Theoretical Study of MgC$_n$, MgC$_n^+$, MgC$_n^-$ ($n = 1-7$) Open-Chain Clusters

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MgC$_n$ ($n = 1-7$) open-chain clusters, as well as their cationic and anionic derivatives, have been studied by means of the B3LYP density functional method. Results for several molecular properties which could help in their possible experimental characterization, such as equilibrium geometries, electronic energies, dipole moments and vibrational frequencies, are provided. MgC$_n$ clusters are predicted to be linear with triplet ground states, with the only exception of MgC$_2$ that has a $^1\Sigma$ ground state. Both cationic and anionic clusters have doublet ground states, except for the first members of the series, MgC$^+$ and MgC$^-$, which are found to have $^4\Sigma$ ground states. The analysis of incremental binding energies shows that both MgC$_n$ and MgC$_n^-$ species exhibit a clear even−odd alternation in stability, n-even clusters being always more stable than n-odd ones. This alternation is also reflected in the electron affinity values, which are higher for n-even clusters. In the case of the cationic clusters, the stability alternation is reversed along the series, and for larger MgC$_n^+$ species n-odd species seem to be more stable.

Introduction

The study of heteroatom-doped carbon clusters containing second-row elements is receiving much attention in recent years, partly due to their interest in astrochemistry. Several binary compounds of the general formula XC$_n$ have been detected in space, 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 other similar molecules could be observed in astronomical objects as structural data for other binary carbides become available. Among the possible new candidates for interstellar molecules, some of the more interesting are those binary carbides formed with metals such as magnesium, aluminum, or sodium, which are relatively abundant in the interstellar medium. As a matter of fact, a few simple molecules containing these elements have already been detected in space, such as MgNC,[9] MgCN,[10] AlCl,[11] AlF,[11] AlNC,[12] or NaCN.[13] Most of these molecules are cyanides or isocyanides, and it is also conceivable that metal carbides could also be formed in space. Therefore, it is important to provide structural information on metal carbides to favor their characterization in laboratory, and an eventual detection in space by radioastronomical observations. Quite recently, we have studied some of these metal carbides, such as AlC$_3$,[14] MgC$_3$,[15] or NaC$_3$[16] to aid in their possible experimental observation.

In addition, heteroatom-doped carbon clusters containing second-row elements are also quite relevant in solid-state chemistry, since they are the basic structural units of new materials with interesting potential applications. In this respect, it is very important to have some knowledge about the behavior of binary carbon clusters as a function of the size of the cluster. This will allow the identification of possible systematic trends that could help to understand the structure of these materials, as well as to have information that could be useful to make extrapolations for some properties (stabilities, ionization potentials, ...) and therefore predictions for larger clusters. Whereas pure carbon clusters and heteroatom-doped carbon clusters containing first-row elements have been extensively studied by theoretical methods, only a few works are devoted to the systematic study of second-row-doped carbon clusters. Some of them have focused on binary carbon clusters with nonmetallic elements, such as C$_n$S,[17] C$_n$P,[18] or C$_n$Cl.[19] Silicon-doped carbon clusters, SiC$_n$ and their cations, have also been the subject of different theoretical studies.[20,21] We have recently carried out a theoretical study of the structures and stabilities of AlC$_n$, AlC$_n^+$, and AlC$_n^-$ clusters.[22]

In the present work, we provide a theoretical study of the MgC$_n$, MgC$_n^+$, and MgC$_n^-$ ($n = 1-7$) open-chain clusters, reporting their equilibrium structures and some spectroscopic data that could be helpful for their eventual experimental detection. In addition, the systematic behavior for their stability, ionization potential, and electron affinity will be discussed. In all reported structures in this work, the magnesium atom occupies a terminal position in the chain. We have also explored other isomers in which Mg is in a central position, but these isomers were always found to lie much higher in energy. For example, in the case of MgC$_3$,[15] the triplet state with the Mg atom in a central position was found to lie more than 70 kcal/mol above the corresponding isomer with Mg at the end of the chain. For the singlet state, the energy difference between both isomers was even higher, about 120 kcal/mol.

We will only report results about open-chain (linear or quasi-linear) clusters, to study possible systematic trends in their properties. Nevertheless, we should point out that cyclic structures might be important for MgC$_n$ clusters. For example we have found in a previous work on MgC$_3$[15] that cyclic and open-chain isomers are quite close in energy, and in fact the predicted ground state is a rhombic isomer. Nevertheless we are currently carrying out a systematic study of cyclic MgC$_n$ clusters in order to identify also possible systematic behaviors, as well as to discuss from a general point of view the competition between open-chain and cyclic structures for the ground state of MgC$_n$, MgC$_n^+$, and MgC$_n^-$ clusters. Therefore the present work is restricted only to open-chain structures.

