohedrenes "*met-cars*", with a $M_8C_{12}^+$ steichiometry.[1−5] Transition metals can also be incorporated into the carbon cage to form "*networked*" metallofullerenes.[6] On the other hand, late transition metals are catalysts for carbon nanotubes formation[7] and finally, rare-earth elements can be trapped inside fullerene cages and form endohedral metallofullerenes.[8] Transition metal carbide clusters have very complicated electronic structures and are interesting to elucidate the nature of interactions between transition metals and carbon, which dictate what type of structures is formed. Therefore, theoretical investigations of small carbon clusters are very useful to obtain information on metal carbon interactions, which are important not only to understand the growth mechanisms of the various metal−carbon nanomaterials but also to obtain insight into their physical and chemical properties in general.

It is well-known that linear and cyclic structures coexist in pure carbon clusters.[9] The addition of a foreign atom to small carbon clusters can lead to changes in both the geometry and electronic properties of these systems. In this respect, the knowledge about the behavior of binary carbon clusters as a function of the size of the cluster will allow the identification of possible systematic trends, which could help one understand the structure of these systems and could be useful to make extrapolations for some properties (stability, ionization energy, ...) and therefore predictions for larger clusters. Whereas pure carbon clusters and heteroatom-doped carbon clusters containing first- and second-row elements have been extensively studied by theoretical methods, only a few works are devoted to the study of transition-metal-doped carbon clusters. In the last years calculations on transition metals clusters, such as YC_n,[10] LaC_n,[10−12] NbC_n,[13] PdC_n^+, PtC_n^+,[14,15] or CrC_n,[16] have been performed. Recently, we have carried out a theoretical study of the CaC_n, CaC_n^+, and CaC_n^- ($n = 1-8$) species.[17,18] In the periodic table scandium is located after calcium atom, making ScC_n and ScC_n^+ systems isoelectronic with CaC_n^- and CaC_n systems, respectively, and therefore, it appears to be interesting to compare the results of both systems. To the best of our knowledge, theoretical studies of scandium-carbides have been performed at different levels of theory only for ScC,[19−21] ScC_2,[22−24] and ScC_3[24,25] systems. In the present work we provide a theoretical study of the ScC_n, ScC_n^+ and ScC_n^- ($n = 1-8$) open-chain clusters, reporting their equilibrium structures and some spectroscopic data. Because of the presence of 3d shells in the scandium atom the number of low-lying electronic states increases for these species, and information on the low-lying electronic states provided in this work could be helpful for their eventual experimental detection. In addition, the systematic behavior for their stability, ionization energy, and electron affinity will be discussed. The present work is restricted to open-chain structures. Nevertheless, we should point out that cyclic structures may be important for ScC_n clusters, as has been found in previous works on ScC_2,[22−24] and ScC_3,[24−25] where a cyclic isomer has be predicted as the ground state. However, we are currently carrying out a systematic study of cyclic ScC_n clusters in order to identify possible systematic behaviors, as well as to discuss the competitions between open-chain and cyclic structures for the ground state of ScC_n, ScC_n^+ and ScC_n^- systems.

Computational Methods

We have employed the same theoretical approach than in our previous studies on second-row heteroatom-doped carbon clusters,[26−30] and in particular in our previous works on CaC_n system.[17,18] Therefore, all our calculations have been made using the density functional theory (DFT). In particular, we selected the B3LYP exchange-correlation functional,[31,32] which has been widely applied to the study of many medium-sized heteroatom-doped carbon clusters, providing structures in good agreement

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with the experimental results.[33] This consists of the Lee−Yang−Parr[34] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[35] The latter is a linear combination of local density approximation, Becke's gradient correction,[36] and the Hartree−Fock exchange energy based on Kohn−Sham orbitals.[37]

Computations are performed using five different basis set. First, as in our previous works we employed both the triple split-valence d-polarized 6-311G(d) basis set (the Wachters[38] and Hay[39] with the scaling factor of Ragavachari and Trucks[40] is used for scandium and the conventional 6-311G(d) basis set[41] for carbon atoms), and the 6-311G+(d) basis set, which also includes diffuse functions. The use of effective core potential methods for the description of clusters reduces significantly the computational time. In particular, we selected Los Alamos ECP plus DZ, LanL2DZ.[42−44] Finally we employed two mixed basis set formed by the LanL2DZ for scandium atom in conjunction to the 6-311G(d) or the 6-311+G(d) basis set for carbon atom, denoted as LAN-6(d) and LAN-6+(d), respectively.

An analysis of the harmonic vibrational frequencies was carried out for all structures. This allows an estimate of 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.[45]

Results and Discussion

We have studied different linear or quasi-linear isomers with the scandium sited at the end of position. We have also made explorations of other possible isomers with the scandium in an intermediate position, but are not presented here since they lie higher in energy, according to the fact that a C−C bond is much stronger than a Sc−C one. In this work we only provide geometrical parameters and other properties, such as vibrational frequencies or dipole moments, computed with three basis sets: 6-311+G(d), LAN-6(d), and LAN-6+(d). The results calculated with both 6-311G(d) and LanL2DZ basis sets can be available upon request. In general, bond distances differences between 6-311+G(d) results and 6-311G(d) or LanL2DZ ones are between 0.01 and 0.02 Å. However, we include results of properties, such as relative stability or ionization energies calculated with the five basis sets in order to analyze systematic trends.

ScC_n Open-Chain Clusters. We have studied different open-chain isomers on both the doublet and quartet ScC_n potential surfaces. In Table 1, we provide the electronic energies, $\langle S^2\rangle$ expectation values, dipole moments, binding energies, and relative energies at the B3LYP/6-311+G(d), B3LYP/LAN-6(d), and B3LYP/LAN-6+(d) levels of theory, for the lowest-lying open-chain ScC_n species on both potential surfaces. These molecular properties might be helpful in an experimental search for these species. In addition, in Figure 1 the optimized geometries for the most stable structures are shown. Results for the computed harmonic vibrational frequencies and rotational constants are given as Supporting Information in Table S1.

TABLE 1: Electronic Energies, $\langle S^2\rangle$ Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Linear ScC_n Clusters with the B3LYP/6-311+G(d) (First Line), B3LYP/LAN-6(d) (Second Line), and B3LYP/LAN-6+(d) (Third Line) Methods

