J. Phys. Chem. A **2003,** *107,* 6317−6325

Theoretical Study of Small MgC_n, MgC_n^+, and MgC_n^- Cyclic Clusters

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Received: May 16, 2003; In Final Form: June 19, 2003

A theoretical study of the MgC_n, MgC_n^+, and MgC_n^- ($n = 2-7$) cyclic clusters has been carried out. Predictions for their electronic energies, rotational constants, dipole moments, and vibrational frequencies have been made at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) levels. MgC_n cyclic clusters generally have singlet ground states, whereas both cationic and anionic clusters have doublet ground states. An even−odd parity effect (n-even clusters being more stable than n-odd ones) is observed for both the neutral and anionic species, whereas in the case of the cations, there is no clear alternation in stability. Ionization potentials exhibit also a clear parity alternation trend, with n-even clusters having larger values than n-odd ones. In the case of electron affinities, initially the same behavior is observed, but for larger members the trend is reversed and n-odd compounds have higher electron affinity. It is also found that neutral clusters prefer cyclic structures over open-chain isomers, especially for high n. On the other hand open-chain ground states are predicted for both anionic and cationic clusters, except for the first members of the series.

Introduction

Small heteroatom-doped carbon clusters containing second-row elements are quite interesting in astrochemistry, because some of these species of general formula XC_n have been detected in space.[1−8] So far most of the binary carbides containing second-row atoms observed in space correspond to silicon and sulfur, but it is expected that other similar molecules could be detected by radioastronomy soon. Of special interest are the binary carbides formed with metals such as magnesium, aluminum, or sodium, which are relatively abundant in the interstellar medium. However, the experimental information on these compounds is rather scarce, and therefore theoretical studies providing structural information on metal carbides are highly valuable. Our group has recently contributed to the study of some of these metal carbides, such as AlC_3,[9] MgC_3,[10] or NaC_3.[11]

Another interesting feature of heteroatom-doped carbon clusters is their behavior as a function of the cluster size. Some knowledge about the variation of different properties of doped carbon clusters with the number of carbon atoms is relevant to understand the structure and characteristics of potential new materials whose basic structural units are binary carbides. In particular, the identification of possible systematic trends might allow extrapolations for larger clusters of some properties such as stabilities, ionization potentials (IP), or electron affinities (EA). Several theoretical studies have dealt with the systematic study of heteroatom-doped carbon clusters containing second-row elements. Of particular relevance for the present work are those studies dealing with the properties of C_nS,[12] C_nP,[13] C_nCl,[14] SiC_n,[15,16] and AlC_n[17] clusters. In some of these studies not only the neutral species have been taken into account but also the properties of their cationic and anionic derivatives have been considered.

We have recently carried out a theoretical study of the structures and stabilities of open-chain MgC_n, MgC_n^+, and MgC_n^- clusters,[18] reporting their equilibrium structures and some spectroscopic data that could be helpful for their eventual experimental detection. A systematic study of their stabilities, IP, and EA allowed us to identify some general trends in most cases. Nevertheless, usually these compounds have low-lying cyclic states, and even in some cases the ground state is cyclic. An almost paradigmatic example is SiC_2, with a C_{2v}-symmetric ground state whose experimental detection[19] was undoubtedly aided by a theoretical study.[20] SiC_3 was also predicted by theory[21] to have a rhomboidal ground state. Theoretical studies have also found cyclic ground states for the magnesium carbides MgC_2[22−24] and MgC_3.[10] A recent theoretical study has also predicted that MgC_3^+ has a rhombic ground state.[25] In the present work we provide a theoretical study of the MgC_n, MgC_n^+, and MgC_n^- ($n = 1-7$) monocyclic clusters to identify possible systematic behaviors. In addition, the competition between open-chain and cyclic structures for the ground state of MgC_n, MgC_n^+, and MgC_n^- clusters will be discussed. We should point out that we have also made explorations of other possible isomers (for example cages) for the smaller clusters of the series. 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 main purposes of our 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.

Computational Methods

As in our previous studies on second-row heteroatom-doped carbon clusters,[14,17,18] we have carried out theoretical calculations using the density functional method (DFT). We have employed the B3LYP exchange-correlation functional,[26,27] which consists of the Lee−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 Khon−Sham[31] orbitals. Other authors have

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10.1021/jp035352h CCC: $25.00

