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Theoretical Study of AlC_n, AlC_n^+, and AlC_n^- ($n = 1-7$) Clusters

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AlC_n, AlC_n^+, and AlC_n^- ($n = 1-7$) clusters have been studied by means of the B3LYP density functional method. Results of their equilibrium geometries, electronic energies, dipole moments, and vibrational frequencies are reported. The energy calculations show that the open-chain linear or quasi-linear isomers with the aluminum atom bound to the end of the carbon chain are the most stable geometry in all cases. For the AlC_n clusters the electronic structure is predicted to be a doublet, with the only exception of AlC. In the AlC_n^+ species, the electronic ground state was found to be alternately a singlet for odd n or a triplet for even n, again with the exception of the first member of the series, and in the AlC_n^- clusters the opposite was found. From the binding energies we can deduce an even−odd parity effect, with n-even clustering atoms being more stable than those with odd ones in the neutral and anionic clusters, whereas in the cations this effect is reversed. The ionization potentials (IP) and electron affinities (EA) also computed show an even−odd alternation with n-even clusters presenting both higher IP and EA than n-odd ones.

Introduction

Heteroatom-doped carbon clusters containing second-row elements have been the subject of study in the last years in part due to its potential interest in both solid state and in gas phase chemistry, particularly in astrochemistry. Although only few binary carbides have been detected in space, CSi,[1] C_2Si,[2] C_3-Si,[3] C_4Si,[4] CS,[5] C_2S,[6] C_3S,[7] and CP,[8] it can be expected that other similar molecules could be observed in astronomical objects. Some new candidates include binary carbides formed with metals such as aluminum, magnesium or sodium. In fact some species containing these metals have already been detected via radioastronomical observations: MgNC,[9] MgCN,[10] AlCl,[11] and AlF.[11]

Carbon is the most abundant organic element in the interstellar space, and aluminum is also quite abundant in stellar atmospheres. Thus, it can be expected that compounds containing these elements may exist in some astrophysical objects, although they have not been observed to date.

Pure carbon clusters and heteroatom-doped carbon clusters obtained from replacement of a carbon atom by a first-row element have been extensively studied, in contrast only few works are devoted to second-row-doped carbon clusters. Aluminum is located before silicon and phosphorus in the periodic table, making the AlC_n^- isoelectronic to neutral C_nSi and C_nP^+ clusters, and therefore it appears interesting to study the neutral, cationic and anionic forms of aluminum-doped carbon clusters in order to compare with other heteroatom-doped carbon clusters for which information exists in the literature.[12]

Recently, we have carried out theoretical studies of the AlC_3[13] and AlC_3^+[14] species and, in contrast with previous work,[15] we predict linear species with $^2\Pi$ and $^1\Sigma$ electronic states respectively, but studies for larger AlC_n clusters have not been found in the literature to date. In this work, we present a theoretical study of the AlC_n, AlC_n^+, and AlC_n^- ($n = 1-7$) species in order to gain some insight into their energies, equilibrium structures and spectroscopic data. In addition the simultaneous study of the AlC_n, AlC_n^+, and AlC_n^- clusters is required in the study of some quantities such as ionization energies or electronic affinities.

Computational Methods

All calculations have been made using the density functional method (DFT). In these DFT calculations the B3LYP exchange−correlation functional[16,17] has been used. This consists of the Lee−Yang−Parr[18] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.[19] The latter is a linear combination of local density approximation, Becke's gradient correction,[20] and the Hartree−Fock exchange energy based on Khon−Sham[21] orbitals. Recently, it has been shown that DFT/B3LYP method appears well-adapted to medium-sized impurity-containing carbon clusters.[22]

The calculations were performed using both the triple split-valence d-polarized 6-311G(d) basis set[23] and the 6-311+G(d) basis set which also includes diffuse functions. In density functional calculations, such basis sets are able to give accurate results.

The equilibrium geometries were characterized by analysis of the harmonic vibrational frequencies. These were computed from analytic second-order derivative techniques and were employed to estimate the zero-point vibrational energy (ZPVE) correction. The harmonic vibrational frequencies also enable us to assess the nature of the stationary points.

Other properties, such as dipole moments, calculated taking the center of mass as origin, and rotational constants were also computed. In addition we give the expected values of $\langle S^2 \rangle$ in order to check spin contamination.

