Theoretical Study of the Structures and Stabilities of Small CaC_n, CaC_n^+, and CaC_n^- (n = 1−8) Cyclic Clusters

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CaC_n, CaC_n^+, and CaC_n^- ($n = 1-8$) monocyclic clusters have been studied using the B3LYP density functional method. Predictions for several molecular properties that could help in possible experimental characterization, such as equilibrium geometries, electronic structures, dipole moments, and vibrational frequencies, have been reported. For the CaC_n monocyclic clusters, the electronic ground state is found to be a singlet for n-even clusters, whereas in the case of n-odd, singlet and triplet states are predicted to lie very close in energy. Both anionic and cationic clusters have doublet ground states, with the only exception of CaC_3^+ that has a $^4B_1$ ground state. An even−odd parity effect, with n-even clusters being more stable than n-odd ones, is found for both neutral and anionic species, whereas in the case of cationic species this effect is slight and reversed. Ionization potentials exhibit also a clear parity alternation trend, with n-even clusters having larger values than n-odd ones. In the case of the electron affinities, a slight variation is found. It is also predicted that all neutral clusters prefer cyclic arrangements, with cyclic isomers being more favored for n-even clusters. Monocyclic ground states are also predicted for the first members of the series in the case of anionic and cationic monocyclic clusters.

Introduction

Considerable interest has been paid in the last years to the structure and properties of small heteroatom-doped carbon clusters containing second-row elements. This has been partly due to their potential relevance in both solid state chemistry and in gas phase chemistry, particularly in astrochemistry. A number of binary compounds corresponding to the general formula XC_n have been detected in space. Up to date, this family of molecules includes compounds such as SiC,[1] SiC_2[2], SiC_3[3], SiC_4,[4] SC,[5] SC_2,[6] SC_3,[7] and PC,[8] and it is expected that, as structural data for other binary carbides become available, new molecules could be detected in the interstellar medium. Some new candidates of this type include binary compounds containing metallic elements such as aluminum, magnesium, sodium, or calcium. In fact a number of molecules containing these metals (mainly cyanides and isocyanides) have already been detected in space.[9−12] Calcium has a similar cosmic abundance to aluminum or sodium, and calcium carbides compounds have been proposed as possible carriers of interstellar radioastronomical lines.[13,14] Nevertheless, no calcium bearing molecules have been observed to date.

In addition, metal carbides corresponding to the same general formula are also relevant in solid-state chemistry, since they correspond to the basic structural units of potentially interesting new materials. Substitution of heteroatom into a pure carbon cluster results in significant changes on the electronic structure, which may eventually be used to elaborate new types of materials with interesting applications. 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, that could help us to understand the structure of these materials and could be useful to make extrapolations for some properties (stability, ionization potential, etc.) and therefore predictions for larger clusters. As a consequence the systematic study of heteroatom-doped carbon clusters containing second-row elements has received considerable attention in recent years. Of particular relevance for this work are those studies dealing with the properties of heteroatom-doped carbon clusters containing metallic elements, such as C_nSi,[15−17] AlC_n,[18] MgC_n,[19] or NaC_n[20] clusters. In most cases, only the open-chain isomers of these clusters have been considered. In addition, systematic studies of cyclic isomers have also been carried out for AlC_n,[21] MgC_n,[22] and NaC_n[20] compounds.

We have recently carried out a theoretical study of the CaC_n[23] clusters considering only open-chain isomers. Nevertheless, usually these compounds have low-lying cyclic states, and even in some cases the ground state is cyclic. Theoretical studies have shown that CaC_2[24] has a cyclic ground state and that CaC_3[25] has a rhomboidal ground state. In addition, a recent theoretical study for the isovalent MgC_n[22] clusters has found that neutral clusters prefer cyclic structures over open-chain isomers, especially for high n. Therefore, cyclic structures could be relevant for these kinds of compounds. In the present work, we present a theoretical study of the CaC_n, CaC_n^+, and CaC_n^- ($n = 1-8$) monocyclic clusters, to study possible systematic trends in their properties. In addition, the competition between open-chain and cyclic structures for the ground state of CaC_n, CaC_n^+, and CaC_n^- clusters will be discussed.

Computational Methods

We have employed the same theoretical approach than in our previous studies on heteroatom doped carbon clusters[18−22] and in particular in our previous work on CaC_n open-chain clusters.[23] Therefore, all our calculations have been made using the density functional theory (DFT), in particular, we selected the B3LYP exchange-correlation functional.[26,27] This consists of the Lee−

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Yang−Parr[28] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[29] The latter is a linear combination of local density approximation, Becke's gradient correction,[30] and the Hartree−Fock exchange energy based on Kohn−Sham orbitals.[31] In these calculations, we used both the triple split-valence d-polarized 6-311G(d) basis set[32] and the 6-311G+(d) basis set, which has an extra set of diffuse functions.

The effect of employing high-level theoretical methods and extension of the basis set on the results of this type of compounds have been analyzed in our previous studies on CaC_2[24] and CaC_3[25] systems. In general, a good agreement between the results obtained with the B3LYP/6-311G(d) level and other more expensive theoretical methods is observed. In addition, other authors have shown that the B3LYP method appears well adapted to medium-sized impurity-containing carbon-clusters.[33]

Harmonic vibrational frequencies were computed for all structures using analytic gradient techniques. These frequencies were employed to estimate the zero-point vibrational energy (ZPVE) correction and enable us to check the nature of stationary points. Other properties, such as dipole moments, calculated taking the center of mass as origin, or rotational constants were also computed.