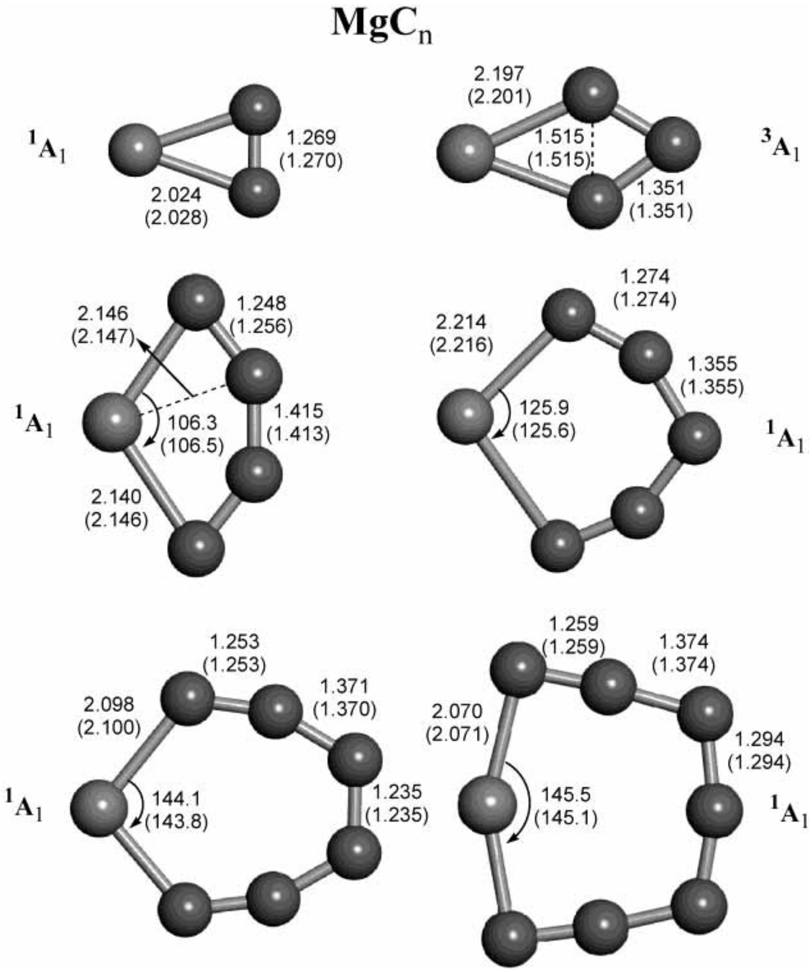

Figure 1. Equilibrium geometries of MgC_n ($n = 1-7$) monocyclic clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in ångstroms and angles in degrees.

shown that the B3LYP method appears well adapted to medium-sized impurity-containing carbon clusters.[32]

In our B3LYP calculations we employed both the triple split-valence d-polarized 6-311G(d) basis set[33] 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.

Harmonic vibrational frequencies were computed for all structures. This allows us not only to estimate the zero-point vibrational energy (ZPVE) correction for each structure but also to assess the nature of the stationary points.

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

Results and Discussion

MgC_n Cyclic Clusters. We have searched for different cyclic MgC_n species on both the singlet and triplet surfaces. We have considered monocyclic structures with the magnesium atom included in the cycle, structures with an exocyclic magnesium atom (with Mg bonded to a carbon cycle through an apex), Mg-capped pure carbon monocyclic structures (with the magnesium atom bonded to a side of a carbon cycle), and structures with a Mg−C chain bonded to a pure carbon cycle. In all cases the monocyclic structure including the Mg atom in the cycle were found to be the lowest-lying one. In Figure 1 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 addition, 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, for the lowest-lying cyclic MgC_n species on the singlet and triplet potential surfaces.

It can be readily seen in Table 1 that for all triplet states the $\langle S^2 \rangle$ values are in all cases very close to the pure spin values, and therefore spin contamination is not a problem for MgC_n cyclic clusters.

As in our previous work on MgC_n open-chain isomers,[18] the inclusion of diffuse functions in the basis set does not seem relevant for the description of cyclic MgC_n structures, because not only the geometrical parameters obtained with both basis sets 6-311G(d) and 6-311+G(d) are virtually coincident (see Figure 1) but also all other properties (see Table 1) are very close.

All MgC_n cyclic clusters are shown in our B3LYP calculations to have closed-shell ground states, with the only exception of MgC_3, which is predicted to have a triplet ground state. This seems to be related with the fact that cyclic C_3 is predicted to have a lowest-lying triplet state,[35] whose interaction with the magnesium atom would result also in a triplet MgC_3 state. In fact, whereas $MgC_3(^3A_1)$ has a transannular C−C distance of 1.515 Å, which suggests that there exists some bonding between both carbon atoms, $MgC_3(^1A_1)$ exhibits a transannular C−C distance of 1.73 Å. Nevertheless, the result for MgC_3 should be taken with caution. We have previously studied this system in detail, employing different theoretical methods.[10] The most reliable levels of theory predict that the ground state should be