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MgC$_n$, MgC$_n^+$, MgC$_n^-$ Open-Chain Clusters

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TABLE 1: Electronic Energies, ⟨S^2⟩ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Linear MgC$_n$ Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	−E (au)	⟨S^2⟩	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants GHz)	ΔE (kcal mol^{-1})
MgC	$^1\Delta$	237.940723		522		3.91	14.231	37.99
		237.943432		514		4.55	14.145	37.39
	$^3\Sigma$	238.001244	2.4924	512	1.39	3.27	14.267	0.00
		238.003005	2.4882	507	1.37	3.67	14.204	0.00
MgC$_2$	$^1\Sigma$	276.127246		41(2)/545/1910	8.61	9.21	5.667	0.00
		276.131167		130(2)/544/1910	8.63	9.77	5.661	0.00
	$^3\Pi$	276.113963	2.0032	134/329/450/1775		4.95	5.014	8.55
		276.117166	2.0033	170/553/446/1772		5.32	5.000	9.11
MgC$_3$	^{1}A′	314.197627		126/212/302/431/1222/1974		4.86	45.528/2.975/2.792	5.09
		314.200811		127/233/303/432/1221/1970		5.33	45.210/2.980/2.796	5.45
	$^3\Pi$	314.206140	2.0171	99/108/278/408/414/1242/1895	14.56	6.16	2.475	0.00
		314.209970	2.0173	108/121/301/420/411/1243/1893	14.55	6.52	2.471	0.00
MgC$_4$	^{1}A′	352.299018		71/192/217/427/511/624/952/1784/2073		11.13	23.241/2.058/1.890	5.95
		352.303869		72/197/211/473/521/622/950/1787/2072		11.75	23.157/2.065/1.896	5.44
	$^3\Pi$	352.308244	2.0156	68/71/140/236/382/444/517/986/1832/2103	21.11	7.60	1.416	0.00
		352.312518	2.0155	81/82/185/250/381/473/531/985/1832/2106	21.07	7.97	1.4141	0.00
MgC$_5$	^{1}A′	390.381527		71/132/176/272/317/424/513/613/799/ 1489/1972/2095		7.06	26.299/1.039/1.000	8.23
		390.385640		74/160/177/287/296/440/507/630/796/ 1512/1973/2165		7.62	25.907/1.042/1.002	8.67
	$^3\Pi$	390.394784	2.0288	64/65/165/179/319/375/360/482/645/ 835/1491/1950/2005	27.25	8.37	0.889	0.00
		390.399300	2.0288	65/67/166/179/331/364/359/500/644/ 834/1492/1950/2000	27.19	8.81	0.888	0.00
MgC$_6$	$^1\Sigma$	428.453270		61(2)/174(2)/295(2)/406/595(2)/777/ 922(2)/1297/1742/2097/2144		21.06	0.621	25.37
		428.459436		58(2)/170(2)/282(2)/403/562(2)/775/ 691(2)/1314/1745/2136/2196		22.42	0.622	24.04
	$^3\Pi$	428.491590	2.0247	52/54/129/139/241/269/341/445/493/ 695/714/720/1252/1889/2059/2143	33.63	9.63	0.595	0.00
		428.496462	2.0244	54/55/135/143/248/271/340/442/487/ 633/650/718/1252/1888/2062/2148	33.56	10.09	0.595	0.00
MgC$_7$	^{1}A′	466.561659		48/78/112/182/211/303/330/423/508/ 569/599/643/800/1111/1612/1919/2074/2147		9.23	21.919/0.467/0.457	9.69
	$^3\Pi$	466.578057	2.0399	45/46/110/116/208/223/326/346/376/ 502/600/640/846/947/1114/1599/1896/2035/2111	39.75	10.31	0.419	0.00

Computational Methods

We have employed the same theoretical approach to that in our previous studies on second-row heteroatom-doped carbon clusters.[19,22] Therefore, all our calculations have been made using the density functional method (DFT), in particular, selecting the B3LYP exchange-correlation functional.[23,24] This consists of the Lee−Yang−Parr[25] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[26] The latter is a linear combination of local density approximation, Becke's gradient correction,[27] and the Hartree−Fock exchange energy based on Khon-Sham[28] orbitals. Other authors have shown that the B3LYP method appears well adapted to medium-sized impurity-containing carbon clusters.[29]

In our B3LYP calculations, we employed both the triple split-valence d-polarized 6-311G(d) basis set[30] and the 6-311+G(d) basis set, which also includes diffuse functions. In density functional calculations such basis sets are usually able to give accurate results.

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.[31]

Results and Discussion

MgC$_n$ Clusters. We have studied different linear or quasi-linear isomers on both the singlet and triplet MgC$_n$ potential surfaces. We have collected in Table 1 some of the most interesting properties, such as harmonic vibrational frequencies, rotational constants, dipole moments, binding energies, and absolute and relative energies, for the lowest-lying open-chain MgC$_n$ species on the singlet and triplet potential surfaces. These molecular properties might be helpful in an experimental search for these species. In addition, the optimized geometries at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) levels of theory for the most stable structures are shown in Figure 1.