isomer	state	$-E$ (au)	$\langle S^2\rangle$	BE (eV)	μ (D)	ΔE (kcal mol^{-1})
ScC	$^2\Pi$	798.590338	1.7203		3.25	1.53
		84.332180	1.7852		3.00	2.32
		84.335538	1.7799		3.21	2.21
	$^4\Pi$	798.592960	3.7626	3.09	3.90	0.00
		84.336110	3.7661	3.18	3.74	0.00
		84.339302	3.7647	3.23	3.88	0.00
ScC_2	$^2\Sigma$	836.750913	0.7533	11.17	8.86	0.00
		122.491907	0.7541	11.24	8.55	0.00
		122.497550	0.7540	11.32	8.90	0.00
	$^4\Delta$	836.700047	3.7679		4.12	31.82
		122.444929	3.7684		3.92	29.39
		122.449150	3.7682		4.18	30.27
ScC_3	$^2\Delta$	874.786854	1.1594		8.97	12.53
		160.528775	1.1795		8.67	11.89
		160.536187	1.1715		9.13	12.16
	$^4\Sigma$	874.807391	3.7745	16.45	9.43	0.00
		160.548281	3.7745	16.55	8.88	0.00
		160.556100	3.7747	16.65	9.34	0.00
ScC_4	$^2\Sigma$	912.926424	0.7553	23.41	12.96	0.00
		198.666456	0.7562	23.52	12.51	0.00
		198.674380	0.7565	23.58	12.97	0.00
	$^4\Pi$	912.887206	3.7640		9.01	23.88
		198.630266	3.7637		8.66	21.85
		198.637583	3.7636		9.10	22.49
ScC_5	$^2\Delta$	950.97568	1.2527		12.09	9.42
		236.717050	1.2739		11.73	8.74
		236.725214	1.2723		12.25	9.01
	$^4\Sigma$	950.991431	3.7936	28.94	12.96	0.00
		236.731782	3.7939	29.08	12.30	0.00
		236.740307	3.7943	29.14	12.83	0.00
ScC_6	$^2\Sigma$	989.101299	0.7592	35.64	16.63	0.00
		274.840990	0.7607	35.76	16.03	0.00
		274.849640	0.7613	35.81	16.63	0.00
	$^4\Pi$	989.071222	3.7724		11.16	18.03
		274.813831	3.7723		10.70	15.85
		274.821713	3.7721		11.24	16.50
ScC_7	$^2\Delta$	1027.159269	1.3245		14.96	7.55
		312.900131	1.3501		14.52	6.70
		312.908826	1.3493		15.13	7.06
	$^4\Sigma$	1027.172024	3.8127	41.33	16.39	0.00
		312.911902	3.8133	41.46	15.62	0.00
		312.920847	3.8139	41.51	16.25	0.00
ScC_8	$^2\Sigma$	1065.277018	0.7647	47.95	20.23	0.00
		351.016395	0.7671	47.97	19.49	0.00
		351.025542	0.7683	48.12	20.19	0.00
	$^4\Pi$	1065.253020	3.7802		13.12	15.58
		350.995182	3.7802		12.56	11.55
		351.003673	3.7798		13.20	12.08

As can be seen in Figure 1, the three basis set considered lead to very similar equilibrium geometries. Furthermore, other properties, such as vibrational frequencies, dipole moments or relative energies, computed with the three basis sets are also very close for all the species, especially the calculated with the 6-311+G(d) and LAN-6+(d) basis sets which are virtually coincident. Therefore, it can be concluded that, for neutral ScC_n clusters, the employment of effective core potentials, in particular LanL2DZ, for the scandium atom gives similar results to the obtained with the 6-311+G(d) basis set. Another general comment that we should make is that all reported structures correspond to true minima on their respective potential surfaces (as can be seen in Table S1), with the only exception of the ScC_2 system. In this case the lowest-lying doublet and quartet isomers correspond, in fact, to saddle points on their respective potential surfaces (corresponding to the transition state for the degenerate rearrangement of the cyclic isomer).

Theoretical studies of diatomic carbide, ScC, have previously been reported at different levels of theory.[20−21] The most complete study of this system is that carried out by Kalemos et al.,[20] where they have studied nine molecular states of ScC within an energy range about 1 eV by ab initio multireference method (MRCI). The ground state has been determined to be $^2\Pi$ and the first excited state, $^4\Pi$, being 1.2 kcal/mol higher in energy. In this study, they pointed out the difficulty to identify

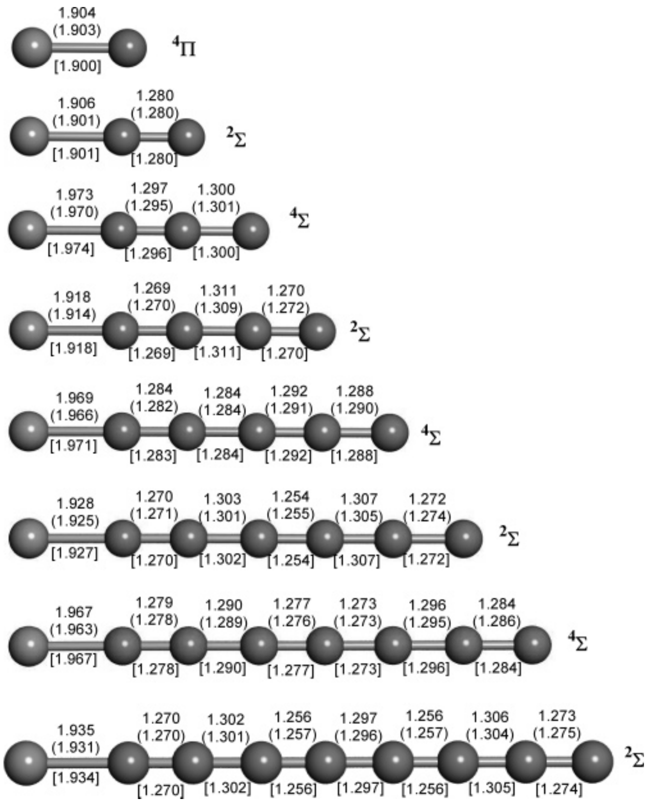

Figure 1. Equilibrium geometries of ScC_n linear clusters at the B3LYP/6-311+G(d), B3LYP/LAN-6(d) (in parentheses) and B3YP/LAN-6+-(d) (in brackets) levels of theory. Distances are given in angstroms.

the ground state due to the complexity, and the near degeneracy of their first four states. Our results predict two doublet states, $^2\Pi$ and $^2\Sigma$, very close in energy (energy differences are 0.39, −2.52, and −1.48 kcal/mol at the B3LYP/6-311+G(d), B3LYP/LAN-6(d), and B3LYP/LAN-6+(d) levels, respectively), and the ground state is predicted to be the $^4\Pi$, lying only 1.53 kcal/mol lower in energy than the $^2\Pi$ state (see Table 1). These discrepancies can be attributed to the multiconfigurational character of the $^2\Pi$ wave function and the fact that correlation energy favors doublet states over quartet ones. More recently, Gutsev el al.[21] in their study on the similarities and differences in the structure of 3d-metal monocarbides provide results for ScC on the doublet surface, using different DFT methods, that are similar to those shown in this study.

According to previous studies of ScC_2 system,[22,23] which have been carried out at the MP2, MP4, CASSCF and MRSDCI levels, in the case of ref 22, and using local and non local spin density functional theories in ref 23, doublet states are most stable that quartet ones, and linear structures on the doublet potential surfaces correspond to transition states. In addition, we have also performed a calculation at the QCISD level with different basis sets for the $^2\Sigma$ state of ScC_2, and the results agree in that the linear geometry corresponds to the transition state for the cyclic rearrangement. The most stable quartet, $^4\Delta$, shown in Table 1, also corresponds to a saddle point at the B3LYP level. MP2 results show that this state corresponds to a true minimum on the quartet surface, whereas at the QCISD level this isomer corresponds to a transition state as in the case of B3LYP results. However, we have located a quasi-linear structure, $^4A'$, lying about 4 kcal/mol above $^4\Delta$, that is a true minima. This minimum can be related to the $^4\Sigma_g{}^+$ state provided by Jackson et al.[23] in their study of ScC_2.

Finally, the linear isomer of ScC_3 system on the doublet surface has been studied by Roszak at al.,[25] at the CASSCF and B3LYP levels using relativistic effective core potentials. The B3LYP results agree with our own results in the prediction of a $^2\Delta$ as the lowest-lying doublet state, but CASSCF predicts a $^2\Pi$ as the most stable one. We have found that $^2\Pi$ lies 6.89 kcal/mol above the $^2\Delta$ state. Nevertheless, according to our results (see Table 1) for this system a $^4\Sigma$ state could be predicted as the ground state.