All calculations reported in this work were carried out with the *Gaussian 98* program package.[24]

We will only present results for the more stable open chain structures. Other geometries were also studied but are not given since they lie much higher in energy. The only exception is the AlC_2 system, where a cyclic structure is shown to be the ground state.[25,26] In the case of AlC_3, although it seems that a linear

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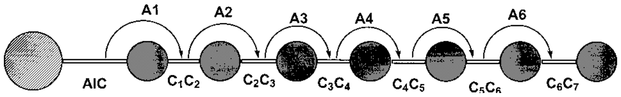
TABLE 1: Equilibrium Geometries of AlC_n ($n = 1-7$) Clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in Parentheses) Levels of Theory[a]



	AlC	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_7	A1	A2	A3	A4	A5	A6
AlC ($^2\Pi$)	1.836												
	(1.838)												
($^4\Sigma$)	1.975												
	(1.977)												
AlC_2 ($^2\Sigma$)	1.886	1.249											
	(1.884)	(1.250)											
($^4A''$)	1.877	1.232						166.0					
	(1.875)	(1.231)						(170.4)					
AlC_3 ($^2\Pi$)	2.021	1.269	1.322										
	(2.026)	(1.269)	(1.321)										
($^4\Sigma$)	1.803	1.288	1.307										
	(1.803)	(1.288)	(1.306)										
AlC_4($^2A'$)	2.001	1.252	1.323	1.285				166.3	182.2	173.5			
	(2.007)	(1.253)	(1.323)	(1.285)				(167.0)	(181.8)	(176.9)			
($^4\Pi$)	1.850	1.236	1.349	1.220									
	(1.851)	(1.236)	(1.349)	(1.221)									
AlC_5 ($^2\Pi$)	2.013	1.251	1.313	1.273	1.304								
	(2.019)	(1.251)	(1.312)	(1.273)	(1.302)								
($^4\Sigma$)	1.796	1.273	1.286	1.289	1.293								
	(1.797)	(1.273)	(1.286)	(1.290)	(1.291)								
AlC_6 ($^2\Pi$)	2.013	1.244	1.326	1.248	1.311	1.287							
($^4\Pi$)	2.010	1.297	1.269	1.317	1.264	1.335							
AlC_7 ($^2\Pi$)	2.011	1.244	1.324	1.252	1.294	1.280	1.297						
($^4\Sigma$)	1.795	1.269	1.291	1.275	1.275	1.294	1.288						

[a] Distances are given in angstroms and angles in degrees.

isomer is the global minimum, other cyclic structures are quite close in energy. However, since they have already been described,[13,25] we will not reconsider them here.

Results and Discussion

AlC_n Clusters. We have studied different linear or quasi-linear isomers on both the doublet and quartet AlC_n potential surfaces. In Table 1 we have collected their optimized geometries at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) levels of theory. In addition Table 2 lists the electronic configurations, harmonic vibrational frequencies, rotational constants, dipole moments, binding energies, and absolute and relative energies for the AlC_n species. These quantities might be helpful in an observational search in the infrared, millimeter, and submillimeter spectra of such clusters.

It can be considered that the B3LYP wave functions are nearly spin-pure since the $\langle S^2\rangle$ values, showed in Table 2, are uniform and in general deviate slightly from the pure spin values, and consequently spin contamination should not be a problem in these cases.

The lowest energy structure for the AlC_n clusters is predicted to be the linear arrangement of nuclei in the doublet electronic ground states, with the exceptions of $n = 1$ where the ground state corresponds to a $^4\Sigma$ electronic state, and $n = 4$ where a nonlinear structure with a $^2A'$ ground state was found.

As can be seen in Table 1, the equilibrium geometries computed from the two basis sets employed in this work were very similar and therefore it can be concluded that diffuse functions are not essential for obtaining these structures and were only employed up to $n = 5$.

For $n = 1$, the computed Al−C distance for the ground state, $^4\Sigma$, is 1.977 Å [6-311+G(d) basis set], a value in agreement with previous calculations obtained by Bauschlicher et al.[27] (1.978 Å) and by Ashman et al.[28] (1.98 Å), and is slightly higher than both experimental values given by Brazier[29] (1.9550 Å) and the value from a previous calculation based on a coupled cluster approach computed by Gutsev et al.[30] (1.9544 Å). For the second member of series AlC_2 ($^2\Sigma$), the Al−C bond distance is 1.884 Å [6-311+G(d) basis set], a value smaller than that in the previous cluster, reflecting a certain degree of π donation from aluminun that confers a small double bond character. Finally, for $n \geq 3$, the Al−C bond length in the ground (doublet) states is always of the order of the prototypical single bond length (≈2.0 Å).