All calculations reported in this work were carried out with the *Gaussian 98* program package.[34]

Results and Discussion

CaC_n Monocyclic Clusters. We have searched for different monocyclic CaC_n species on both the singlet and triplet surfaces. We have also made explorations of other possible isomers (for example structures with an exo-cyclic calcium atom) for the smaller clusters of the series and they were found to lie higher in energy, and it is expected that for small-size clusters they will not be competitive. Nevertheless, one of the 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. In Table 1, we provide the electronic energies, $\langle S^2 \rangle$ expectation values, harmonic vibrational frequencies, rotational constants, dipole moments, binding energies, and relative energies at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) levels of theory for the lowest-lying cyclic CaC_n species on the singlet and triplet 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.

It can be readily seen in Table 1 that for all cyclic species reported in this work the B3LYP wave functions have $\langle S^2 \rangle$ expectation values close to the pure spin values. Therefore, spin contamination should not be a problem in these cases. It can also be seen that all of the reported structures have all of their frequencies real, thus confirming that they are true minima on the respective potential surface. On the other hand, geometrical parameters, and other properties, such as vibrational frequencies or dipole moments, computed with both basis sets, 6-311G(d) and 6-311+G(d), are virtually coincident for all species. Therefore, it can be concluded, as in the case of open-chain isomers,[23] that inclusion of diffuse functions is not essential for the description of cyclic CaC_n structures.

As can be seen in Table 1, all n-even cyclic clusters have a singlet ground state, and the energy difference between singlet and triplet states has a slight tendency to decrease as the number of carbon atoms increases, except for the first member of the series (n=2), that shows a small difference. For n-odd cyclic clusters, singlet and triplet states are very close in energy, and we have found that for $n = 3$ and 7 the ground state corresponds to a $^3B_1$. In the case of CaC_5, a $^1A_1$ state is predicted to lie only 0.7 kcal/mol lower in energy than the corresponding triplet one. Nevertheless, for n-odd clusters, both states should be quite close in energy, and therefore, both could be accessible to experimental detection. The effect of cyclation on n-even CaC_n linear clusters is a destabilization of the triplet states with respect to the singlets ones, whereas singlet states lower their energy with respect to triplet states for n-odd CaC_n linear clusters. On the other hand, the isovalent MgC_n cyclic clusters[22] have singlet ground states (except for $n = 3$), and therefore, the substitution of magnesium for a calcium atom favors triplet states for n-odd clusters, whereas the effect is the opposite in the case of n-even ones.

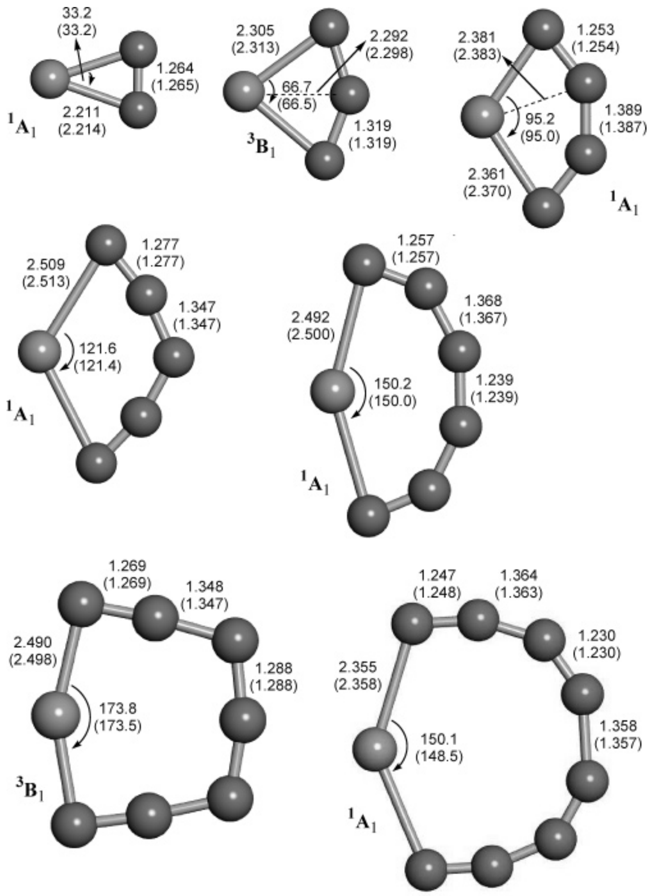

Figure 1. Equilibrium geometries of CaC_n monocyclic clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

There are some interesting features of the geometrical parameters for CaC_n cyclic clusters. It can be seen in Figure 1 that all C−C bond distances are between the range 1.23−1.39 Å following a pattern that resembles the behavior found in the case of open-chain isomers,[23] with a clear alternation of C−C bond distances ($C_{odd}-C_{even}$ distances shorter than $C_{even}-C_{odd}$ ones). On the other hand, the Ca−C distances are in general longer for the cyclic structures. An analysis of the Ca−C distances shows that there is a sort of π-type interaction between the calcium and the entire carbon unity, except in the case of CaC_8 where the main interaction is with the terminal carbons. For example, it is clear in CaC_6 that the Ca−C_1, Ca−C_2, and Ca−C_3 distances (2.492, 2.488, and 2.522 Å, at the B3LYP/6-