It is readily seen in Table 1 that ScC_n clusters show a clearly alternation in stability between doublet and quartet states. Neutral clusters with *n*-odd have quartet ground states, whereas *n*-even neutral clusters present doublet ground states (*n* being the number of carbon atoms). The doublet-quartet energy difference is large for *n*-even, and in both cases (*n*-even and *n*-odd species) it decreases with *n*, with the only exception being ScC, where the behavior is different since carbon is only bonded to scandium. This alternation between doublet and quartet states for ScC_n clusters can be related to their electronic configuration. Neutral scandium-doped carbon clusters have $4n + 3$ valence electrons, and the corresponding electronic configurations can be generalized as

$$\{\text{core}\}1\sigma^2...1\pi^4...\left(\frac{n}{2}\right)\pi^4(n+2)\sigma^1 \quad n\text{-even clusters}$$

$$\{\text{core}\}1\sigma^2...1\pi^4...\left(\frac{n+1}{2}\right)\pi^2(n+2)\sigma^1 \quad n\text{-odd clusters}$$

except for ScC: $\{\text{core}\}1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1$.

Thus, the ScC_n clusters contain $2n + 3$ valence σ-electrons and $2n$ valence π-electrons, with the only exception of the smallest member, ScC. $2n + 2$ of the total σ-electrons fully occupy $n + 1$ orbitals, and the valence σ-electron remaining lead to a half-filled σ-orbital, $(n + 2)\sigma^1$. For the species with even *n*, the $2n$ valence π-electrons constitute a closed shell and the configurations result in $^2\Sigma$ electronic states. However, for the clusters with odd *n*, two of the $2n$ π-electrons are distributed over a pair of degenerate π-orbitals, corresponding to a half-filled π-orbital, $((n + 1)/2)\pi^2$, so that the lowest energy state of this configuration is $^4\Sigma$. For *n*-odd clusters this electronic configuration also results in the lowest-lying doublet state, $^2\Delta$, whereas in the case of *n*-even clusters the lowest-lying quartet state is obtained upon $(n/2)\pi^4 \rightarrow (n + 3)\sigma$ or 1δ promotion. This fact is consistent with the larger doublet quartet energy differences (in absolute values) found for *n*-even clusters. It is interesting to comment that in the case of the isoelectronic $CaC_n{}^-$ species, the same lowest-lying electronic states have been obtained.[17]

As can be seen in Figure 1, the ScC_n clusters with *n*-even present smaller Sc−C distances (1.906 Å for ScC_2 to 1.935 Å for ScC_8) than these with *n*-odd ones (1.973Å for ScC_3 to 1.967Å to ScC_7). The C−C bond distances are all in the range 1.25−1.31Å, and can be assimilated to moderately strong double bonds typical of cumulene structures. Nevertheless, it can be observed a clear alternation in the C−C bond distances, C_{odd}−C_{even} being shorter than C_{even}−C_{odd}, suggesting that there is some poliacetylenic character in these compounds.

In the case of *n*-even ScC_n clusters the unpaired electron is mainly located at the scandium atom and the dominant valence structure contributing to their description could be summarized as

$$^{\bullet}\text{Sc}{=}\text{C}({=}\text{C})_{n-2}{=}\text{C}: \quad n\text{-even clusters}$$

For *n*-odd ScC_n clusters ($n \geq 3$), the spin density for scandium atom is found to be close to $1.7e^-$, and the rest of the spin density is distributed among the odd carbon atoms, mainly at

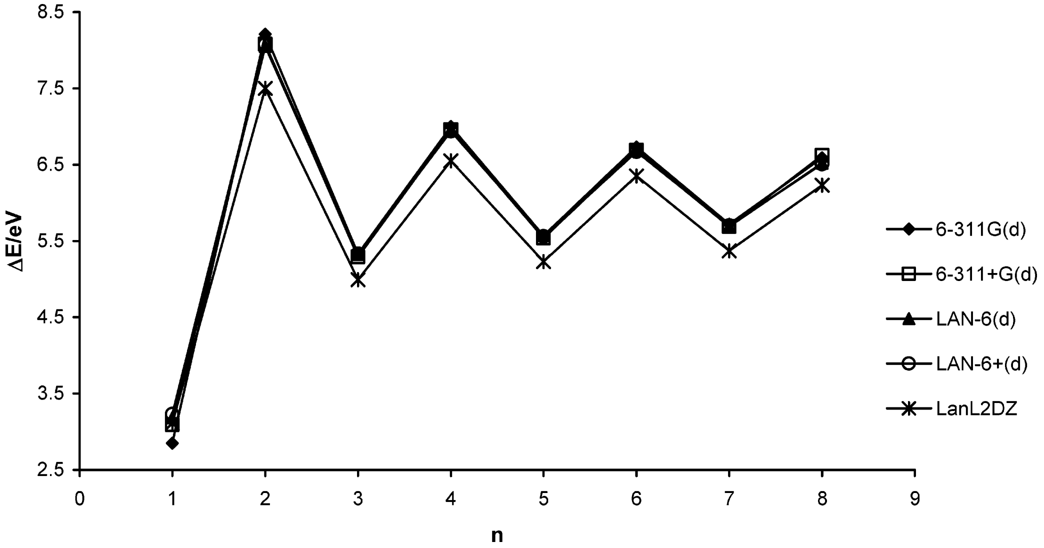

Figure 2. Incremental binding energies (eV) for the ScC_n linear clusters vs the number of carbon atoms.

the terminal one. Consequently, the valence structures contributing to the description of these clusters can be depicted as

$${}^{\bullet}\dot{S}c-(C\equiv C)_{(n-1)/2}-\dot{C}:$$

$${}^{\bullet}\dot{S}c-\dot{C}(=C)_{n-2}=C: \quad n\text{-odd clusters}$$

$${}^{\bullet}Sc=\dot{C}(-C\equiv C)_{(n-3)/2}-C\equiv C^{\bullet}$$

The population analysis shows that the Sc−C bond has a high ionic character, as has been discussed in previous works.[20,22] There is a substantial charge transfer from scandium to the carbon chain, although this is in part compensated by a certain degree of $p_\pi \rightarrow d_\pi$ back-donation. This delocalization of the π electrons toward the scandium atom contributes to the linearity of these species. In fact, the positive charge bearing the scandium atom is between +0.66 and +0.80, according to our results of the Mulliken population analysis. As a consequence of the large ionic character of the Sc−C bond, in all case high dipole moments are found for the ground states and this might help in their possible detection. In Table 1, we can see that the dipole moments increase with the number of carbon atoms.

To discuss the relative stability of the ScC_n clusters with different sizes, we will employ, as we made in previous works,[17,18,26−30] the concept of incremental binding energy. Pascoli and Lavendy[46] suggested that this magnitude could be useful for studying this kind of compounds. In our case, the incremental binding energy is defined as the change in energy associated with the process:

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

and 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 neutral ScC_n clusters calculated with the five basis sets are shown as a function of the number of carbon atoms. It is readily seen in Figure 2 that we obtain a similar behavior with the different basis sets employed in this work, and the results are virtually the same with the only exception of LanL2DZ basis set where incremental binding energies are systematically lower along the series (about −0.5 eV). The same trends are found in the computed incremental binding energies with the different basis sets for ScC_n^+ and ScC_n^- clusters. From Figure 2 we can see that there is an even−odd alternation, n-even clusters being more stable than n-odd ones. This parity effect can be attributed to the number of available valence electrons. As we pointed out before, the ScC_n clusters contain $2n + 3$ valence σ-electrons and $2n$ valence π-electrons. The occupation of the σ-orbitals is the same for n-even and n-odd, and therefore the stability alternation is associated with the number of available π-electrons. For n-even, the $2n$ valence π-electrons fully populate $n/2$ π-orbitals, resulting in a π^4 electronic configuration, whereas for odd n the highest occupied molecular orbital with π-symmetry is half-filled, resulting in a π^2 electronic configuration. As it is well-known, the fully filled π-orbitals are energetically much more stable than the half-filled π-orbitals, and therefore, n-even clusters are more stable than the adjacent n-odd ones.