It should be pointed out that for some of the structures reported in this work, for example, those with $^2\Pi$ or $^3\Pi$ electronic states, the B3LYP method (as well as single-reference based methods such as HF, MP2, QCISD, etc.) provides nondegenerate π frequencies. On the other hand, for the $^1\Sigma$, $^2\Sigma$, and $^4\Sigma$ linear states studied in this work it is possible to obtain degenerate π frequencies,[32] and these are denoted in Tables 1−3 as (2). 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 Tables 1−3, since all structures have real frequencies, with the only exception of the $^2\Sigma$ state of MgC$_2^+$ which has imaginary frequencies when obtained with the 6-311G(d) basis set but is a true minimum with the 6-311+G(d) basis set). Since we are interested in predicting properties for structures that could be

TABLE 2: Electronic Energies, $\langle S^2 \rangle$ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Linear MgC$_n^+$ Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	-E (au)	$\langle S^2 \rangle$	vibrational frequencies (cm^{-1})	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
MgC$^+$	$^2\Pi$	237.706658	0.9641	406		3.92	12.220	0.45
		237.707130	0.9608	407		3.97	12.235	0.41
	$^4\Sigma$	237.707802	3.7527	591	1.12	5.87	15.574	0.00
		237.708203	3.7528	590	1.10	5.92	15.574	0.00
MgC$_2^+$	$^2\Sigma$	275.841541	0.7771	68i(2)/588/2071	8.55	9.19	5.774	0.00
		275.842806	0.7770	113(2)/588/2070	8.50	9.24	5.777	0.00
	^{4}A″	275.772639	3.7616	144/275/1506		2.19	144.000/4.667/4.521	42.19
		275.773204	3.7619	143/274/1497		2.21	144.862/4.661/4.516	42.29
MgC$_3^+$	$^2\Sigma$	313.921063	0.7510	79(2)/239/549(2)/1244/2185	14.49	4.173	2.171	0.00
		313.922578	0.7509	114(2)/239/590(2)/1243/2185	14.42	4.227	2.172	0.00
	^{4}A″	313.882596	3.8153	142/386/407/471/1323/1778		8.24	214.434/2.751/2.716	23.39
		313.883619	3.8153	139/390/410/464/1324/1768		8.35	230.493/2.742/2.710	23.61
MgC$_4^+$	^{2}A	352.016735	0.8037	69/152/231/429/458/500/1008/1624/1934	20.93	15.12	194.095/1.538/1.530	0.00
		352.018975	0.7969	68/156/231/414/467/494/1012/1638/1944	20.84	15.80	338.237/1.519/1.515	0.00
	$^4\Sigma$	351.988574	3.7895	61(2)/114(2)/257/428(2)/960/1626/2106		5.17	1.297	17.31
		351.990551	3.7896	65(2)/137(2)/257/460(2)/960/1626/2107		5.26	1.298	17.62
MgC$_5^+$	$^2\Sigma$	390.117352	0.7515	68(2)/164(2)/260/412(2)/633(2)/816/1498/2093/2274	27.39	5.72	0.847	0.00
		390.119662	0.7515	71(2)/166(2)/260/415(2)/665(2)/816/1499/2092/2274	27.27	5.83	0.848	0.00
	$^4\Sigma$	390.069265	3.8602	90(2)/265(2)/447/474(2)/677(2)/898/1593/1754/1973		14.56	0.935	30.44
		390.071311	3.8601	87(2)/253(2)/447/440(2)/579(2)/897/1590/1758/1973		14.67	0.934	30.06
MgC$_6^+$	^{2}A	428.205334	1.0266	55/68/125/163/230/368/372/458/509/561/ 713/1251/1831/1971/2079	33.63	16.86	121.752/0.624/0.621	0.00
	$^4\Sigma$	428.189371	3.8140	47(2)/116(2)/225(2)/261/415(2)/612(2)/ 696/1249/1762/2016/2145		6.83	0.573	10.31
		428.192102	3.8139	48(2)/113(2)/223(2)/262/413(2)/649(2)/ 696/1250/1763/2015/2148		6.97	0.574	
MgC$_7^+$	^{2}A′	466.311543	0.7606	47/68/111/159/194/281/287/367/498/534/ 611/614/693/1119/1595/2036/2116/2197	40.26	12.26	148.529/0.427/0.425	0.00
	$^4\Sigma$	466.255804	3.9019	54(2)/144(2)/274(2)/388/430(2)/627(2)/ 705/1152/1221(2)/1659/1697/2014/2045		18.37	0.433	37.24
		466.258401	3.9017	55(2)/141(2)/270(2)/387/409(2)/525(2)/ 707/755(2)/1150/1663/ 1694/2011/2043		18.51	0.432	
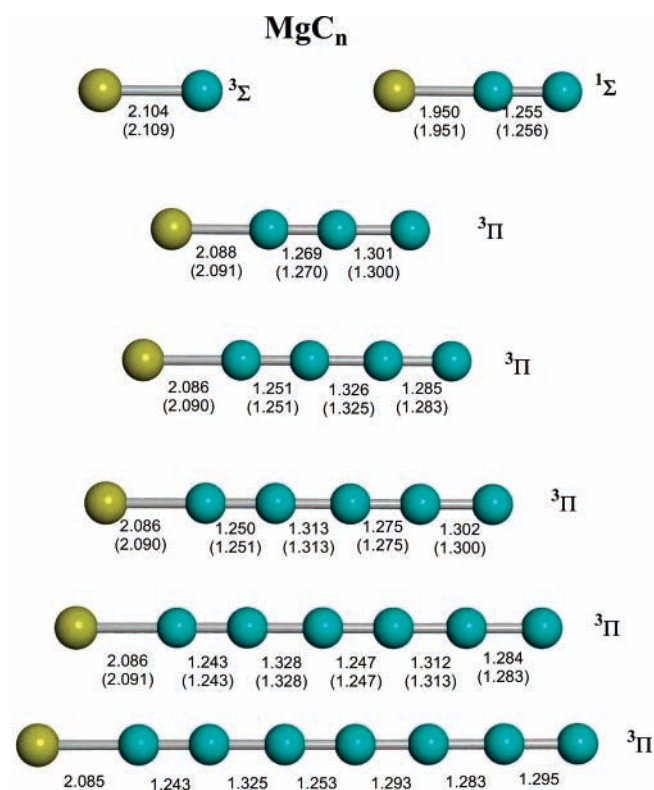
Figure 1. Equilibrium geometries of MgC$_n$ ($n = 1-7$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