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 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	$^1A_1$	276.153486		410/602/1766	9.31	8.17	52.266/11.400/9.359	0.00
		276.155318		402/598/1763	9.28	8.45	52.215/11.359/9.329	0.00
	$^3A_1$	276.133865	2.0127	215/439/1849		2.37	52.723/9.135/7.786	11.92
		276.135069	2.0128	212/434/1856		2.51	52.727/9.100/7.760	12.32
MgC_3	$^1A_1$	314.189373		317/322/344/499/1273/1476		4.01	27.987/5.466/4.573	6.67
		314.191623		317/321/345/502/1270/1475		4.34	28.035/5.476/4.581	6.41
	$^3A_1$	314.201066	2.0062	230/260/427/873/1209/1634	14.41	2.39	36.697/5.297/4.629	0.00
		314.202712	2.0067	230/253/423/871/1204/1632	14.34	2.60	36.675/5.282/4.617	0.00
MgC_4	$^1A_1$	352.321662		259/396/418/418/493/555/988/1884/2008	21.43	5.84	10.020/6.138/3.806	0.00
		352.324343		259/403/411/414/491/554/988/1880/2004	21.36	6.04	10.000/6.123/3.798	0.00
	$^3A_2$	352.282474	2.0087	61/78/197/350/369/505/680/1706/2027		2.33	7.434/5.388/3.124	23.75
		352.285422	2.0088	51/106/191/349/382/503/977/1707/2029		2.50	7.389/5.372/3.110	22.84
MgC_5	$^1A_1$	390.394792		169/220/312/334/362/409/535/682/969/1250/1755/1830	27.26	4.57	6.589/4.080/2.520	0.00
		390.398586		177/220/315/337/362/406/531/677/968/1250/1757/1830	27.18	4.76	6.556/4.083/2.516	0.00
	$^3B_1$	390.387101	2.0817	158/230/365/412/441/468/523/647/966/1313/1643/1772		3.61	6.809/4.170/2.586	4.98
		390.389780	2.0805	157/228/366/410/438/464/517/644/966/1314/1643/1772		3.74	6.797/4.164/2.582	5.65
MgC_6	$^1A_1$	428.517744		150/180/282/332/376/404/430/439/529/573/942/1168/1910/2002/2041	34.34	2.11	4.512/3.080/1.861	0.00
		428.520573		146/178/283/330/377/396/428/443/527/569/942/1168/1909/2000/2038	34.20	2.25	4.496/3.080/1.828	0.00
	$^3A''$	428.464937	2.0397	115/174/213/267/387/480/537/538/583/687/930/1067/1567/1805/1842		4.05	3.774/3.449/1.804	32.33
		428.467748	2.0388	144/175/217/270/395/464/528/512/579/674/932/1072/1550/1769/1830		4.32	3.769/3.441/1.802	32.26
MgC_7	$^1A_1$	466.589909		102/164/172/225/321/357/418/466/515/519/616/659/929/1045/1378/1702/1906/1910	40.12	3.41	2.839/2.472/1.321	0.00
		466.593589		100/163/172/227/334/362/416/464/517/522/614/657/929/1045/1376/1702/1905/1910	39.97	3.64	2.828/2.474/1.320	0.00
	$^3B_1$	466.581868	2.1330	118/131/149/176/374/375/380/431/484/497/589/627/903/1067/1494/1499/1862/1864		2.17	2.843/2.437/1.312	4.50
		466.585046	2.1314	117/133/147/175/372/377/387/430/489/495/586/623/904/1069/1493/1502/1861/1864		2.36	2.827/2.441/1.310	4.80

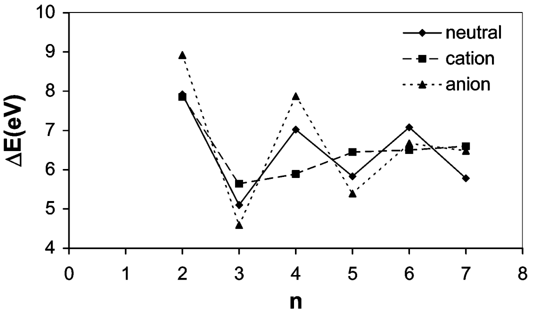

Figure 2. Incremental binding energies (eV) for the MgC_n, MgC_n^+, and MgC_n^- monocyclic clusters vs the number of carbon atoms.

in fact rhombic, but the $^1A_1$ and $^3A_1$ states were found to be almost isoenergetic (with an energy difference of less than 1 kcal/mol at the coupled-cluster level of theory). Therefore it seems that in this case the energy difference between both states is somewhat overestimated by the B3LYP method. In any case it is clear from Table 1 that the energy difference between singlet and triplet states is much lower for n-odd MgC_n clusters than for n-even ones.

It is apparent in Figure 1 that there is a trend in Mg−C distances to shorten as n increases, indicating a higher degree of participation of the Mg atom in the bonding for larger clusters. It can also be seen in Figure 1 that the C−C bond lengths exhibit a behavior quite similar to that found for the open-chain isomers,[18] with an alternation of C−C bond distances because $C_{odd}-C_{even}$ distances being shorter than the $C_{even}-C_{odd}$ ones. On the other hand for small pure carbon clusters C_n there is a prevalence of cumulenic structures,[36] and all C−C bond distances are quite similar. Another interesting feature of the geometrical parameters of the MgC_n clusters is that the Mg−C distances suggest that there is a certain change from $n = 5$ in the type of interaction between the Mg and the C_n unit. An analysis of this interaction shows that for MgC_2, MgC_3, and MgC_4 there seems to be a π-type interaction with either a C−C bond ($n = 2$, 3) or with the entire carbon unit ($n = 4$). As a consequence, it is clear, for example, in MgC_4 that the $Mg-C_1$ and $Mg-C_2$ distances are virtually the same, suggesting that in fact there is a similar interaction between Mg and the contiguous carbon atoms than between Mg and the second next carbon atoms. Therefore, for small MgC_n clusters there seems to be a certain trend for magnesium to interact with the entire carbon chain, rather than just with the carbon atoms at the end of the chain.

Following the suggestion by Pascoli and Lavendy,[13] the relative stability of cyclic MgC_n clusters will be discussed in terms of the incremental binding energies.[37] The incremental binding energy can be defined as the change in energy associated to the process

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

and can be computed as the consecutive binding energy differences between adjacent MgC_n and MgC_{n-1} clusters.

In Figure 2 the incremental binding energy for the different cyclic MgC_n clusters are shown as a function of the number of carbon atoms. As in the case of the open-chain isomers,[18] it is clearly seen that there is an even−odd alternation, n-even clusters being more stable than n-odd ones. However, the variation in the incremental binding energies is much higher than in the case of the open-chain clusters. For the latter the incremental binding energies for $n > 3$ were found to take values around 6.1−6.5 eV, therefore having variations of less than 0.5 eV for consecutive members in the series. On the other hand, for monocyclic clusters the variations in the incremental binding energies for consecutive members is as much as twice that value.