The isoelectronic CaC_n^- clusters[17] exhibit a rather similar behavior, and in both systems the incremental binding energies difference decrease monotonically when the number of carbon atoms increase. This shows that the parity effect is less pronounced for larger clusters.

ScC_n^+ Open-Chain Clusters. The molecular properties (absolute and relative energies, S^2 expectation values, and dipole moments) for the lowest-lying singlet, triplet and quintet states for ScC_n^+ open-chain clusters are given in Table 2, whereas the corresponding vibrational frequencies and rotational constants are included as Supporting Information in Table S2. In addition, in Figure 3 the geometrical parameters for the ground states are shown. In general, all the structures reported in Table 2 are true minima in their respective potential energy surface, with the only exception of the singlet state of ScC_2^+, which, as in the case of neutral system, corresponds to the transition state of cyclic rearrangement (see Table 2S). The same behavior was found employing wave function-based methods. As can be seen in Table 2, spin-contamination does not seem a problem for studying ScC_n^+ state with the B3LYP method, because The $\langle S^2 \rangle_o$ values of the wave functions are relatively close to the pure spin values. The results computed with the different basis sets show the same behavior than for the neutral clusters.

Only the first member of the series, ScC^+, has been theoretically studied.[19,21] Kerkines and Mavridis[19] found that the ground state of ScC^+ is a $^3\Pi$ and the lowest-lying singlet and quintet states correspond to a $^1\Sigma$ and $^5\Delta$ symmetry and are located 14.9 and 12.7 kcal/mol, respectively, above the ground state, computed at the MRCI + Davison correction level of theory. As shown in Table 2, our results for the ScC^+ system at the B3LYP level of theory predict the same order for the

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

isomer	state	$-E$ (au)	$\langle S^2 \rangle$	BE (eV)	μ (D)	ΔE (kcal mol^{-1})
ScC^+	$^1\Sigma$	798.327970			4.88	17.98
		84.073551			4.87	17.65
		84.075825			4.78	17.59
	$^3\Pi$	798.356346	2.0343	3.22	5.62	0.00
		84.101355	2.0439	3.65	5.60	0.00
		84.103560	2.0404	3.67	5.55	0.00
	$^5\Delta$	798.341232	6.0027		5.28	9.27
		84.088543	6.0024		5.33	7.84
		84.089688	6.0025		5.29	8.49
ScC_2^+	$^1\Sigma$	836.487119		10.56	10.25	0.00
		122.232676		11.04	9.85	0.00
		122.235401		11.04	10.04	0.00
	$^3\Delta$	836.462604	2.0256		7.66	15.63
		122.211028	2.0256		7.48	13.80
		122.212575	2.0255		7.57	14.59
	$^5\Delta$	836.360015	6.0148		2.82	79.56
		122.106858	6.0141		3.33	78.96
		122.110083	6.0143		3.30	78.35
ScC_3^+	$^1\Delta$	874.532387			12.06	15.09
		160.278283			11.69	15.56
		160.252259			11.91	15.54
	$^3\Sigma$	874.556397	2.0316	16.19	11.88	0.00
		160.303061	2.0330	16.74	11.47	0.00
		160.306977	2.0328	16.73	11.69	0.00
	$^5\Delta$	874.506994	6.0647		8.06	31.07
		160.255581	6.0638		7.89	29.94
		160.257811	6.0641		7.98	30.93
ScC_4^+	$^1\Sigma$	912.663941		22.84	15.09	0.00
		198.408866		23.38	14.53	0.00
		198.413332		23.35	14.85	0.00
	$^3A'$	912.641079	2.0435		13.80	13.57
		198.388471	2.0464		13.43	11.50
		198.391701	2.0438		13.78	12.26
	$^5\Pi$	912.574810	6.0299		8.12	54.24
		198.320791	6.0290		8.73	53.89
		198.325559	6.0294		8.29	53.67
ScC_5^+	$^1\Delta$	950.721015			16.66	12.86
		236.466280			16.14	13.29
		236.471170			16.49	13.29
	$^3\Sigma$	950.741416	2.0613	28.72	16.29	0.00
		236.487496	2.0643	29.33	15.74	0.00
		236.492294	2.0638	29.25	16.08	0.00
	$^5\Delta$	950.696814	6.1163		11.28	27.66
		236.445051	6.1154		11.06	26.47
		236.447943	6.1157		11.20	27.38
ScC_6^+	$^1\Sigma$	988.842194		35.16	19.48	0.00
		274.586882		25.79	18.76	0.00
		274.592046		25.67	19.21	0.00
	$^3A'$	988.828125	2.0374		18.52	7.73
		274.574693	2.0462		18.20	6.75
		274.579000	2.0378		18.68	6.95
	$^5\Pi$	988.776360	6.0447		11.48	39.46
		274.521578	6.0436		12.20	40.80
		274.526998	6.0441		11.71	39.64
ScC_7^+	$^1\Delta$	1026.905763			21.10	11.50
	$^1A'$	312.650443			20.45	11.70
		312.655930			20.92	11.91
	$^3\Sigma$	1026.923833	2.0929	41.15	20.52	0.00
		312.669338	2.0979	41.85	19.84	0.00
		312.674707	2.0971	41.70	20.31	0.00
	$^5\Delta$	1026.883291	6.1634		14.63	24.94
		312.631010	6.1626		14.33	23.97
		312.634479	6.1629		14.52	24.75
ScC_8^+	$^1\Sigma$	1065.020990		47.59	23.69	0.00
	$^1A'$	350.765377		48.21	22.83	0.00
		350.771155		48.02	23.40	0.00
	$^3\Pi$	1065.013104	2.0463		22.56	4.53
		350.759056	2.0471		22.69	3.35
		350.764060	2.0469		23.11	3.40
	$^5\Pi$	1064.970311	6.0584		14.73	30.24
		350.714821	6.0572		15.57	33.82
		350.720595	6.0574		15.10	29.28