eventually characterized by experimental studies, we focused our work on obtaining true minima. However, in a few cases there may exist apparently other species lying lower in energy, although they are in fact saddle-points. This is for example the case for MgC$_2$, since it is possible to obtain a $^3\Sigma$ state that lies lower in energy than our reported $^3\Pi$ structure, but has imaginary bending frequencies. When the basis set is increased up to 6-311+G(3df), two degenerate imaginary bending frequencies are still obtained. Therefore, it seems quite safe to consider that this state is not a true minimum. Following the associated normal mode, no stable open-chain isomer could be found, since all our attempts collapsed into the triplet cyclic isomer. Therefore, the lowest-lying triplet open-chain minimum is the reported $^3\Pi$ structure.

With the only exception of the first member of the series, MgC, all $\langle S^2 \rangle$ values for the triplet states are very close to the pure spin values, and therefore spin contamination does not seem to be a problem for studying MgC$_n$ open-shell states with the B3LYP method.

As can be seen in Figure 1, the inclusion of diffuse functions in the basis set has a negligible effect on the geometrical parameters of the neutral clusters. Furthermore, the computed relative energies with both basis sets are also quite close, and therefore it can be concluded that diffuse functions are not essential for the description of neutral MgC$_n$ species.

The lowest-lying structure for all MgC$_n$ open-chain clusters is found to be linear, and in all cases, with the only exception of MgC$_2$, corresponding to a triplet state. Our results for MgC are basically in reasonable agreement with the previous studies of Castro et al.[33] and Bauschlicher et al.,[34] that also predicted a $^3\Sigma^-$ ground state. Boldyrev and Simons[35] carried out a detailed

TABLE 3: Electronic Energies, ⟨S²⟩ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for Linear MgC$_n^-$ Clusters with the B3LYP/6-311G(d) (first line) and B3LYP/6-311+G(d) (second line) Methods