MgC_n^+ Cyclic Clusters. The main properties for the lowest-lying doublet and quartet states of MgC_n^+ monocyclic clusters are given in Table 2. In addition, the equilibrium geometries for the ground states are shown in Figure 3. As in the case of their neutral analogues, the inclusion of diffuse functions in the basis set has no important effects on the computed properties, including the geometrical parameters.

All cationic monocyclic clusters, as in the case of their open-chain counterparts,[18] have doublet ground states, and the energy difference between doublet and quartet states is always high enough as to be confident in that prediction. Nevertheless, there seems to be a tendency to decrease such energy difference as the number of atoms increases.

Comparing the geometrical parameters of monocyclic MgC_n^+ clusters with their neutral counterparts it can be concluded that Mg−C distances are slightly lengthened for n-even clusters, whereas for n-odd clusters the Mg−C bond distances are in general slightly shortened. Nevertheless, there are no drastic differences in the bond lengths between the neutral and cationic clusters. Perhaps the most important difference is that for the latter the Mg−C distances for second next carbon atoms are no longer close to the Mg−C distances for contiguous carbon atoms, as was observed for the neutral analogues. This lengthening of $Mg-C_2$ distances is, for example, quite evident in MgC_4^+. This effect is also reflected in the much smaller $\angle$CMgC angles that are observed for the cationic clusters compared with their neutral counterparts. Therefore upon ionization there seems to be a preference for magnesium to bond to the carbon atoms at the end of the carbon chain rather than to the entire carbon unit.

We should point out that for MgC_2^+ and MgC_3^+ the quartet states have one imaginary frequency. Our attempts to obtain true minima for these cationic clusters, following the normal modes associated to the imaginary frequencies led to open-chain isomers. Therefore we have included the values for the cyclic lowest-lying quartets for comparison purposes, although they are not true minima.

The incremental binding energies for MgC_n^+ clusters are also shown in Figure 2. The cationic clusters exhibit a very different behavior than their neutral analogues. With the exception of the first point ($n = 2$), which has a very large value (in part due to the low stability of MgC^+) that is virtually the same than for neutral MgC_2, the variations found for the incremental binding energies for consecutive members in the series are much smaller than for the neutral clusters. Furthermore, there seems to be no parity alternation effect, because the incremental binding energies increase monotonically from 5.6 eV (MgC_3^+) to 6.6 eV (MgC_7^+).

MgC_n^- Cyclic Clusters. The main properties for the lowest-lying doublet and quartet states of monocyclic MgC_n^- anions are given in Table 3, whereas the geometries for the ground states are shown in Figure 4. As expected, it can be seen that the inclusion of diffuse functions in the basis set is more important than for the neutral and cationic clusters, although their effect on geometrical parameters and harmonic vibrational frequencies is not particularly high. On the other hand, binding energies for anionic clusters are more sensitive to the inclusion of diffuse functions. In the case of the neutral clusters, inclusion of diffuse functions generally results in a modification of binding energies of about 0.5%, whereas for the anionic clusters variations of about 2% in the binding energies are usually observed. Therefore it seems that inclusion of diffuse functions

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 Monocyclic 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^+	$^2A_1$	275.857182	0.7695	311/554/1797	8.98	7.66	51.970/14.470/8.715	0.00
		275.857657	0.7695	310/553/1797	8.92	7.68	51.970/14.470/8.715	0.00
	$^4B_1$	275.765665	3.7619	185i/179/1636		2.67	48.407/5.631/5.044	56.22
		275.766235	3.7622	184i/178/1636		2.67	48.407/5.631/5.044	56.15
MgC_3^+	$^2A_1$	313.924893	0.7631	300/393/506/561/1307/1618	14.62	8.76	33.930/5.936/5.052	0.00
		313.925865	0.7632	300/392/506/563/1305/1617	14.53	8.81	33.930/5.936/5.052	0.00
	$^4B_2$	313.866685	3.7590	178i/88/143/1002/1168/1622		5.31	44.943/3.323/3.094	35.72
		313.867758	3.7599	176i/90/140/1103/1168/1621		5.40	44.944/3.306/3.079	35.66
MgC_4^+	$^2B_2$	352.002659	0.8043	97/314/340/408/477/520/1107/1817/1974	20.50	5.72	8.056/6.749/3.672	0.00
		352.003632	0.8039	88/314/339/412/476/518/1106/1817/1972	20.39	5.71	8.056/6.749/3.672	0.00
	$^4B_1$	351.950830	3.7899	211/211/222/236/318/470/1143/1341/1875		4.08	6.918/5.907/3.186	31.05
		351.951927	3.7901	204/211/221/236/316/469/1143/1341/1875		4.07	6.918/5.907/3.186	30.98
MgC_5^+	$^2A_1$	390.099390	0.7913	134/181/266/299/312/402/448/592/1020/1411/1824/1856	26.95	4.60	5.891/4.256/2.471	0.00
		390.100703	0.7909	137/181/269/299/312/401/445/592/1019/1410/1825/1856	26.81	4.59	5.898/4.251/2.470	0.00
	$^4A_2$	390.053925	3.8392	155/189/373/396/473/479/562/637/1095/1290/1639/1705		5.94	5.471/4.360/2.426	28.89
		390.055100	3.8389	153/188/373/396/473/478/561/637/1095/1290/1639/1705		5.95	5.471/4.360/2.426	28.96
MgC_6^+	$^2A'$	428.201363	0.7838	80/169/175/255/283/331/360/424/503/523/1043/1327/1871/1931/1989	33.49	5.06	3.516/3.319/1.707	0.00
		428.202634	0.7825	111/168/199/258/283/327/360/425/500/523/1044/1326/1867/1931/1983	33.31	5.15	3.535/3.330/1.706	0.00
	$^4A_2$	428.163103	3.8381	167/178/190/268/347/472/503/555/584/652/972/1189/1469/1766/1855		5.99	3.790/3.021/1.681	23.87
		428.164512	3.8379	166/177/189/268/348/471/501/554/575/649/972/1189/1468/1766/1855		6.02	3.793/3.017/1.680	23.69
MgC_7^+	$^2A''$	466.304541	0.8052	97/143/166/189/228/327/358/361/481/490/519/544/983/1155/1630/1682/1931/1960	40.09	5.35	2.791/2.226/1.242	0.00
		466.306137	0.8041	78/144/166/185/226/326/356/356/480/490/515/540/984/1157/1641/1680/1928/1960	39.89	5.45	2.804/2.214/1.240	0.00
	$^4A''$	466.256205	3.8589	76/145/158/169/357/394/401/422/486/501/560/613/966/1180/1427/1675/1743/1828		5.64	2.763/2.235/1.235	30.14
		466.257862	3.8586	77/145/157/168/360/395/399/421/490/499/559/613/967/1179/1426/1677/1743/1826		5.66	2.763/2.235/1.235	30.13