TABLE 1: Electronic Energies, $\langle S^2 \rangle$ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for Monocyclic CaC$_n$ Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	$-E$(a.u)	$\langle S^2 \rangle$	vibrational frequencies (cm^{-1})	BE (eV)	μ (D)	rotational constants (GHz)	ΔE, kcal mol^{-1}
CaC$_2$	$^1A_1$	753.693216		391/554/1827	10.85	10.62	52.706/7.510/6.573	0.00
		753.695883		382/551/1823	10.86	11.01	52.673/7.483/6.552	0.00
	$^3A_1$	753.649432	2.0130	201/381/1859		3.11	53.067/5.821/5.245	27.00
		753.651069	2.0134	197/375/1857		3.35	53.052/5.789/5.219	27.65
CaC$_3$	$^1A_1$	791.724919		221/408/520/973/1064/1384		13.06	41.676/3.922/3.585	5.04
		791.731206		230/405/520/989/1033/1421		13.37	41.483/3.915/3.577	4.39
	$^3B_1$	791.732829	2.0540	322/456/490/613/1224/1411	15.74	10.13	13.107/6.282/4.247	0.00
		791.737990	2.0522	315/449/482/609/1223/1427	15.78	10.47	13.094/6.232/4.223	0.00
CaC$_4$	$^1A_1$	829.891249		272/329/412/442/480/598/1002/1885/2014	23.78	8.60	5.977/5.794/2.942	0.00
		829.895595		268/321/406/440/482/597/1002/1881/2012	23.77	8.81	5.955/5.767/2.930	0.00
	$^3A''$	829.813649	2.0110	69/147/220/315/395/524/990/1698/2004		3.33	5.423/4.454/2.447	47.16
	$^3A_2$	829.816969	2.0096	52/147/217/317/391/523/987/1697/2011		3.50	5.401/4.444/2.438	47.81
CaC$_5$	$^1A_1$	867.941408		143/210/304/304/332/370/549/652/901/1328/1777/1845	29.00	7.36	5.154/3.369/2.037	0.00
		867.946239		147/205/302/305/331/370/546/649/900/1327/1781/1847	28.95	7.55	5.128/3.369/2.033	0.00
	$^3B_1$	867.940818	2.0777	76/232/320/372/380/441/488/601/923/1408/1599/1756		6.49	5.115/3.471/2.068	0.20
		867.944784	2.0763	61/230/313/366/380/438/485/598/922/1407/1601/1757		6.62	5.105/3.458/2.062	0.70
CaC$_6$	$^1A_1$	906.071935		119/256/264/295/315/387/418/467/516/577/850/1197/1894/1996/2101	36.29	3.75	4.771/2.246/1.527	0.00
		906.075930		114/255/260/289/313/386/412/468/514/565/849/1197/1893/1995/2099	36.19	3.80	4.768/2.238/1.523	0.00
	$^3B_2$	906.001469	2.0316	9/134/216/251/409/420/424/542/550/673/904/1067/1622/1867/1892		7.32	3.080/2.671/1.430	43.26
	$^3A''$	906.005448	2.0315	35/137/221/252/411/412/420/539/542/664/902/1071/1616/1857/1876		7.47	3.032/2.738/1.445	43.29
CaC$_7$	$^1A_1$	944.118476		72/80/101/207/287/336/370/375/485/502/516/641/899/1044/1399/1727/1942/1955		7.28	2.204/2.007/1.050	3.34
		944.123494		74/78/100/209/296/346/366/372/481/496/524/638/900/1044/1399/1726/1942/1955		7.57	2.208/1.992/1.047	2.90
	$^3B_1$	944.122750	2.1014	94/121/142/164/288/320/347/355/432/453/453/597/817/1092/1530/1573/1838/1861	41.54	1.64	3.648/1.709/1.164	0.00
		944.127119	2.0999	92/123/140/163/284/314/349/356/431/451/484/606/816/1092/1529/1577/1838/1863	41.41	1.61	3.643/1.703/1.161	0.00
CaC$_8$	$^1A_1$	982.237755		80/81/103/149/270/290/309/387/394/410/439/483/490/505/797/996/1300/1980/2026/2107/2152	48.38	4.39	1.663/1.603/0.816	0.00
		982.242472		77/83/103/149/267/290/303/367/389/407/435/473/483/498/798/996/1302/1976/2023/2101/2148	48.23	4.65	1.637/1.611/0.812	0.00
	$^3B_1$	982.184164	2.0332	23/102/105/146/235/271/357/361/374/414/423/494/582/618/794/1018/1281/1629/1857/1866/2030		1.19	2.604/1.372/0.899	32.52
		982.188773	2.0327	27/101/103/145/238/269/355/358/390/410/428/507/581/620/795/1019/1291/1629/1858/1866/2030		1.20	2.590/1.370/0.896	32.75

311+G(d) level, respectively) are all very close, suggesting that in fact there is a similar interaction between Ca and each of the carbon atoms. Therefore, for CaC$_n$ clusters ($n = 2-7$), there seems to be a certain trend for calcium to interact with the entire

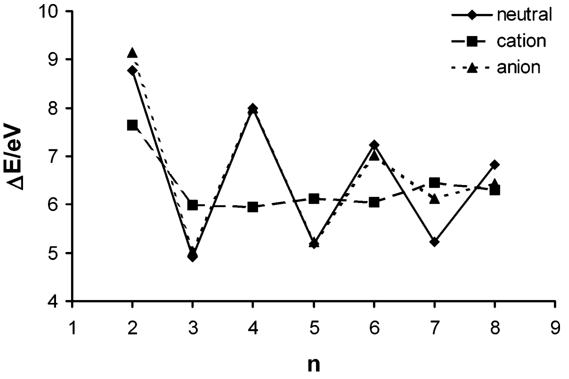

Figure 2. Incremental binding energies (eV) for the CaC_n, CaC_n^+, and CaC_n^- monocyclic clusters vs the number of carbon atoms.

carbon chain, rather than just with the carbon atoms at the end of the chain.

It is also worth mentioning that in general cyclic CaC_n clusters are characterized by high dipole moments, as a consequence of the high ionic character of the Ca−C bond, with the calcium atom bearing in most cases a relatively high positive charge. As expected, dipole moments of monocyclic clusters are much lower than the corresponding open-chain species (except for $n = 3$). In general, the dipole moment decreases with the number of carbon atoms.