isomer	state	−E (au)	⟨S²⟩	vibrational frequencies (cm⁻¹)	binding energies (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol⁻¹)
MgC$^-$	$^2\Pi$	238.009450	1.5302	549		1.44	15.157	20.54
		238.016853	1.6621	527		2.21	14.863	21.59
	$^4\Sigma$	238.041889	3.7568	415	3.10	0.85	12.939	0.00
		238.050984	3.7629	403	2.93	0.19	12.849	0.00
MgC$_2^-$	$^2\Sigma$	276.216259	0.7543	59/60/505/1895	11.64	4.69	5.455	0.00
		276.226653	0.7546	133(2)/502/1896	11.46	5.99	5.435	0.00
	$^4A''$	276.118265	3.7619	183/369/1373		1.44	6173.688/4.945/4.941	60.64
		276.129377	3.7636	192/378/1398		2.16	6028.060/4.936/4.962	60.05
MgC$_3^-$	$^2A''$	314.275068	0.9169	103/276/373/386/1208/1758	17.06	1.68	107.081/2.599/2.537	0.00
		314.284051	0.9733	102/227/367/418/1201/1747	16.81	2.34	106.874/2.610/2.548	0.00
	$^4\Sigma$	314.265611	3.7775	142(2)/442(2)/469/1261/1756		5.53	2.559	6.72
		314.276301	3.7800	143(2)/451/452/469/1260/1737		6.88	2.559	5.64
MgC$_4^-$	$^2\Sigma$	352.413632	0.7530	48/49/244(2)/440/554(2)/1001/1949/2127	24.55	9.00	1.466	0.00
		352.425533	0.7526	68(2)/254/255/437/550/553/995/1950/2120	24.35	10.35	1.463	0.00
	$^4\Delta$	352.332273	3.7585	87/98/259/299/361/432/539/968/1723/1993		1.51	1.404	50.41
		352.342119	3.7592	92/99/270/301/362/453/547/967/1718/1989		1.54	1.404	51.70
MgC$_5^-$	$^2A''$	390.478290	1.1661	63/144/174/310/382/392/469/554/785/1474/1840/1901	30.15	4.06	51.237/0.952/0.935	0.00
	$^4\Sigma$	390.473861	3.8024	75(2)/203(2)/402/415(2)/580(2)/849/1499/1845/1897		8.62	0.903	3.56
		390.484445	3.8047	65(2)/193(2)/401/404(2)/527(2)/846/1504/1865/1998		10.07	0.902	
MgC$_6^-$	$^2\Sigma$	428.607338	0.7529	47(2)/136(2)/283(2)/377/532(2)/739/809(2)/1243/1955/2119/2200	37.35	12.09	0.604	0.00
		428.618702	0.7525	50(2)/139(2)/279(2)/375/511(2)/736/651(2)/1236/1957/2117/2197	37.09	13.52	0.603	0.00
	$^4\Delta$	428.527748	3.7810	45/66/114/168/207/318/338/449/484/638/756/691/1258/1764/1930/1958		4.01	0.594	48.42
		428.537307	3.7801	60/63/156/158/292/305/342/418/472/538/664/702/1252/1759/1904/2016		4.68	0.594	49.96
MgC$_7^-$	$^2A''$	466.673050	1.3976	44/83/105/202/217/329/383/394/488/513/597/673/676/1091/1610/1748/1964/2025	43.00	7.40	43.273/0.439/0.435	0.00
	$^4\Sigma$	466.672000	3.8282	50(2)/126(2)/239(2)/354/413(2)/576(2)/660/981(2)/1112/1621/1766/1958/2021		11.68	0.421	2.26
		466.682583	3.8303	48(2)/124(2)/231(2)/353/393(2)/504(2)/658/660(2)/1108/1618/1750/1953/2012		13.17	0.421	

analysis of the nature of bonding in this species, concluding that MgC is a singly bound species with two unpaired nonbonding electrons (π^2) essentially localized on the carbon atom. This is the same description provided by the B3LYP method according to the spin densities calculated at this level of theory. The bonding in this species seems to involve a dative bond from the magnesium 3s electron-pair to the empty $2p_z$ orbital of the carbon atom, therefore corresponding to the following valence-bond picture:

$$Mg : \rightarrow \overset{\bullet}{\underset{\bullet}{C}} :$$
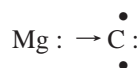
The singlet lowest-lying state observed for $n = 2$ also agrees with the theoretical studies of Green,[36] Woon,[37] and Boldyrev and Simons,[38] since all of them predict also a singlet ground state for the linear MgCC isomer. The geometrical parameters found for this species, with a relatively short Mg−C bond length, are compatible with the following dominant valence-bond structure:

$$Mg = C = C :$$
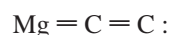
This $^1\Sigma$ state is predominant over the $^3\Pi$ state associated essentially to the valence-bond structure:

$$\bullet Mg - \overset{\bullet}{C} = C :$$

For $n \geq 3$, the lowest-lying state is $^3\Pi$, with very similar Mg−C bond distances, which can be ascribed to a single bond. The C−C distances are all in the range 1.24−1.33 Å, and therefore can be assimilated to moderately strong and typical double bonds, characteristic of cumulene structures:

$$\bullet Mg - \overset{\bullet}{C}(= C)_{n-2} = C : \quad n = 3, 4, 5, 6$$
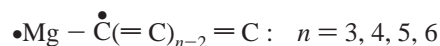
In all cases, we find spin densities for magnesium greater than 0.9e, but for C$_1$ usually the spin density is around 0.4−0.5e, the rest of the spin density distributed among the other carbon atoms, mainly at terminal carbon for n odd clusters. This fact, together with the clear alternation of the C−C bond distances, C$_{odd}$−C$_{even}$ shorter than C$_{even}$−C$_{odd}$, suggest that, as in the case
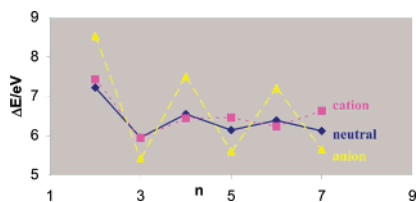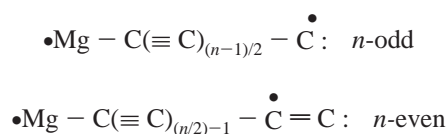
Figure 2. Incremental binding energies (eV) for the MgC_n, MgC_n^+, and MgC_n^- clusters vs the number of carbon atoms.

of the AlC_n clusters,[22] there is some polyacetylenic character with alternant triple C−C bonds starting in the C_1−C_2 bond:

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

$$\bullet Mg - C(\equiv C)_{(n/2)-1} - \overset{\bullet}{C} = C : \quad n\text{-even}$$

Dipole moments are in all cases quite high, reflecting the high ionic character of the Mg−C bonds. Furthermore, the dipole moment increases regularly with the number of carbon atoms for the triplet states, which are the ground states except for $n = 2$.