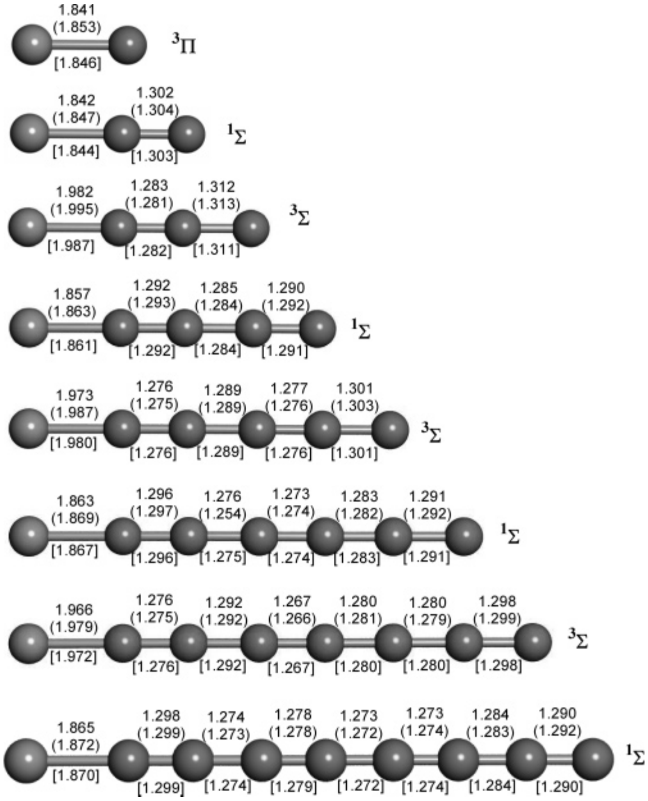

Figure 3. Equilibrium geometries of ScC_n^+ linear clusters at the B3LYP/6-311+G(d), B3LYP/LAN-6(d) (in parentheses) and B3YP/LAN-6+(d) (in brackets) levels of theory. Distances are given in angstroms.

lowest-lying states. Gustev et al.,[21] in their systematic study of XC^+ (X = 3d-metal), also agree in the assignment of the ground state for ScC^+ employing a DFT method. Finally, the binding energy that we have calculated at the B3LYP/6-311+G(d) (74.25 kcal/mol) is very close to the experimental value given by Clemmer et al.[47](77.0 ± 1.4 kcal/mol).

It is generally observed in Table 2 that n-odd clusters (except for ScC^+, where the scheme is different since carbon is only bonded to scandium) have triplet ground states, whereas n-even ones present singlet ground states. The energy difference (in absolute value) between singlet and triplet states decreases slightly along the series as the corresponding triplet−quintet energy difference for n-odd clusters. However, the singlet−quintet energy difference decreases significantly when n increases in the case of n-even cationic clusters. This alternation in stability between singlet and triplet states in ScC_n^+ clusters can be related to their electronic configuration. The electronic configuration for the cationic clusters can be obtained from that of the neutral by removing an electron from their frontier orbital. In both cases, n-even and n-odd cationic clusters, the electron is subtracted from the $(n + 2)\sigma$ orbital of the corresponding neutral system. The electronic configurations for ScC_n^+ can be summarized as

$$\{\text{core}\}1\sigma^2 ... 1\pi^4 ... (n+1)\sigma^2 \left(\frac{n}{2}\right)\pi^4 \quad n\text{-even clusters}$$

$$\{\text{core}\}1\sigma^2 ... 1\pi^4 ... (n+1)\sigma^2 \left(\frac{n+1}{2}\right)\pi^2 \quad n\text{-odd clusters}$$

except ScC^+: $\{\text{core}\}1\sigma^2 2\sigma^2 1\pi^3$.

There are $2n + 2$ valence σ-electrons and $2n$ valence π-electrons. When n is even, the $2n$ π-electrons fully occupy $(n/2)$ π-orbital and corresponds to a $^1\Sigma$ state. In the case of n-odd

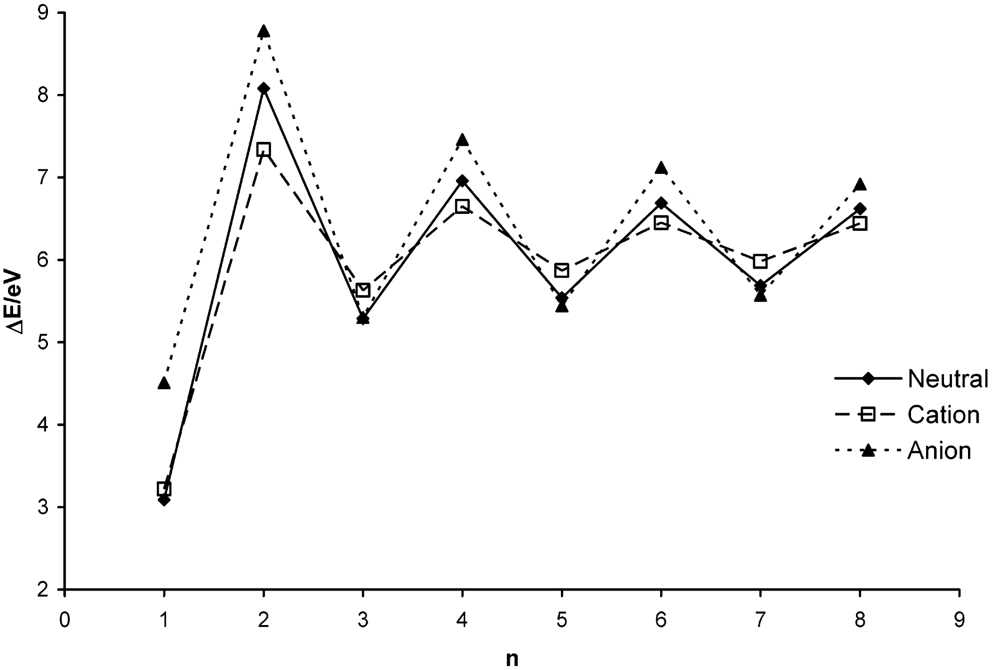

Figure 4. Incremental binding energies (eV) for the ScC_n, ScC_n^+, and ScC_n^- linear clusters vs the number of carbon atoms.

two of the π-electrons are distributed over a pair of degenerate π-orbitals, leading to a half-filled π-orbital and a $^3\Sigma$ electronic state. Singlet states for *n*-odd cationic clusters correspond to the same electronic configuration than triplet states, and the lowest-lying quintet state is obtained from triplet upon $(n + 1)\sigma \rightarrow 1\delta$ excitation. In the case of *n*-even ScC_n^+ clusters, with the only exception of ScC_2^+, triplet states have $^3\Pi$ ($^2A'$) symmetry, and quintet states correspond to $^5\Pi$ symmetry and are obtained from singlet configuration upon a $(n/2)\pi \rightarrow (n + 2)\sigma$ or $(n/2)\pi \rightarrow (n + 2)\sigma$ $((n + 2)/2)\pi$ promotion, respectively.

The main difference in the geometries with respect to their neutral counterparts is that the Sc−C bond decreases for *n*-even ScC_n^+ clusters, whereas in the case of *n*-odd cationic clusters increases slightly. The C−C distances have values close to typical cumulenic structures and some acetylenic character, which is reflected in the alternation of C−C distances, mainly in *n*-odd clusters. In the case of the *n*-even cationic clusters the most important valence structure is a cumulene-type structure:

$$^{+}\mathrm{Sc{=}C({=}C)_{\mathit{n}-2}{=}C{:}} \quad n\text{-even clusters}$$

where the short Sc−C bond lengths can be assigned to a double bond.

In the case of *n*-odd cationic clusters we have found a spin density for scandium close to 1.0 e$^-$, and the rest of the spin density is distributed among the carbon chain, mainly at the terminal carbon atom, which bears an electron density about 0.5 e$^-$. Consequently, the most important valence bond structures contributing to their description are

$$^{+}\dot{\mathrm{S}}\mathrm{c{-}(C{\equiv}C)_{(\mathit{n}-1)/2}{-}\dot{C}{:}} \quad n\text{-odd clusters}$$

$$^{+}\dot{\mathrm{S}}\mathrm{c{-}\dot{C}({=}C)_{\mathit{n}-2}{=}C{:}}$$

In the ScC_n^+ clusters our results of the Mulliken population analysis show that the scandium atom bears a positive charge in the range +1.30 to +1.45, related to the higher electronegativity of carbon respect to scandium atom. As in the case of neutral systems, dipole moments (taking the center of mass as the origin) are very high and increase with the number of carbon atoms.