As in our previous studies on open-chain and monocyclic clusters,[18−23] the relative stability of monocyclic CaC_n compounds will be discussed, following the suggestion by Pascoli and Lavendy,[35] in terms of the incremental binding energies.[36] The incremental binding energy can be defined as the change in energy accompanying the following process:

$$CaC_n \rightarrow CaC_{n-1} + C \tag{1}$$

and can be computed as the consecutive binding energy differences between adjacent CaC_n and CaC_{n-1} clusters. The results for the incremental binding energy for the different cyclic CaC_n clusters, as a function of the number of carbon atoms are shown in Figure 2. From this figure, it can be observed that there is a clear even−odd alternation, n-even clusters being more stable than n-odd ones. This is the same behavior found for open chain CaC_n clusters.[23] As in the case of the isovalent MgC_n systems,[19−22] the variation in the incremental binding energies for cyclic CaC_n clusters is higher than for the open-chain ones. It should be remembered that the computed incremental binding energies are in fact enthalpies for the corresponding process (1), as in similar theoretical studies on related systems. Nevertheless, for possible comparisons with experiments, perhaps Gibbs energies could be more appropriate, since the temperature could be large. However, we have estimated the entropy change, and consequently the Gibbs energies, associated with process (1) and the conclusions are very similar. The same trend observed in Figure 2 is found, because in fact all values for the different clusters decrease in a uniform way, around 0.38−0.42 eV.

CaC_n^+ Monocyclic Clusters. The molecular properties for the lowest-lying doublet and quartet states of CaC_n^+ monocyclic clusters are given in Table 2, whereas the geometrical parameters for the ground states are shown in Figure 3. In general, we can see in Table 2 that all of the structures reported are true minima on the doublet and quartet potential energy surface, and their corresponding $\langle S^2 \rangle_0$ values are relatively close to the pure spin values. Therefore, spin contamination does not seem to be a problem for studying CaC_n^+ monocyclic states with the B3LYP method. On the other hand, the inclusion of diffuse functions in the basis set has no important effects on the computed properties, including geometrical parameters.

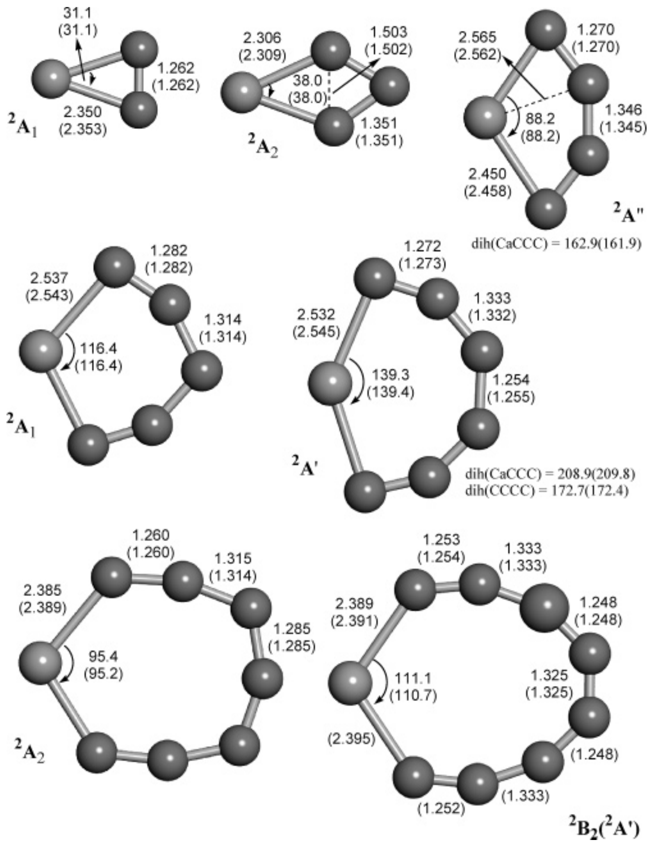

Figure 3. Equilibrium geometries of CaC_n^+ monocyclic clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

In all cases, the lowest-lying cationic species corresponds to a doublet electronic state. The doublet-quartet energy difference in general decreases with increasing n, as in the case of their open-chain counterparts.[23] Nevertheless, energy differences show a clear even−odd alternation for open-chain clusters. Comparing the geometries of the cationic clusters with their neutral counterparts, it can be observed that Ca−C distances are slightly lengthened (except in the case of CaC_7^+). However the most important difference is the much smaller ∠CCaC angles that are observed for the cationic clusters compared with their neutral counterparts. This is also reflected in the lengthening of Ca−C distances for second next carbon atoms respect to that observed for the neutral analogues (see CaC_4 and CaC_4^+ in Figures 1 and 3, respectively). Therefore, upon ionization, the calcium atom shows a preference to bond to the carbon atoms at the end of the carbon chain rather than to the entire carbon unit. On the other hand, the C−C distances follow the same patterns observed for the neutral CaC_n clusters, with values close to typical cumulenic structures and some acetylenic character, which is reflected in the alternation of C−C distances (into the range 1.248 and 1.350 Å).

In Figure 2, the incremental binding energies for the different CaC_n^+ clusters are also represented. The incremental binding energies are very similar for cationic clusters (the values change from 5.95 eV (CaC_4^+) to 6.45 eV (CaC_7^+)), except for the first point ($n = 2$) which has a very large value, in part due to the low stability of CaC^+. Furthermore, it is seen that there is a slight parity alternation effect, and in contrast with neutral