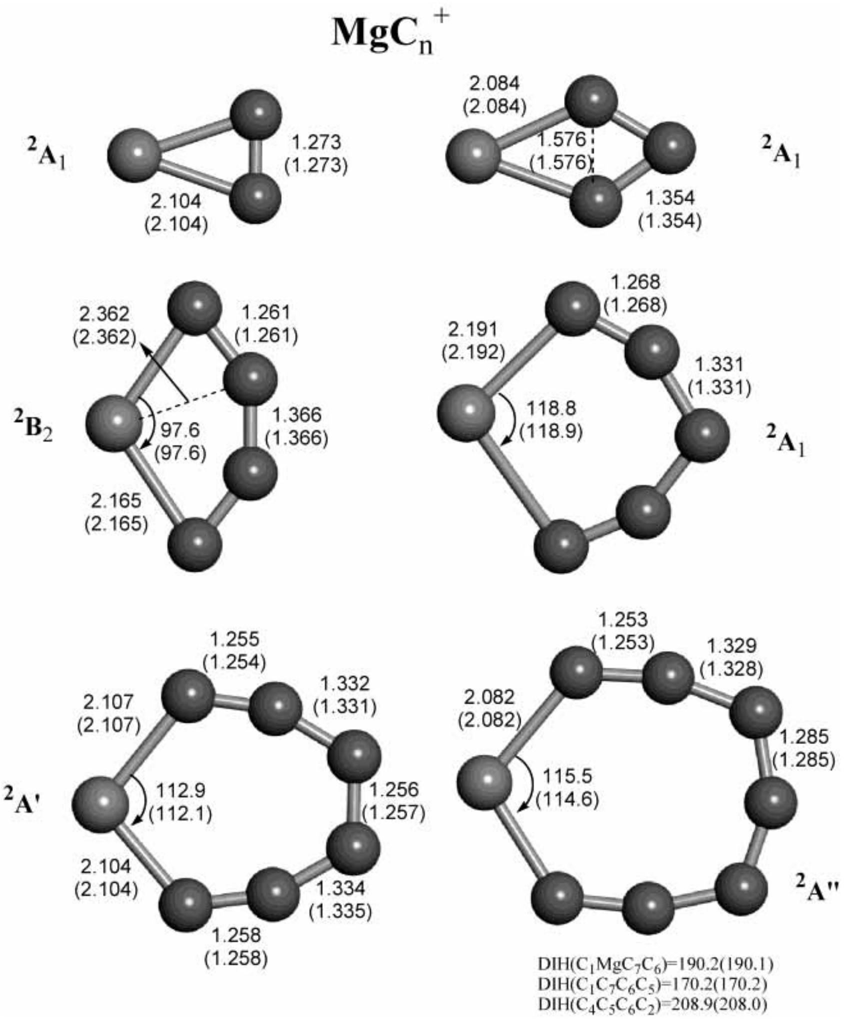

Figure 3. Equilibrium geometries of MgC_n^+ ($n = 1-7$) monocyclic clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in ångstroms and angles in degrees.

is comparatively more important for energetic values than for geometrical parameters. Another magnitude that is sensibly affected by inclusion of diffuse functions for the anionic clusters is the dipole moment (in some cases the difference between dipole moments computed with both basis sets is higher than 50%).

As a general trend there are no large differences in the geometrical parameters between neutral and anionic species. Perhaps one of the most significant differences is observed for MgC_4^-, where the distances between magnesium and second carbon atoms are even smaller than the Mg−C distance for contiguous carbon atoms. Therefore it seems that the extra electron favors the π-interaction between Mg and the carbon unit. It is also generally observed for anionic clusters that there is a trend to increase the ∠CMgC angles, compared with the corresponding values for the neutral species, just the opposite behavior that was found for the cationic clusters.