Compared with the isoelectronic CaC_n clusters, *n*-even clusters have the same ground state, whereas *n*-odd CaC_n clusters have a $^3\Pi$ ground state corresponding to the electronic configuration $\pi^1\sigma^1$. The stabilization of the HOMO π-orbital respect to σ-orbital in scandium clusters is related to the fact that in the π-orbital there is a participation of the $3d_\pi$-type atomic orbital of scandium atom.

The incremental binding energies for the different ScC_n/ScC_n^+/ScC_n^- clusters as a function of the number of carbon atoms calculated at the B3LYP/6-311+G(d) are shown in Figure 4. It is readily seen that there is a clear even−odd alternation in stability, *n*-even ScC_n^+ clusters being more stable than *n*-odd ones. This behavior resembles very much the situation for the neutral clusters, but with small variations in incremental binding energies between consecutive species for the cationic clusters. As in the case of neutral ScC_n system, this parity effect can be attributed to the number of available valence π-electrons, mainly the electron number in π-type highest occupied molecular orbital (HOMO). As we pointed out before, *n*-even ScC_n^+ clusters result in a π^4 electronic configuration, while for *n*-odd ones the highest occupied π-type orbital is half-filled, π^2 electronic configuration. Therefore, the fully filled π-orbitals (*n*-even cationic clusters) are energetically more stable than the half-filled ones (*n*-odd cationic clusters). The addition of an electron in the $(n + 2)\sigma$ orbital to give neutral clusters, makes the parity effect larger for ScC_n than in the case of cationic ScC_n^+ clusters.

ScC_n^- Open-Chain Clusters. The main properties for the lowest-lying singlet, triplet and quintet states of open-chain ScC_n^- clusters are given in Table 3, whereas geometries for the ground states are shown in Figure 5. As in previous sections, the vibrational frequencies and rotational constants for the lowest-lying singlet triplet and quintet states of anionic clusters are given as Supporting Information in Table S3. The effect of employing effective core potentials to describe scandium atoms on the geometrical parameters, harmonic frequencies, dipole moments, and binding energies is not particularly important. Similar results are found in the case of neutral and cationic systems. However, relative energies for anionic clusters are most sensitive to the inclusion of effective core potentials in the basis sets, as can be seen in Table 3.

TABLE 3: Electronic Energies, $\langle S^2\rangle$ Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Linear ScC$_n^-$ Clusters with the B3LYP/6-311+G(d) (First Line), B3LYP/LAN-6(d) (Second Line), and B3LYP/LAN-6+(d) (Third Line) Methods

isomer	state	$-E$ (au)	$\langle S^2\rangle$	BE (eV)	μ (D)	ΔE (kcal mol^{-1})
ScC$^-$	$^1\Sigma$	798.623556			1.35	9.90
		84.366850			0.82	8.90
		84.370167			1.62	8.64
	$^3\Pi$	798.639176	2.0823	4.51	0.02	0.00
		84.380876	2.1074	4.39	0.54	0.00
		84.383776	2.1042	4.44	0.09	0.00
	$^5\Pi$	798.599991	6.0279		0.28	24.11
		84.342362	6.0496		0.97	23.70
		84.345151	6.0413		0.00	23.74
ScC$_2^-$	$^1\Sigma$	836.823328		13.29	4.46	0.00
		122.561639		13.11	3.59	0.00
		122.568535		13.23	4.63	0.00
	$^3\Delta$	836.803568	2.0033		7.75	12.23
		122.545716	2.0035		6.39	9.80
		122.553456	2.0036		7.75	9.28
	$^5\Pi$	836.711341	6.0121		2.09	69.73
		122.458205	6.0115		2.01	65.35
		122.462449	6.0123		1.80	66.54
ScC$_3^-$	$^1\Delta$	874.856814			3.75	14.58
		160.595307			2.76	14.26
		160.604086			3.92	14.32
	$^3\Sigma$	874.879968	2.0283	18.59	4.30	0.00
		160.617927	2.0276	18.43	3.25	0.00
		160.626829	2.0281	18.56	4.44	0.00
	$^5\Delta$	874.859840	6.0292		8.44	12.47
		160.600959	6.0273		7.07	10.49
		160.610423	6.0288		8.50	10.01
ScC$_4^-$	$^1\Sigma$	913.017507		26.05	7.53	0.00
		198.753533		25.87	6.28	0.00
		198.764101		26.01	7.74	0.00
	$^3\Delta$	913.004746	2.0034		11.82	7.85
		198.744278	2.0038		10.12	5.57
		198.755401	2.0035		11.88	5.14
	$^5\Delta$	912.918300	6.0149		2.18	61.14
		198.664914	6.0072		2.88	54.34
		198.673154	6.0073		4.40	55.73
ScC$_5^-$	$^1\Delta$	951.059108			5.97	12.50
		236.796284			4.70	12.10
		236.806555			6.11	12.46
	$^3\Sigma$	951.078704	2.0497	31.49	6.88	0.00
		236.815281	2.0486	31.36	5.53	0.00
		236.825826	2.0495	31.48	7.01	0.00
	$^5\Delta$	951.065490	6.0567		11.81	8.02
		236.805462	6.0511		10.08	5.64
		236.816311	6.0532		11.84	5.56
ScC$_6^-$	$^1\Sigma$	989.204586		38.61	10.36	0.00
		274.939897		38.46	8.87	0.00
		274.951556		38.56	10.55	0.00
	$^3\Delta$	989.196525	2.0032		15.43	4.83
		274.935320	2.0037		13.49	2.06
		274.947250	2.0034		15.43	1.85
	$^5\Pi$	989.122662	6.0219		9.07	49.91
		274.862848	6.0225		7.15	46.09
		274.873119	6.0247		9.18	47.10
ScC$_7^-$	$^1\Delta$	1027.252842			8.13	11.36
		312.989275			6.65	10.86
		313.000214			8.26	11.03
	$^3\Sigma$	1027.270343	2.0725	44.18	9.40	0.00
		313.006260	2.0710	44.06	7.84	0.00
		313.017497	2.0724	44.12	9.53	0.00
	$^5\Delta$	1027.261679	6.0790		15.04	5.04
		313.001122	6.0761		13.07	1.87
		313.012513	6.0784		15.02	1.74
ScC$_8^-$	$^1\Sigma$	1065.389664		51.10	13.14	0.00
		351.124577		50.93	11.49	0.00
		351.136742		51.02	13.34	0.00
	$^3\Delta$	1065. 384835	2.0030		18.85	2.65
		351.123277	2.0034		16.76	−0.95
		351.135648	2.0031		18.84	−1.04
	$^5\Pi$	1065.319718	6.0394		13.19	41.11
		351.058797	6.0408		10.89	37.64
		351.072043	6.0125		13.83	36.07