TABLE 2: Electronic Energies, ⟨S^2⟩ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for Monocyclic CaC$_n^+$ Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	$-E$(a.u)	⟨S^2⟩	vibrational frequencies (cm^{-1})	BE (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
CaC_2^+	$^2A_1$	753.431522	0.7694	248/471/1847	9.91	8.63	52.906/6.574/5.847	0.00
		753.435393	0.7697	246/469/1846	9.85	8.67	52.911/6.560/5.837	0.00
	$^4A_2$	753.296112	3.7568	383/413/1220		7.25	41.830/6.321/5.491	84.18
		753.297510	3.7570	380/405/1225		7.24	41.999/6.280/5.463	83.85
CaC_3^+	$^2A_1$	791.513390	0.7555	253/368/447/883/1253/1635	15.93	9.47	37.296/3.781/3.433	0.00
		791.514890	0.7555	254/365/444/883/1251/1634	15.84	9.53	37.318/3.771/3.425	0.00
	$^4A_1$	791.385979	3.7903	193/388/533/550/1094/1280		8.25	12.172/5.378/3.730	78.81
		791.387887	3.7900	190/384/534/548/1094/1282		8.29	12.163/5.360/3.720	78.55
CaC_4^+	$^2A''$	829.593735	0.7831	186/251/300/370/460/547/1083/1780/1920	21.90	7.51	6.236/4.852/2.740	0.00
		829.595506	0.7817	198/246/292/366/459/547/1080/1775/1920	21.79	7.52	6.200/4.854/2.735	0.00
	$^4A''$	829.513933	3.7958	211/217/307/398/405/567/1091/1306/1766		7.91	7.260/3.833/2.509	49.18
		829.515639	3.7958	209/214/304/398/403/566/1089/1306/1766		7.93	7.242/3.834/2.507	49.22
CaC_5^+	$^2A_1$	867.679962	0.7853	119/191/254/263/316/398/426/539/947/1447/1832/1853	28.06	12.27	4.616/3.415/1.963	0.00
		867.682029	0.7850	120/193/251/262/313/397/425/537/945/1447/1834/1853	27.93	12.26	4.619/3.404/1.960	0.00
	$^4A_2$	867.623199	3.8224	135/160/300/373/411/492/492/612/1087/1252/1663/1740		7.96	5.308/2.678/1.781	35.81
		867.624972	3.8221	132/159/299/371/410/488/491/611/1086/1252/1663/1740		7.97	5.297/2.678/1.779	35.98
CaC_6^+	$^2A'$	905.764906	0.7813	117/147/232/261/286/333/407/439/463/532/888/1277/1792/1943/2026	34.13	4.55	4.120/2.278/1.477	0.00
		905.767121	0.7794	113/153/229/258/281/330/411/435/465/522/885/1275/1790/1942/2026	33.99	4.48	4.151/2.261/1.475	0.00
	$^4A_2$	905.724192	3.8205	115/127/171/246/335/372/394/525/581/644/958/1185/1484/1789/1871		8.03	3.513/2.009/1.278	25.05
		905.726216	3.8203	114/125/169/245/336/369/393/524/563/641/957/1184/1483/1789/1872		8.04	3.504/2.012/1.278	25.17
CaC_7^+	$^2A_2$	943.863330	0.7930	99/123/177/188/196/299/357/366/376/399/521/524/988/1173/1678/1722/1890/1972	40.61	8.41	2.726/1.429/0.937	0.00
		943.865794	0.7925	90/123/176/185/196/298/352/363/372/397/519/524/988/1172/1679/1721/1888/1972	40.42	8.41	2.729/1.425/0.936	0.00
	$^4A''$	943.814304	3.8422	69/113/126/159/318/354/355/394/460/476/478/596/945/1173/1433/1687/1754/1835		7.79	2.492/1.548/0.955	30.30
		943.816707	3.8417	68/112/125/159/316/353/459/354/394/474/478/596/946/1173/1432/1686/1754/1835		7.81	2.493/1.544/0.953	30.38
CaC_8^+	$^2B_2$	981.956927	0.7713	32/105/113/168/169/263/277/326/369/393/424/431/449/463/871/1073/1410/1922/19932036/2061	46.93	7.23	1.853/1.197/0.727	0.00
	$^2A'$	981.959514	0.7710	55/106/112/168/170/262/273/325/328/391/415/431/435/465/871/1072/1409/1919/1989/2033/2059	46.71	7.27	1.858/1.191/0.726	0.00
	$^4B_1$	981.914599	3.8261	54/104/111/171/260/265/266/364/369/374/420/557/560/574/868/1052/1332/1473/1821/1872/2065		8.60	1.882/1.153/0.715	25.96
		981.917390	3.8258	52/104/112/171/260/265/265/361/367/378/418/550/559/572/868/1052/1332/1473/1820/1871/2063		8.65	1.885/1.149/0.714	25.90

clusters, *n*-odd clusters being more stable than *n*-even ones. Linear CaC_n^+ clusters[23] also show a smooth parity alternation effect, but *n*-even clusters are the most stable ones.

CaC_n^- Monocyclic Clusters. Finally, we have also studied the anionic cyclic clusters. Their main properties are given in Table 3 and the optimized geometries for the lowest-lying species are shown in Figure 4. All anionic species reported in this work are true minima, with the only exception of the quartet state of CaC_7^-, which has an imaginary frequency at the B3LYP/6-311+G(d) level of theory. However, the quartet state of $CaC_7^-(^4B_1)$ lies clearly higher in energy than the corresponding doublet. Except for $^2B_1$ of CaC_5^-, the $\langle S^2\rangle_0$ values, shown in Table 3, deviate slightly from the pure spin values, always less than 2%, and consequently, it can be considered that spin contamination should not be significant in these cases. As expected, it can be seen that the inclusion of diffuse functions