All MgC_n^- cyclic clusters have doublet ground states. Usually, the energy difference with the lowest-lying quartet is quite high (especially for *n*-even clusters). The only exception is MgC_3^-, where we find the doublet state lying slightly lower in energy than the quartet when the 6-311G(d) basis set is employed, but the $^2A_1$ and $^4B_1$ states are virtually isoenergetic when diffuse functions are employed in the calculation.

The incremental binding energies for the anionic clusters are shown in Figure 2. It can be readily seen that incremental binding energies for MgC_n^- cyclic clusters follow the same general patterns as their neutral analogues. Again *n*-even clusters are more stable than *n*-odd ones, but now the incremental binding energies vary even more drastically for consecutive members in the series than for neutral MgC_n cyclic clusters, especially for small *n*. Therefore MgC_n^- cyclic clusters follow generally the same trends observed for their open-chain counterparts.

Our results for the cationic and anionic clusters allow to estimate the ionization potentials (IP) and electron affinities (EA) for MgC_n cyclic clusters. IPs and EAs were computed as the energy difference (including ZPVE corrections) between the neutral and positively and negatively, respectively, charged clusters, and the results are shown in Figure 5. It can be readily seen that, as in the case of the open-chain MgC_n clusters, cyclic clusters have IPs and EAs that exhibit only smooth variations along the series. The IPs are all around 8 eV, whereas EAs take values close to 2 eV. Ionization potentials show a parity alternation trend, with *n*-even clusters having larger IP. In the case of EAs, the same behavior is observed for small *n*, but an inversion in the trend is observed from $n = 5$, and for the larger clusters *n*-odd compounds have higher EA.

The energy differences between cyclic and open-chain isomers for MgC_n, MgC_n^+, and MgC_n^- clusters are shown in Figure 6. In that figure a negative value means that the cyclic isomer is more stable than the corresponding open-chain one. As a general trend cyclic isomers are favored over open-chain isomers, especially for larger clusters, in the case of neutral

TABLE 3: Electronic Energies, $\langle S^2 \rangle$ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for Monocyclic 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^-	$^2A_1$	276.230833	0.7535	312/530/1821	12.02	2.85	52.551/10.357/8.652	0.00
		276.237724	0.7538	291/517/1813	11.76	3.33	52.433/10.260/8.581	0.00
	$^4B_2$	276.126237	3.7583	319/372/1684		1.82	51.397/8.666/7.416	65.22
		276.137219	3.7592	288/379/1713		3.19	51.740/8.723/7.465	62.72
MgC_3^-	$^2A_1$	314.258529	0.7544	248/262/274/721/1063/1389	16.62	0.42	35.507/5.113/4.470	0.00
		314.265396	0.7557	251/272/275/681/1053/1376	16.32	1.05	35.816/5.223/4.558	0.00
	$^4B_1$	314.256714	3.7895	183/409/436/603/1153/1435		2.06	12.434/9.105/5.256	1.52
		314.266385	3.7882	174/401/433/590/1154/1445		2.55	12.435/9.012/5.225	−0.21
MgC_4^-	$^2A_1$	352.410467	0.7511	170/226/269/441/456/565/928/1875/2032	24.48	1.26	8.789/5.422/3.353	0.00
		352.420209	0.7511	155/233/259/438/465/567/927/1868/2025	24.23	1.66	8.700/5.394/3.330	0.00
	^4A	352.303674	3.7656	175/231/288/393/435/603/945/1417/1788		0.54	7.304/6.266/3.451	66.03
		352.313236	3.7661	168/224/282/391/432/593/950/1415/1779		0.38	7.272/6.253/3.434	66.12
MgC_5^-	$^2B_1$	390.468235	0.9498	122/200/278/358/393/409/547/641/943/1296/1619/1748	29.88	1.59	7.179/3.748/2.462	0.00
		390.478850	0.8721	114/204/291/377/398/404/551/648/946/1287/1618/1754	29.60	2.47	7.148/3.805/2.483	0.00
	$^4B_1$	390.450279	3.7989	157/158/260/325/363/373/488/651/924/1238/1717/1848		1.62	5.810/3.921/2.341	11.18
		390.458530	3.7987	149/152/253/315/354/365/483/645/921/1243/1715/1843		1.50	5.820/3.898/2.334	12.53
MgC_6^-	$^2B_2$	428.575515	0.7679	175/188/245/288/416/437/534/553/629/639/897/1004/1643/1834/1838	36.54	3.28	4.300/3.216/1.840	0.00
		428.585572	0.7677	172/184/245/288/423/437/527/546/617/631/896/1010/1639/1836/1839	36.22	3.91	4.284/3.215/1.837	0.00
	$^4A''$	428.520815	3.7814	103/146/206/241/358/367/391/473/530/639/963/1103/1533/1821/1841		1.93	3.624/2.908/1.624	33.46
		428.529682	3.7799	114/133/217/244/346/349/378/485/528/621/961/1107/1524/1815/1836		1.69	3.577/2.937/1.622	34.26
MgC_7^-	$^2A_2$	466.674154	0.7777	99/121/168/190/410/421/433/447/522/540/626/677/896/1002/1349/1612/1843/1856	43.03	2.18	3.196/2.353/1.355	0.00
		466.684453	0.7775	95/127/166/187/411/427/429/454/515/534/622/670/895/1006/1351/1612/1841/1855	42.68	2.67	3.179/2.353/1.352	0.00
	$^4B_1$	466.628800	3.8748	71/108/123/130/314/326/361/365/401/452/470/537/913/1078/1476/1483/1874/1879		3.67	2.551/2.158/1.169	27.24
		466.638307	3.8722	78/105/122/129/313/321/368/368/399/451/475/534/912/1079/1477/1490/1869/1876		3.70	2.546/2.160/1.168	27.77