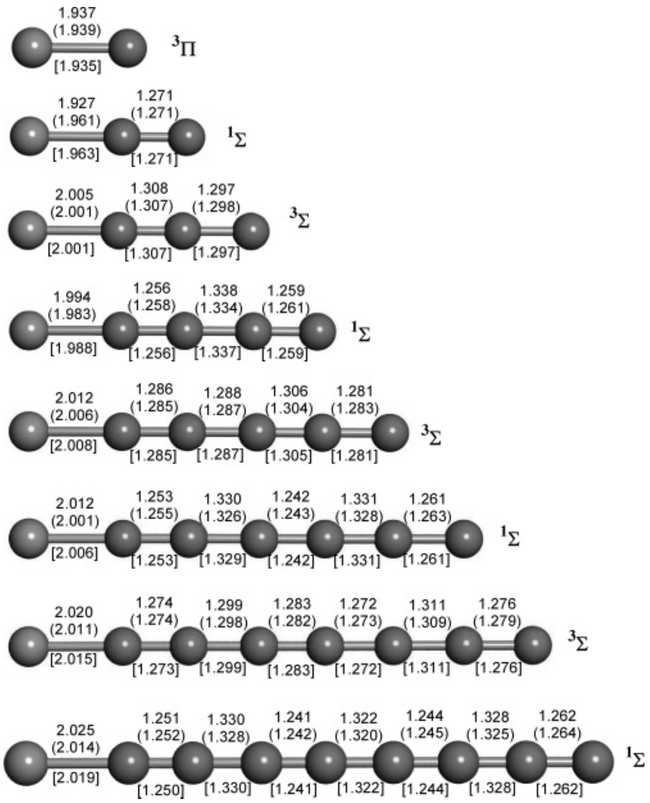

Figure 5. Equilibrium geometries of ScC$_n^-$ linear clusters at the B3LYP/6-311+G(d), B3LYP/LAN-6(d) (in parentheses) and B3YP/LAN-6+(d) (in brackets) levels of theory. Distances are given in angstroms.

There are only available theoretical results for linear SC$_2^-$ and ScC$_3^-$. In a recent study Hendrickx and Clima[24] at the CASPT2 level of theory predicted a $^1\Sigma$ as the lowest-lying linear isomer with a $^3\Delta$ and $^3\Pi$ lying 22.08 and 23.31 kcal/mol above the singlet state, respectively. We have found the same order of states, but the energy differences between singlet and triplet states are lower ($^3\Delta$ and $^3\Pi$ are about 12.23 and 15.85 kcal/mol, respectively, higher in energy than $^1\Sigma$ at the B3LYP/6-311+G(d) level). In the case of the ScC$_3^-$ system, Roszak et al.[25] made a study of the different isomers of this system, but for the linear structure, they only provide results for a $^3\Pi$ state. We have found that the ground state of the ScC$_3^-$ system corresponds to a $^3\Sigma$ symmetry. In addition we have also located the $^3\Pi$ state reported by Roszak et al.,[25] but at the B3LYP/6-311+G(d) level is lying about 13.98 kcal/mol above the ground state.

From Table 3, it is readily seen that the clusters with *n*-odd have triplet ground states, whereas *n*-even clusters present singlet ground states. This behavior can be connected with the electronic configuration. Anionic linear clusters have one more electron than their corresponding neutrals. The extra electron is incorporated to the $(n + 2)\sigma$ orbital of their neutral counterpart. Consequently, the electronic configurations for linear ScC$_n^-$ clusters can be generalized as

$$\{\text{core}\}1\sigma^2...1\pi^4...\left(\frac{n}{2}\right)\pi^4(n+2)\sigma^2 \quad n\text{-even clusters}$$

$$\{\text{core}\}1\sigma^2...1\pi^4...(n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^2 \quad n\text{-odd clusters}$$

except for ScC$^-$: $\{\text{core}\}1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3$.

The electronic distribution for *n*-odd clusters with a half-filled π-type valence orbital, results in a $^3\Sigma$ state, whereas the

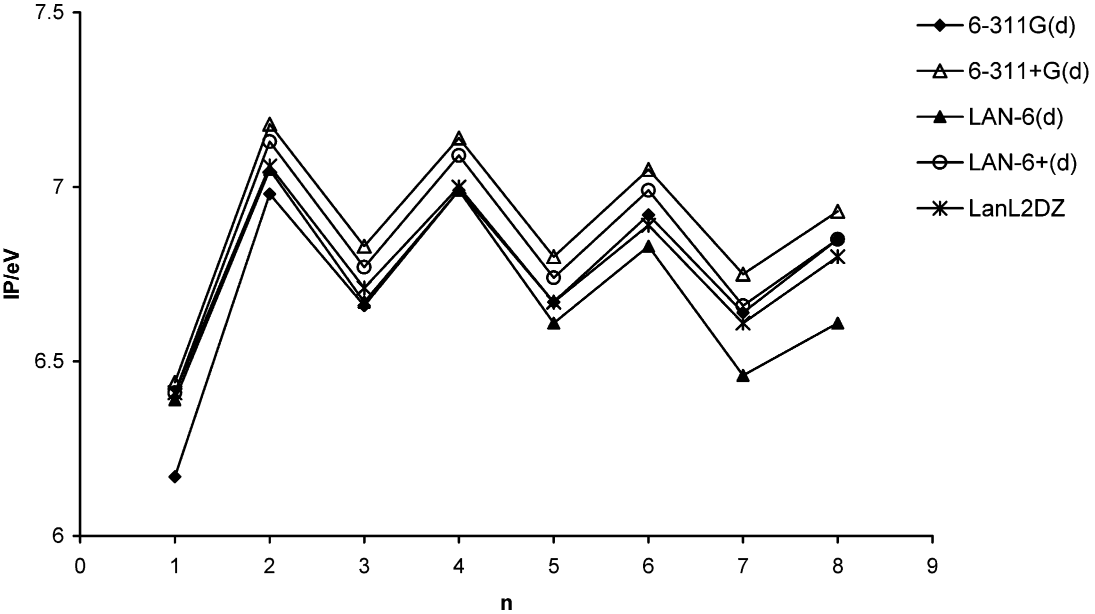

Figure 6. Ionization energies (IP) and electron affinities (EA), in eV, of ScC_n linear clusters vs the number of carbon atoms.

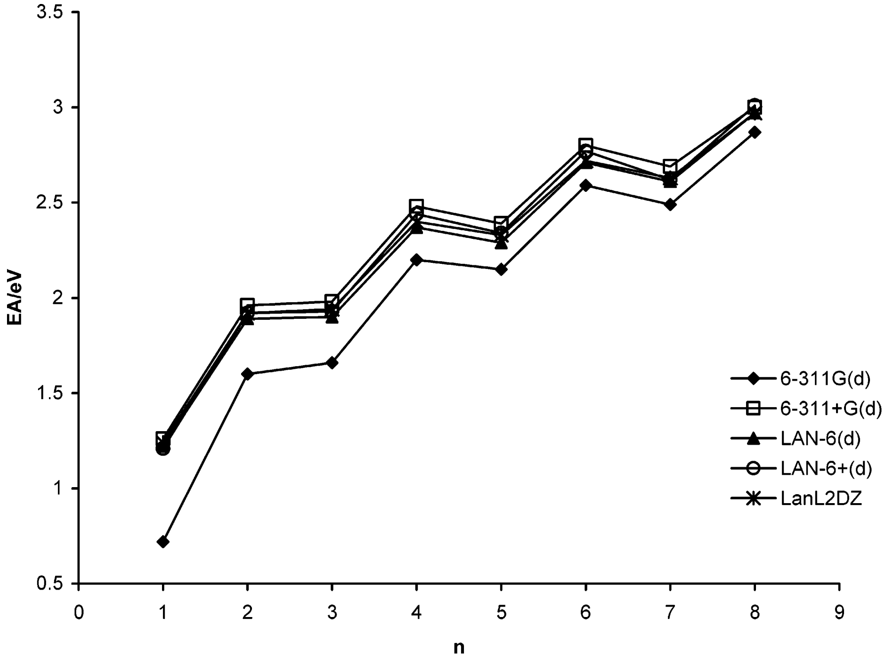

Figure 7. Electron affinities (EA), in eV, of ScC_n linear clusters vs the number of carbon atoms.