TABLE 3: Electronic Energies, ⟨S^2⟩ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for Monocyclic CaC$_n^-$ Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	−E(a.u)	⟨S^2⟩	vibrational frequencies (cm^{-1})	BE (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
CaC$_2^-$	^{2}A$_1$	753.742790	0.7519	313/470/1847	12.36	3.61	52.846/6.778/6.007	0.00
		753.749115	0.7519	300/462/1838	12.30	3.72	52.745/6.745/5.980	0.00
	^{4}B$_2$	753.647745	3.7600	181/329/1843		1.69	52.944/5.504/4.985	59.25
		753.657061	3.7609	177/326/1852		2.68	53.015/5.504/4.986	57.41
CaC$_3^-$	^{2}A$_1$	791.781997	0.7508	218/352/446/980/1097/1429		3.95	41.482/3.645/3.350	2.42
		791.791912	0.7504	222/349/443/1001/1080/1446		4.43	41.328/3.638/3.343	2.62
	^{4}B$_1$	791.785343	3.7957	238/399/444/572/1192/1452	17.33	2.25	12.732/5.618/3.898	0.00
		791.795513	3.7937	232/398/443/566/1192/1466	17.34	2.40	12.721/5.559/3.868	0.00
CaC$_4^-$	^{2}A$_1$	829.943537	0.7503	205/241/295/396/481/584/953/1891/2040	25.38	1.13	5.553/5.144/2.670	0.00
		829.953297	0.7503	200/245/289/393/489/583/954/1884/2033	25.35	1.13	5.541/5.108/2.658	0.00
	^{4}A′	829.833439	3.7604	108/249/306/326/414/630/968/1380/1841		0.98	5.608/5.128/2.679	67.35
	^{4}B$_2$	829.845593	3.7593	63/289/304/299/391/519/986/1368/1874		1.75	5.508/5.175/2.668	66.19
CaC$_5^-$	^{2}B$_1$	867.993583	1.3152	90/205/217/228/387/401/508/555/878/1370/1641/1771	30.59	2.23	4.987/3.164/1.936	0.00
		868.005075	1.1267	82/194/244/217/393/407/528/569/882/1355/1645/1772	30.56	3.86	5.098/3.218/1.973	0.00
	^{4}B$_1$	867.987697	3.8145	81/173/200/282/370/427/442/579/874/1387/1639/1790		1.28	4.603/3.233/1.899	3.68
		867.997554	3.8137	76/173/189/277/374/429/440/572/871/1393/1640/1788		1.36	4.619/3.194/1.888	4.62
CaC$_6^-$	^{2}A$_1$	906.115673	0.7503	94/100/134/245/270/325/410/457/470/547/785/1177/1906/2004/2145	37.29	2.41	4.561/1.921/1.352	0.00
		906.126109	0.7503	91/101/128/249/269/325/412/464/468/540/783/1177/1906/2007/2142	37.57	2.44	4.555/1.907/1.344	0.00
	^{4}A$_2$	906.041720	3.7707	94/104/208/245/294/326/342/535/553/596/915/1091/1561/1834/1877		0.96	2.973/2.374/1.320	45.70
		906.052639	3.7721	91/107/201/249/289/321/353/522/543/591/913/1093/1561/1836/1879		0.90	2.960/2.377/1.318	45.37
CaC$_7^-$	^{2}A$_2$	944.200431	0.7770	74/89/175/193/278/315/358/361/373/502/522/679/793/1013/1431/1686/1850/1882	43.79	1.67	3.957/1.666/1.172	0.00
		944.212247	0.7767	67/94/160/185/276/312/366/372/380/500/516/675/793/1017/1432/1683/1848/1880	43.70	1.88	3.934/1.664/1.170	0.00
	^{4}B$_1$	944.161970	3.8368	21/66/85/132/195/203/335/353/383/394/419/534/753/1070/1534/1639/1850/1889		3.50	3.841/1.394/1.023	23.11
		944.173041	3.8353	8i/68/79/141/192/202/342/368/380/389/467/544/752/1071/1535/1644/1853/1894		3.58	3.837/1.387/1.019	23.69
CaC$_8^-$	^{2}A$_1$	982.300493	0.7697	97/136/137/179/218/245/312/349/394/396/407/484/556/606/759/947/1221/1693/1907/1927/1991	50.28	0.84	2.991/1.329/0.920	0.00
		982. 311677	0.7690	94/130/137/171/227/241/306/366/389/398/414/502/553/601/759/950/1222/1693/1903/1926/1987	50.15	0.73	2.982/1.322/0.916	0.00
	^{4}B$_2$	982. 240259	3.8089	14/71/137/179/221/255/309/356/383/404/441/454/548/613/738/971/1249/1348/1674/1755/2022		0.80	3.007/1.309/0.912	36.63
		982.251605	3.8084	10/68/133/175/225/250/304/365/378/415/457/455/547/610/738/792/1249/1352/1673/1756/2023		0.73	2.997/1.304/0.909	36.53

in the basis set is more important than for the neutral and cationic clusters, although their effect on geometrical parameters, harmonic vibrational frequencies, energies, and dipole moments is not particularly high in this case. Therefore, it seems that inclusion of diffuse functions are comparatively more important for linear CaC$_n^-$ clusters than for cyclic ones.

It is readily seen in Table 3 that all anionic clusters have doublet ground states, with the only exception being CaC$_3^-$.

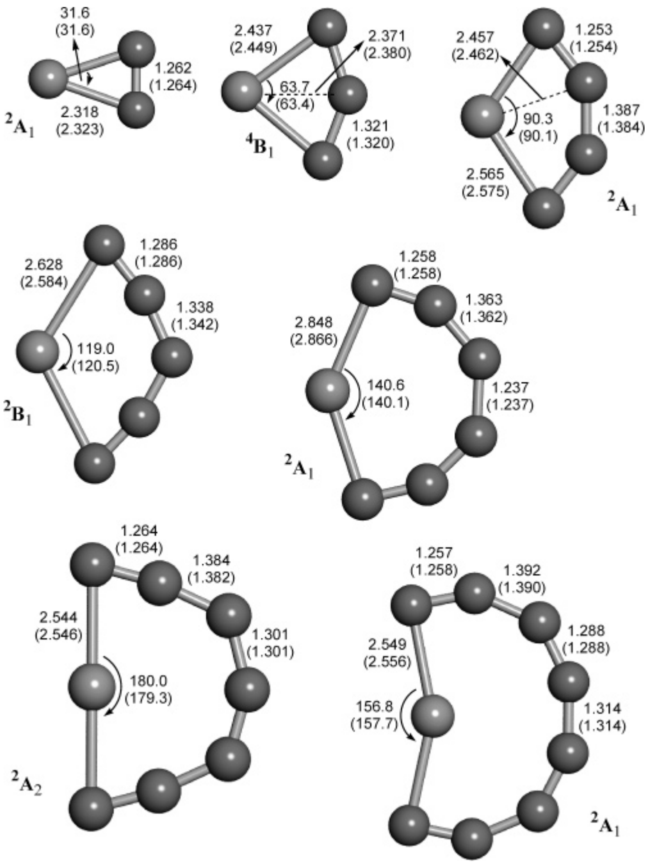

Figure 4. Equilibrium geometries of CaC_n^- monocyclic clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