To discuss the relative stability of MgC_n clusters, we will employ, as we made in the cases of the AlC_n and C_nCl compounds,[19,22] the concept of incremental binding energy. Pascoli and Lavendy[18] suggested in their study of the structure and stability of C_nP clusters that this magnitude could be useful for studying this kind of compound. In our case, the incremental binding energy is defined as the change in energy associated with the process:

$$MgC_n \rightarrow MgC_{n-1} + C$$

The incremental binding energy for the different MgC_n clusters as a function of the number of carbon atoms is shown in Figure 2. It is readily seen in this figure that the incremental binding energy for the neutral clusters varies only smoothly, except for the first members of the series, taking values around 6.1−6.5 eV for $n \geq 4$. In any case, it is clear that there is a small even−odd alternation in stability for neutral MgC_n clusters, n-even clusters being more stable than n-odd ones. This fact can be rationalized in terms of the electronic configuration. Even though all clusters with $n > 2$ have $^3\Pi$ ground states, n-even species have $\sigma^1\pi^3$ electronic configurations, resulting in a somewhat more stable structure than in the case of n-odd species, since for the latter the electronic configuration is $\sigma^2\sigma^1\pi^1$.

MgC_n^+ Clusters. The equilibrium geometries for the lowest-lying states of MgC_n^+ clusters are shown in Figure 3, whereas their corresponding properties ($\langle S^2 \rangle$, vibrational frequencies, dipole moments, rotational constants, and both binding and relative energies) are given in Table 2.

All cationic clusters have doublet ground states, with the only exception of MgC^+. In this case, the quartet state lies slightly lower (about 0.4 kcal/mol) than the doublet one. The doublet-quartet energy difference increases with n for n-odd clusters, whereas decreases for n-even species. The main difference observed between the results with both basis sets is that linear MgC_2^+ is not a true minimum at the B3LYP/6-311G(d), since it has a degenerate imaginary π frequency. However, with the 6-311+G(d) basis set all its frequencies are real. In all other cases, an almost negligible effect is observed upon inclusion of diffuse functions.

The main difference in the geometries with respect to their neutral counterparts is that most of the larger cationic clusters
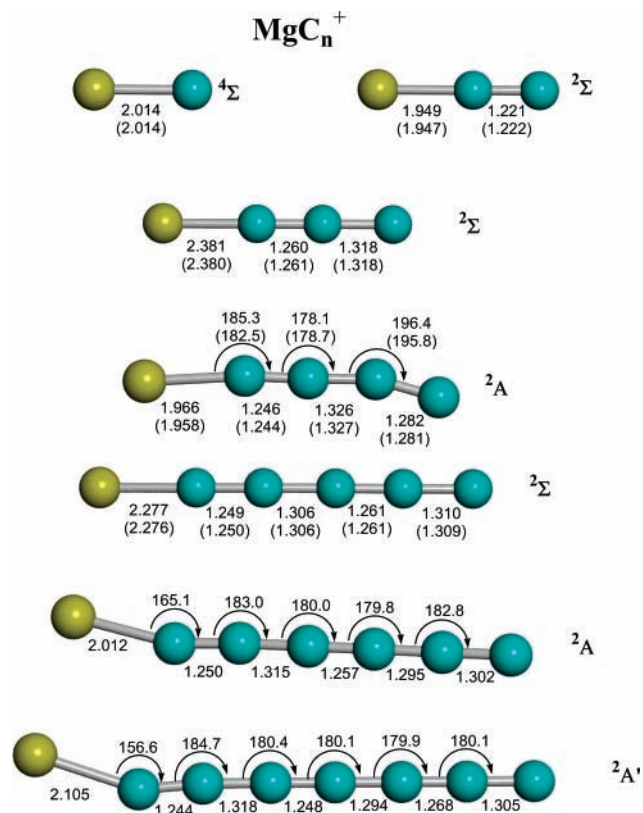

Figure 3. Equilibrium geometries of MgC_n^+ ($n = 1-7$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in angstroms and angles in degrees.

are found to adopt nonlinear geometries. However, the C−C distances follow the same patterns observed for the neutral MgC_n clusters, with values close to typical cumulenic structures and some acetylenic character which is reflected in the alternation of C−C distances.