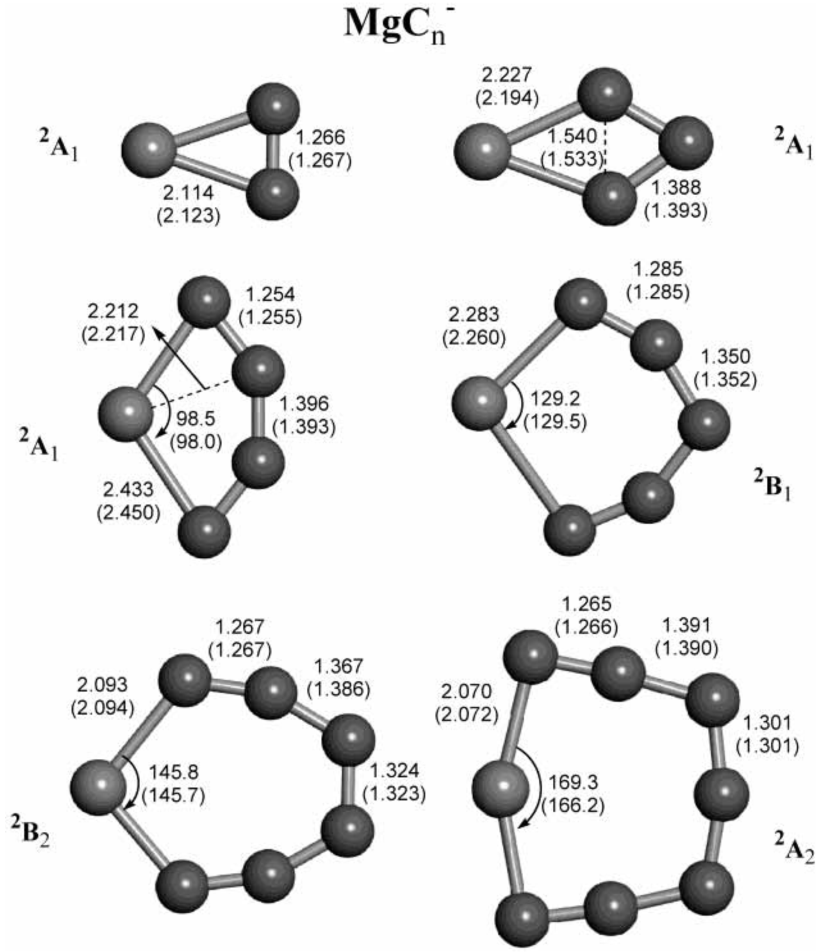

Figure 4. Equilibrium geometries of MgC_n^- ($n = 1-7$) monocyclic clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory. Distances are given in ångstroms and angles in degrees.

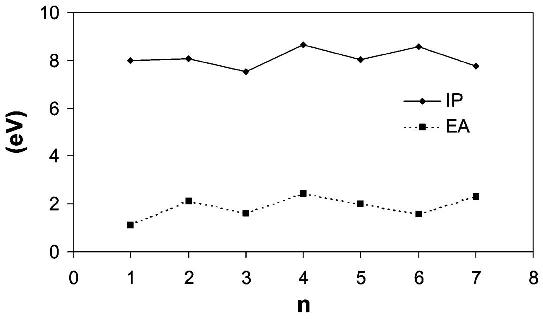

Figure 5. Ionization potentials (IP) and electron affinities (EA), in eV, of MgC_n monocyclic clusters vs the number of carbon atoms.

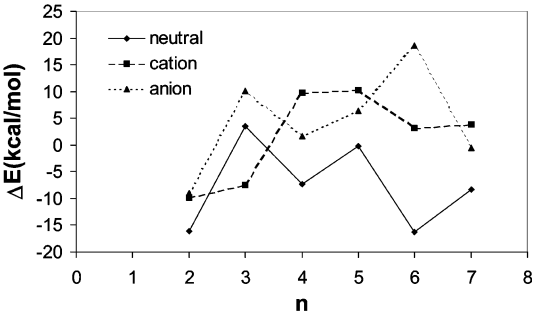

Figure 6. Energy separation (kcal/mol) between the monocyclic and open-chain structures for the MgC_n clusters as a function of the number of carbon atoms. A negative value indicates that the open-chain isomer is less stable than the corresponding cyclic one.

species. It is also clear that there is an even−odd alternation for the neutral clusters, cyclic isomers being comparatively more stable for n-even clusters than for n-odd ones. This is undoubtedly related to the fact that for pure carbon clusters n-even species have monocyclic ground states.[37] Raghavachari and Binkley[37] pointed out that for C_n clusters the stability of monocyclic structures over linear forms is the highest for those species with completely filled π orbitals (taking into account both out-of-plane and in-plane π orbitals). Because for MgC_n clusters the magnesium atom does not contribute with π electrons, the number of π electrons is the same as for C_n clusters, and therefore the same rule for stability of cyclic isomers (n even) is retained.