Usually, the energy difference between the lowest-lying quartet state and the doublet ground state is quite high (especially for *n*-even clusters). Nevertheless, in the case of CaC_3^- and CaC_5^-, doublet and quartet states lie very close in energy, and therefore, some of them could also be accessible to experimental observations. When comparing with linear CaC_n^- clusters,[23] we can see that, except for CaC_3^-, in the case of *n*-odd clusters doublet states are stabilized upon cyclation and become the ground state.

Concerning the geometrical parameters, it can be seen in Figure 4 that in general there are not drastic differences in the bond lengths between neutral and anionic species. Perhaps the most important difference is that for CaC_n^- clusters the distances Ca−C between calcium atom and all of the carbon atoms of the C_n unit are very similar. This fact shows that for anionic clusters there is a certain preference for calcium to interact with the entire carbon chain. As an example, in the case of the largest clusters reported in this work, CaC_8^-, the Ca−C distances from Ca atom to C_1, C_2, C_3, and C_4 carbon atoms are 2.556, 2.498, 2.783, and 2.546 Å, respectively at the B3LYP/6-311+G(d) level of theory. Therefore, it seems that adding an electron in cyclic CaC_n clusters favors the π interaction.

In Figure 2, the incremental binding energies for the anionic clusters are also shown. It can be seen that incremental binding energies for the CaC_n^- species follow the same general pattern than for the neutral clusters, with a clear even−odd alternation; the *n*-even clusters being more stable than the corresponding odd $n - 1$ and $n + 1$ ones. With the exception of the two last points ($n = 7$ and 8), the variations found for the incremental binding energies for consecutive members in the same series are virtually the same than for the neutral clusters. In the case of $n = 7$ and 8, the parity alternation effect is smaller than for the neutral ones. The CaC_n^- cyclic clusters follow generally the same trends observed for their open-chain counterparts[23] and magnesium isovalent clusters.[22]

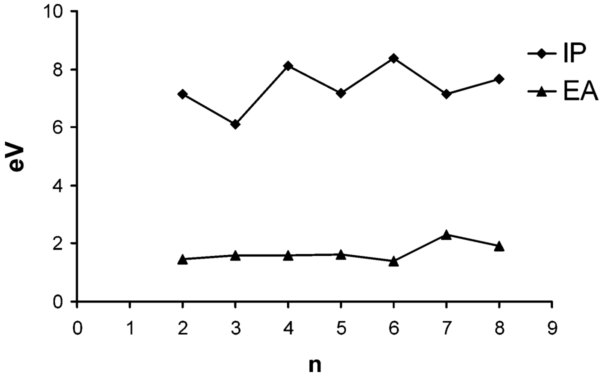

Figure 5. Ionization potentials (IP) and electron affinities (EA), in eV, of CaC_n monocyclic clusters vs the number of carbon atoms.

Ionization Potentials and Proton Affinities. The computed energies for cationic and anionic CaC_n clusters allow us to estimate the corresponding ionization potentials (IP) and electron affinities (EA). The IPs and EAs for CaC_n cyclic clusters as functions of the number of carbon atoms are shown in Figure 5. Since these properties 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 vertical IP and EA.

As can be seen in Figure 5, there is a clear even−odd alternation in the IPs, *n*-even clusters having higher IP than *n*-odd ones. This behavior is related to the stability of CaC_n/CaC_n^+ clusters. As it was predicted out CaC_n clusters present a large even−odd alternation effect, with *n*-even clusters being more stable than *n*-odd ones. On the other hand, the parity effect in the case of CaC_n^+ clusters is the opposite (*n*-odd clusters are more stable than *n*-even ones) and much less pronounced. Both effects result in a clear even−odd alternation in IPs, with *n*-even species presenting higher IPs than *n*-odd ones. CaC_n cyclic clusters exhibit a similar behavior to that found for the open-chain isomers.[23] It is also clear from Figure 5 that the variations found for the IPs for consecutive members in the series are much higher than for the open-chain clusters.

From Figure 5, it can be observed that the EAs vary only slightly when the number of carbon atoms increases (EAs take values close to 1.5 eV). Nevertheless, this situation changes from $n = 6$, and there is an even−odd alternation effect in EAs, with *n*-odd clusters having higher EA. This result is different to that found in the case of open-chain systems and can be related to the stability of CaC_n/CaC_n^- clusters. As it was shown in Figure 2, CaC_n and CaC_n^- clusters present a similar even−odd alternation effect up to $n = 6$ (incremental binding energies are very close), which is reflected in the uniformity of the first EAs values.

Finally, compared to their magnesium isovalent clusters,[22] IPs and EAs exhibit a rather similar parity effect. The main difference is that MgC_n compounds have a small parity effect in the EA curve for all the series.