As expected in all cases the positive charge is mainly located at the magnesium atom. Bearing in mind the description of the neutral clusters, the loss of an electron could give rise in linear geometries either to $^2\Sigma$ or $^2\Pi$ states. The dominant valence-bond structures in each case are, respectively, as follows:

$$\overset{+}{\bullet Mg} \leftarrow : \; C(=C)_{n-2} = C : \qquad ^2\Sigma$$

$$\overset{+}{Mg} - \overset{\bullet}{C}(=C)_{n-2} = C : \qquad ^2\Pi$$
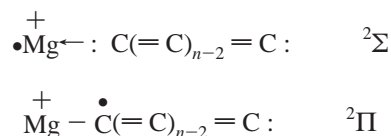
For large MgC_n^+ species, the first one of these descriptions is favored, as illustrated by the large spin density at magnesium, and consequently the Mg−C bond has a high dative character.

The incremental binding energies for MgC_n^+ clusters are also shown in Figure 1. It is readily seen that incremental binding energies for the cations take values of the same magnitude than for their neutral counterparts. In fact, for the first members of the series the values are very close (with differences smaller than 0.2 eV) and the behavior is quite similar, with n-even clusters being more stable than n-odd ones. Nevertheless, this situation changes from $n = 5$, for which an inversion in the tendency of incremental binding energies is observed, with n-odd clusters being more stable.

MgC_n^- Clusters. The geometrical parameters for the lowest-lying states of MgC_n^- anions are shown in Figure 4, whereas their corresponding properties are given in Table 3. With the only exception of the first member of the series, MgC^-, all
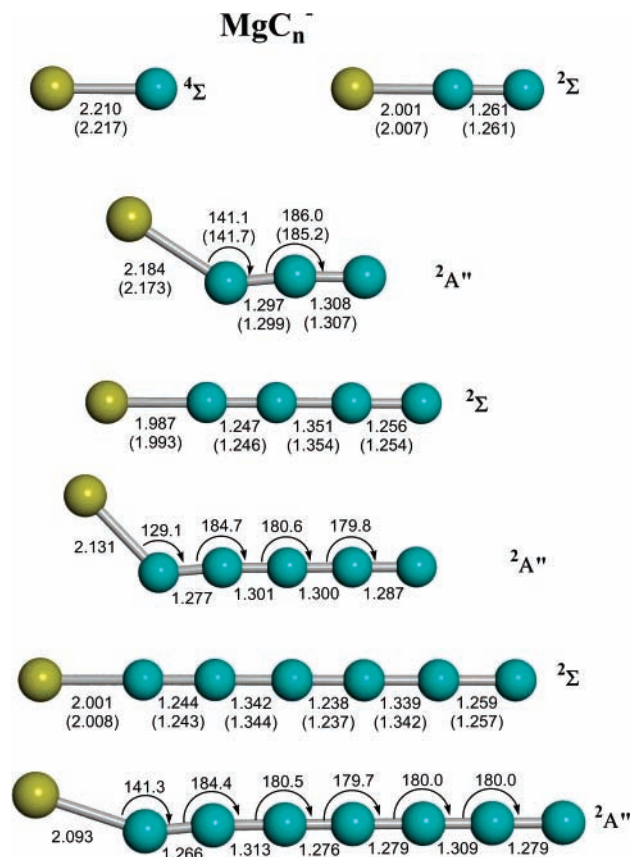
MgC$_n$, MgC$_n^+$, MgC$_n^-$ Open-Chain Clusters

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Figure 4. Equilibrium geometries of MgC$_n^-$ ($n = 1-7$) 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.

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

MgC$_n^-$ clusters have doublet ground states. Furthermore, it is observed that *n*-even clusters prefer linear geometries with $^2\Sigma$ states, whereas *n*-odd species deviate form linearity and correspond to $^2A''$ electronic states.

These observations can be rationalized bearing in mind the electronic configurations for their neutral counterparts, namely, $\sigma^1\pi^3$ for *n*-even species and $\sigma^2\sigma^1\pi^1$ for odd *n*. Adding an electron for *n*-even clusters produces a $\sigma^1\pi^4$ electronic configuration ($^2\Sigma$ electronic state), which is favored over the $^2\Pi$ state ($\sigma^2\pi^3$), since the π orbital has a bonding character and therefore full occupation of the highest-lying π-bonding set is accomplished. The quartet state, corresponding to a $\sigma^1\pi^3\pi^1$ electronic configuration, is much less stable (see their relative energies in Table 3) since the electron enters in a π antibonding orbital. On the other hand, for *n*-odd species adding an electron to the parent neutrals results either in $\sigma^2\sigma^2\pi^1$ ($^2\Pi$ state) or $\sigma^2\sigma^1\pi^2$ ($^4\Sigma$ state). In the former case, the new electron occupies a nonbonding σ orbital essentially located at magnesium, although much of the negative charge is donated to the adjacent carbon atom, whereas in the latter it enters in a π orbital distributed essentially among C$_1$ and the terminal carbon atom. In the case of the $^2\Pi$ states, nonlinear geometries are preferred and finally $^2A''$ states are obtained. Both doublet and quartet electronic states are quite close in energy for *n*-odd clusters, with $^2A''$ states being slightly more stable than the quartet state, although the energy difference decreases with *n*.