$2n$ valence π-electron fully occupy the $(n/2)\pi$ orbital, corresponding to a $^1\Sigma$ state for the n-even members. It can be also observed from Table 3, that for n-odd clusters energy differences of singlet and quintet states respect to triplet one are very similar and decrease along the series. According to our results, with the only exception of the first member of the series, ScC^-, quintet states are always more stable than singlet ones. On the other hand, quintet states are very high in energy for n-even clusters, however the energy differences between singlet and triplet states are smaller and decrease with n. In fact, for the last member of the series, ScC_8^-, singlet and triplet states are very close in energy, and therefore, both states could be accessible to experimental detection.

There are some interesting features on the geometrical parameters for ScC_n^- clusters shown in Figure 5. In the first place, the Sc−C distances for anionic clusters are larger than that observed for the neutral and cationic counterparts. It is also worth mentioning that, for n-odd species all C−C bond distances are rather close and always in the range 1.27−1.31 Å, typical of cumulenic structures. In the case of n-even clusters a clear alternation in the C−C bond distances is observed, with values in the range 1.24−1.34 Å, showing that in this case there is a relatively high polyacetylenic character. Consequently, the dominant valence structure contributing to their description could be summarized as

$$:\mathrm{Sc}-\dot{\mathrm{C}}(=\mathrm{C})_{n-2}=\dot{\underline{C}}: \quad n\text{-odd clusters}$$

$$:\mathrm{Sc}-(\mathrm{C}\equiv\mathrm{C})_{n-2}-\mathrm{C}\equiv\underline{C}: \quad n\text{-even clusters}$$

The incremental binding energies for ScC_n^- clusters shown in Figure 4, exhibit also a similar behavior to that found for the neutral and cationic systems, with n-even clusters being comparatively much more stable than n-odd ones. This parity effect, as in the case of neutral and cationic clusters, can be attributed to the electron number in π-type highest occupied molecular orbital (HOMO). A ground state corresponding to a fully occupied set of π-orbitals (π,^{4} singlet state for n-even ScC_n^- clusters) is energetically much more favorable than a half-filled set (π^2, triplet state for n-odd ScC_n^- clusters). We can also see in Figure 4 that ScC_n^- clusters show variations in the incremental binding energies for consecutive member of the series higher than their neutral analogues. In anionic clusters, the fact that the $(n + 2)\sigma$ orbital is fully occupied stabilize n-even clusters respect to the neutral ones.

Ionization Energies and Electron Affinities. The computed energies for cationic and anionic ScC_n clusters allow one to estimate the ionization energies (IP) and the electron affinities (EA) of the different ScC_n clusters. These properties are calculated in the adiabatic form, from the total energies of the neutral and charged species at their optimized geometries including the zero-point vibrational corrections. In Figure 6, the IP values as a function of the number of carbon atoms are depicted. Results for the five basis set employed in this work are included. The corresponding EA results are shown in Figure 7.

It can be readily seen in Figure 6, that linear ScC_n clusters have IPs that exhibit only smooth variations along the series, the IPs values are all around 7 eV. Ionization energies show a parity alternation trend, with n-even clusters having larger IP. This behavior is related to the stability of ScC_n/ScC_n^+ clusters. As has been pointed out ScC_n clusters present a stronger even−odd alternation stability effect than ScC_n^+ ones, and this is reflected in an even−odd alternation effect in IP. When comparing the results obtained with the different basis sets, in general, we can see that the same behavior has been found. But taking as reference the results obtained with the most complete basis set, 6-311+G(d), we can realize that the LAN-6+(d) basis set give similar values along the series, whereas the 6-311G(d) and LAN-6(d) are quite different at the first part and at the end of the series, respectively. This fact shows the importance of the inclusion of diffuse functions in the basis set (for carbon and scandium atoms) for the determination of ionization energies. Finally we can see that the LanL2DZ shows a behavior more close to that found for the 6-311+G(d) basis set than the 6-311G(d) and LAN-6(d) basis sets.

From Figure 7, it can be observed that EAs increase along the series (EAs take values from 1.26 to 3.00 eV), and show a clear even−odd alternation with higher values for n-even species. These results can also be related to the stability of ScC_n/ScC_n^- clusters. The much higher stability of n-even ScC_n^- clusters with respect to their neutral counterparts is reflected in the behavior of EAs. It is interesting to note that all the basis sets employed in this work, with the only exception being the 6-311G(d) one, give very similar results for the variation of EAs with the number of carbon atoms. It can be concluded that inclusion of diffuse functions in the basis set for the scandium atom is important for calculating electron affinities in this system. On the other hand, the results obtained when we include in the basis set effective core potentials for the carbon and scandium atoms are very close to that obtained with the 6-311+G(d) basis set.

In general, we can see that for both ionization energies and electron affinities, the results obtained when we employ effective core potentials for both carbon and scandium atoms are quite close to that obtained with the 6-311+G(d) basis set. This fact can be useful for the predictions of these properties in larger ScC_n systems.

Conclusions

A theoretical study of small open-chain ScC_n, ScC_n^+, and ScC_n^- ($n = 1-8$) clusters, has been carried out with DFT methods. In particular, we have employed the B3LYP method with five different basis sets. Comparing the results obtained with the different basis sets, it can be concluded that inclusion of diffuse functions in the basis set of scandium atom is relevant for computing molecular properties of this system. On the other hand, the utilization of effective core potentials for scandium atom, in particular LanL2DZ, in conjunction with the 6-311+G(d) basis set for carbon atoms, gives results very close to that obtained when we employ the 6-311+G(d) for all the atoms.

All open-chain ScC_n, ScC_n^+, and ScC_n^- clusters have linear ground states, with the only exceptions of ScC_2 and ScC_2^+ where the linear structures correspond to a transition state. For the linear neutral clusters an alternation in stability between doublet and quartet states is found, n-odd neutral clusters have quartet ground states, $^4\Sigma$, whereas n-even neutral clusters present doublet ground states, $^2\Sigma$. In the case of both cationic and anionic species, an even−odd alternation is also found, n-odd clusters presenting triplet ground states $^3\Sigma$ (except for ScC^+ and ScC^- where the ground states are $^3\Pi$), and n-even ones having singlet ones, $^1\Sigma$.

The relative stability of the different clusters has been discussed employing the concept of incremental binding energy. All neutral, cationic, and anionic species exhibit a clear even−odd parity effect in stability, n-even clusters being more stable than n-odd ones. The parity effect is stronger for anionic clusters and less pronounced for cationic ones. This alternation in stability can be explained in terms of the number of their valence π-electrons. The ionization energies and electron affinities also exhibit an even−odd alternation effect, with n-odd clusters having both smaller ionization energies and electron affinities than n-even. It is also shown that the electron affinity increases along the series.

In addition, predictions for several molecular properties of the ScC_n, ScC_n^+, and ScC_n^- clusters, such as vibrational frequencies, rotational constants, and dipole moments, which could help in their possible experimental detection, have also been made.

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Supporting Information Available: Vibrational frequencies and rotational constants for ScC_n, ScC_n^+, and ScC_n^- clusters (Tables S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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