On the other hand both cationic and anionic clusters do not follow the same pattern. In both cases cyclic isomers are favored for the first members of the series ($n = 2$ and $n = 3$ for the cations, and $n = 2$ for the anions), but for higher n we find that the preferred arrangement is the open chain.

Conclusions

A theoretical study of small cyclic MgC_n, MgC_n^+, and MgC_n^-, clusters, has been carried out with DFT methods. In particular we have employed the B3LYP method with the 6-311G(d) and 6-311+G(d) basis sets. Comparing the results obtained with both basis sets, it can be concluded that inclusion of diffuse function is only relevant for the anionic clusters, especially for computing dipole moments and binding energies.

According to our theoretical calculations the most stable cyclic isomers are those monocyclic compounds where the magnesium atom is also forming the ring. In general, MgC_n

clusters have singlet ground states, although triplet states are quite close in energy for *n*-odd clusters. Both cationic and anionic clusters have doublet ground states. An even−odd parity effect (*n*-even clusters being more stable than *n*-odd ones) is observed for both the neutral and anionic species, whereas in the case of the cations, no systematic variations are observed. Ionization potentials exhibit a clear parity alternation trend, with *n*-even clusters having larger values for the IP. Electron affinities follow the same trend for small *n*, but for higher members (from $n = 5$) the trend is reversed and *n*-odd compounds have higher EA.

Concerning the competition between open-chain and cyclic isomers, our theoretical calculations suggest that for small neutral clusters there is a preference for cyclic structures, especially for high *n*. A parity effect is also observed in this case, cyclic isomers being much favored for *n*-even clusters. Conversely, for both anionic and cationic clusters the smallest members of the series are found to be cyclic, but open-chain ground states are predicted for higher *n*.

We hope that the predictions for different molecular properties (vibrational frequencies, rotational constants, dipole moments) of small cyclic MgC_n, MgC_n^+, and MgC_n^- clusters could help in their possible experimental detection.

Acknowledgment. This research has been supported by the Ministerio de Ciencia y Tecnología of Spain (Grant BQU2001-3660-C02-02) and by the Junta de Castilla y León (Grant VA085/03). A.C. gratefully acknowledges a fellowship from the Junta de Castilla y León (Consejería de Educación y Cultura).

References and Notes

(1) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Thadeus, P.; Vrtilek, J. M. *Astrophys. J. Lett*. **1989**, *341*, L25.

(2) Thaddeus, P.; Cummins, S. E.; Linke, R. A. *Astrophys. J. Lett*. **1984**, *283*, L25.

(3) Apponi, A. J.; McCarthy, M. C.; Gottlieb, C. A.; Thadeus, P. *Astrophys. J*. **1999**, *516*, L103.

(4) Ohishi, M.; Kaifu, N.; Kawaguchi, K.; Murakami, A.; Saito, S.; Yamamoto, S.; Ishikawa, S.; Fujita, Y.; Shiratori Y.; Irvine, W. H. *Astrophys. J. Lett*. **1989**, *345*, L83.

(5) Turner, B. E. *Astrophys. J*. **1973**, *186*, 123.

(6) Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki H.; Kaifu, N. *Astrophys. J*. **1987**, *317*, L115.

(7) Yamamoto, S.; Saito, S.; Kawaguchi, K.; Kaifu, N.; Suzuki H.; Ohishi, M. *Astrophys. J*. **1987**, *317*, L119.

(8) Guelin, M.; Cernicharo, J.; Paubert, G.; Turner , B. E. *Astron. Astrophys.* **1990**, *230*, L9.

(9) Barrientos, C.; Redondo, P.; Largo, A. *Chem. Phys. Lett.* **2000**, *320*, 481.

(10) Redondo, P.; Barrientos, C.; Largo, A. *Chem. Phys. Lett.* **2001**, *335*, 64.

(11) Barrientos, C.; Redondo, P.; Largo, A. *Chem. Phys. Lett.* **2001**, *343*, 563.

(12) Lee, S. *Chem. Phys. Lett.* **1997**, *268*, 69.

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

(14) Largo, A.; Cimas, A.; Redondo, P.; Barrientos, C. *Int. J. Quantum Chem.* **2001**, *84*, 127.

(15) Fye, J. L.; Jarrold, M. F. *J. Phys. Chem. A* **1997**, *101*, 1836.

(16) Pascoli, G.; Lavendy, H. *Int. J. Mass Spectrom. Ion Processes* **1998**, *173*, 41.

(17) Largo, A.; Redondo, P.; Barrientos, C. *J. Phys. Chem. A* **2002**, *106*, 4217.

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

(19) Michalopoulos, D. L.; Geusic, M. E.; Langridge-Smith, P. R. R.; Smalley, R. E. *J. Chem. Phys.* **1984**, *80*, 3556.

(20) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1984**, *80*, 3552.

(21) Alberts, I. L.; Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1990**, *93*, 5046.

(22) Green, S. *Chem. Phys. Lett.* **1984**, *112*, 29.

(23) Woon, D. E *Astrophys. J.* **1996**, *456*, 602.

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

(25) Barrientos, C.; Redondo, P.; Largo, A. *Int. J. Quantum Chem*. **2002**, *86*, 114.

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

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

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

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

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

(31) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(32) Pascoli, G.; Lavendy, H. *Int J. Mass Spectrom.* **1998**, *181*, 11.

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

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

(35) Whiteside, R. A.; Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. von R. *Chem. Phys. Lett.* **1981**, *80*, 547.

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

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