There are some interesting features of the geometrical parameters for MgC$_n^-$ clusters. In the first place, 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. On the other hand, for *n*-even clusters a clear alternation in the C−C bond distances is observed, with values in the range 1.24−1.35
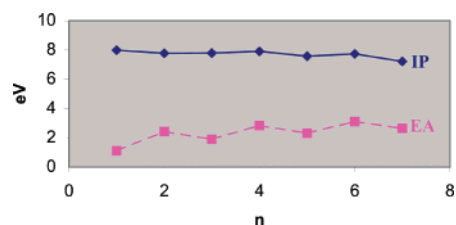
Å, showing that in this case there is a relatively high polyacetylenic character. Undoubtedly, this polyacetylenic character is related with the preference for linear geometries observed for *n*-even species. It is also worth mentioning that, whereas for *n*-odd MgC$_n^-$ species the Mg−C distance remains close (or is even slightly lengthened) to that observed for the neutral counterpart, in the case of *n*-even clusters the Mg−C distance is shortened as a consequence of a more favorable π-donation toward magnesium from a fully occupied π-bonding set resulting from a $\sigma^1\pi^4$ electronic configuration.

Diffuse functions have only a minor effect on the geometrical parameters and vibrational frequencies. However, contrary to what is observed for the neutral and cationic clusters, inclusion of diffuse functions in the basis set has a significant influence on dipole moments with variations up to 1.5 D between 6-311G(d) and 6-311+G(d) values, as can be seen in Table 3. The effect of diffuse functions on binding energies is also nonnegligible, with differences that are always around 0.2 eV.

In Figure 1, the incremental binding energies for the anionic clusters are also shown. It is readily seen that there is a clear even−odd alternation in stability, *n*-even MgC$_n^-$ clusters being more stable than *n*-odd ones. This behavior resembles very much the situation for the neutral clusters, but with much larger variations in incremental binding energies between consecutive species for the anionic clusters. This behavior is a consequence of the electronic configurations of the MgC$_n^-$ species discussed above, since $^2\Sigma$ states for *n*-even clusters, corresponding to full occupation of the π-bonding set, are comparatively much more stable than $^2A''$ states for *n*-odd MgC$_n$ species resulting from a $\sigma^2\sigma^2\pi^1$ electronic configuration in linear geometries.

Finally, we have computed the ionization potentials (IP) and electron affinities (EA) of the different MgC$_n$ clusters. These properties are computed from the total energies of the neutral and charged species and therefore include zero-point vibrational corrections, and the results, as functions of the number of carbon atoms, are shown in Figure 5. It can be seen that initially the IP is slightly higher for *n*-odd clusters, but an inversion in its behavior is observed from $n = 4$. In any case, the variations in the IPs are rather smooth, all values being in the range 7.2−8.0 eV. On the other hand, larger variations are observed for EAs. The much higher stability of *n*-even MgC$_n^-$ clusters is reflected in the behavior of EAs, where a clear even−odd alternation is evident with higher values for *n*-even species.

Conclusions

MgC$_n$ ($n = 1-7$) open-chain clusters, as well as their cationic and anionic derivatives, have been studied employing density functional theory, in particular through the B3LYP method with the 6-311G(d) and 6-311+G(d) basis sets.

All neutral clusters have linear ground states, corresponding to a triplet state, with the only exception of MgC$_2$ which has a $^1\Sigma$ ground state. In the case of both cationic and anionic species, all clusters have doublet ground states, except the special cases of MgC$^+$ and MgC$^-$ that are found to have $^4\Sigma$ ground states.

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The relative stability of the different clusters has been discussed employing the concept of incremental binding energy. For both neutral and cationic species, there is a smooth variation in the incremental binding energies with the size of the cluster, whereas in the case of anionic systems the variations in stability are much more pronounced. Both MgC_n and MgC_n^- species exhibit a clear even−odd parity effect in stability, n-even clusters being always more stable than n-odd ones, a fact closely related to their electronic configuration. The same behavior is observed for small cationic clusters, but this tendency is reversed from $n = 5$, and for larger MgC_n^+ clusters n-odd species seem to be more stable. This inversion is also reflected in the ionization potentials, a property that shows small variations with the size of the molecule. On the other hand, much larger variations are experimented by the electron affinity of MgC_n clusters, and also a clear even−odd alternation is observed in this case. As a consequence of their higher stability for the anionic species, n-even clusters have larger electron affinities.

In addition, predictions for several molecular properties of the MgC_n, MgC_n^+, and MgC_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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