Linear-Cyclic Stability. The energy differences between cyclic and open-chain isomers for CaC_n clusters and their cationic and anionic derivatives are shown in Figure 6. A positive value indicates that the cyclic isomer is more stable than the open-chain isomer. It can be seen in Figure 6 that all neutral clusters are predicted to prefer cyclic arrangements, and therefore, it seems that cyclic neutral species could be the most favorable to be characterized in experimental studies. It is also clear that there is a clear even−odd alternation, *n*-even cyclic

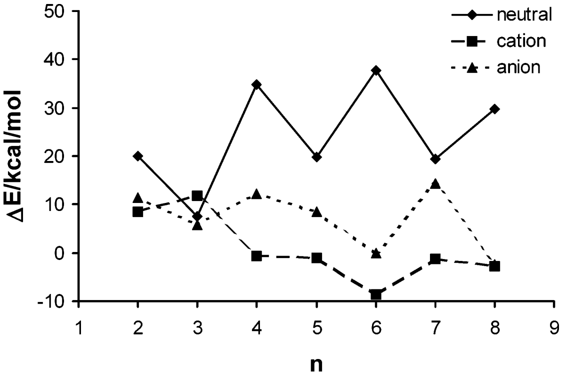

Figure 6. Energy separation between the monocyclic and open-chain structures for the CaC_n clusters as a function of n. A positive value indicates that the monocyclic isomer is more stable than the corresponding open-chain one.

clusters being comparatively more stable than n-odd ones. The same behavior was found for MgC_n clusters[22] and can be related to the stability of pure carbon clusters. The fact that for pure carbon clusters n-even species have monocyclic ground states was explained in terms of the number of π electrons.[36] The stability of monocyclic C_n structures over linear forms is the highest for those species with completely filled π orbitals. In the case of CaC_n clusters, there is almost a net transfer of two electrons from the calcium atom to the carbon chain, and therefore, these species can be viewed as resulting from the interaction of C_n^{2-} with Ca^{2+}. For example, this has been studied in detail for CaC_2,[24] where the ionic character of the interaction is clearly shown by a topological analysis of the charge density. In the case of CaC_n clusters, we have also analyzed the electronic charge density in terms of Bader's theory.[37] The results also show that the Ca−C_n bonding is essentially electrostatic, with bond critical points characterized by rather small electronic density and positive values of the Laplacian of charge density. The small degree of covalency can be mainly assigned to π-(C_n) → 3d(Ca) back-donation. The shape of the HOMO of the C_n^{-2} unit slightly favors the cyclic arrangement for n-even clusters over n-odd ones, because for the former the fully occupied HOMO π set has opposite signs on both sides of the chain, thus making more favorable the overlapping with d(Ca) orbitals. On the other hand, the partially occupied HOMO of the C_n^{-2} unit for n-odd clusters is mainly located at the end of the chain and at the central atom and is also symmetric with respect to the central carbon atom, thus making less favorable the side interaction with calcium than for n-even clusters.

A different behavior is found for the CaC_n^+ and CaC_n^- clusters, where the cyclic isomer (except in the case of CaC_3^+) is comparatively less stable than in the case of CaC_n clusters. The first two members of the CaC_n^+ series, $n = 2$ and 3, are predicted to prefer cyclic arrangements, and for the rest of the series, except CaC_6^+ (where the open-chain isomer is 8.1 kcal/mol more stable than the cyclic ones), open-chain and cyclic isomers are very close in energy. In these cases, inclusion of polarization functions in the basis set favors open-chain isomers (ΔE for CaC_4^+, CaC_5^+, CaC_7^+, and CaC_8^+ change from 0.26, 0.29, 0.33, and 0.26 kcal/mol, at the B3LYP/6-311G(d) to −0.71,−1.04, −1.30, and −2.79 kcal/mol, at the B3LYP/6-311+G(d) level, respectively). Nevertheless, both structures lie close in energy, and therefore could be accessible to experimental observation. On the other hand, anionic CaC_n^- clusters are predicted to prefer cyclic isomers, except for $n = 6$ and 8. For CaC_6^- and CaC_8^-, the cyclic and linear isomers are nearly isoenergetic. As in the case of cationic clusters, open-chain isomers lie lower in energy only when the 6-311+G(d) basis set was employed.

Compared to their magnesium isovalent clusters,[22] CaC_n, CaC_n^+, and CaC_n^- exhibit the same pattern, and in fact, the corresponding lines are nearly parallel. However, for the calcium clusters, the stability of the cyclic isomers is lower than for their magnesium analogues; therefore, substitution of magnesium for calcium atom in heteroatom-doped carbon clusters favors cyclic arrangements over open-chain ones.

Conclusions

Density functional theory calculations have been carried out for CaC_n, CaC_n^+, and CaC_n^- ($n = 1-8$) monocyclic clusters by the employment of the B3LYP method with the 6-311G(d) and 6-311+G(d) basis sets. Predictions for the geometrical parameters and other molecular properties that could be useful for an eventual experimental characterization have been provided. One of the most interesting features of the geometrical parameters, especially for anionic clusters, is that there is a certain tendency for calcium to interact with the entire carbon chain, rather than just with the carbon atoms at the end of the chain.

According to our calculations, all n-even cyclic CaC_n clusters have singlet ground states, whereas in the case of n-odd clusters, singlet and triplet states are very close in energy. In the case of both cationic and anionic species, all structures have doublet ground states, except for CaC_3^- that is found to have $^4B_1$ ground state. The relative stability of the different clusters has been discussed employing the concept of incremental binding energies. For both neutral and anionic species, there is a clear even−odd alternation in the clusters stability, with n-even clusters being more stable than n-odd ones. For the cationic clusters a slight alternation stability effect is found, although with opposite behavior (n-odd clusters being more stable than n-even ones). Ionization potentials exhibit a clear parity alternation trend, with n-even clusters having the larger IPs than n-odd ones. Electron affinities vary only slightly when the number of carbon atoms increases.

One of the most interesting results of the present work concerns the competition between linear and cyclic isomers. According to our theoretical calculations all neutral clusters are predicted to prefer cyclic arrangements, with cyclic isomers being much favored for n-even clusters. In the case of cationic and anionic clusters the smallest members of the series are found to be also cyclic, but open-chain and cyclic structures are, in general, very close in energy for high n. Substitution of magnesium by a calcium atom in heteroatom doped carbon clusters favors cyclic arrangements over open-chain ones. Therefore, cyclic structures are important for calcium-doped carbon clusters, and could be possible experimental targets.

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