The C−C distances, running from 1.24 to 1.32 Å, can be assimilated to moderately strong double bonds underlying a clear π bonding in the corresponding structures, and are typical of cumulene structures:

$$:\mathrm{Al}{-}\dot{\mathrm{C}}({=}\mathrm{C})_{n-2}{=}\mathrm{C}:\quad n = 3, 4, 5, 6, 7$$

with two lone pairs both on the aluminun atom and on the terminal carbon at the other extremity, and an unpaired electron residing at C_1. Nevertheless, in all cases, we observed an alternation of the C−C bond distances, $C_{odd}-C_{even}$ shorter than $C_{even}-C_{odd}$, suggesting that there is some polyacetylenic character with alternant triple C−C bonds starting in the C_1-C_2 bond:

$$:\mathrm{Al}{-}\mathrm{C}({\equiv}\mathrm{C})_{(n-1)/2}{-}\dot{\mathrm{C}}:\quad \text{n odd}$$

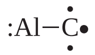
$$:\mathrm{Al}{-}\mathrm{C}({\equiv}\mathrm{C})_{(n/2-1)}{-}\dot{\mathrm{C}}{=}\mathrm{C}:\quad \text{n even}$$

The quartet states present a shorter Al−C bond distance than the doublet ones except in $n = 1$, where the quartet corresponds to the ground state.

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 AlC_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})
AlC	$^2\Pi$	280.316410	0.9829	758	1.98	3.03	18.051	29.33
		280.317896	0.9744	753		3.38	18.010	29.56
	$^4\Sigma$	280.362850	3.7540	627		1.83	15.603	0.0
		280.364698	3.7553	621		2.11	15.562	0.0
AlC_2	$^2\Sigma$	318.495736	0.7600	86/88/512/1845	10.67	3.98	5.654	0.0
		318.498324	0.7602	96/96/514/1844		4.26	5.659	0.0
	$^4A''$	318.394972	3.7759	50/601/1921		1.93	1831.506/5.819/5.801	63.28
		318.397025	3.7767	51/604/1954		1.92	3891.494/5.787/5.778	63.65
AlC_3	$^2\Pi$	356.565380	0.7643	66/70/239/379/414/1241/1921	16.37	3.58	2.418	0.0
		356.568952	0.7645	67/69/257/385/409/1241/1919		3.95	2.412	0.0
	$^4\Sigma$	356.526313	3.7718	155/155/127/127/588/1319/1925		7.71	2.684	25.47
		356.530215	3.7722	156/157/430/430/590/1322/1924		8.22	2.685	25.26
AlC_4	$^2A'$	394.666639	0.7720	38/145/218/326/409/461/991/1814/2041	22.91	4.85	403.864/1.403/1.398	0.0
		394.670563	0.7675	33/129/232/315/453/447/988/1817/2075		5.32	544.535/1.395/1.391	0.0
	$^4\Pi$	394.571147	3.8060	101/122/337/349/488/1054/1082/1370/2025/2121		2.71	1.480	63.65
		394.573721	3.8052	107/124/340/352/487/796/1052/1412/2024/2118		2.74	1.479	64.09
AlC_5	$^2\Pi$	432.753752	0.7744	49/50/152/161/307/361/360/464/653/840/1491/1967/2008	29.05	5.09	0.860	0.0
	$^2A''$	432.758002	0.7746	51/154/159/314/355/356/454/647/838/1492/1965/2014		5.55	0.859	0.0
	$^4\Sigma$	432.709509	3.7865	85(2)/210(2)/384(2)/485/553(2)/940/1539/1964/2068		10.77	0.915	28.61
		432.714126	3.7869	85/86/211/213/386/387/485/543/547/939/1540/1963/2067		11.38	0.915	28.68
AlC_6	$^2\Pi$	470.850115	0.7725	41/47/108/130/213/260/340/415/489/660/682/725/1256/1883/2042/2134	35.43	6.13	0.575	0.0
	$^4\Pi$	470.776622	0.7989	32/35/74/106/219/250/283/337/427/453/667/712/1202/1570/1823/2058		5.03	0.568	44.44
AlC_7	$^2\Pi$	508.936984	0.7842	39/39/98/102/197/209/324/333/366/476/588/646/708/831/1118/1596/1897/2038/2108	41.57	6.46	0.404	0.0
	$^4\Sigma$	508.889925	3.8029	53(2)/136(2)/235(2)/379(2)/408/528(2)/680(2)/725/1181/1634/1937/2059/2113		13.65	0.421	30.09

It should be noted that for both n-odd and n-even the first members of the series do not follow the general patterns observed for the rest of the series. From Table 2 it can be observed that, except for $n = 1$, doublet states are more stable than their corresponding quartet, with energy differences higher than 25 kcal/mol. It can also be seen that the energy difference between doublet and quartet states remains also unaffected by the employment of diffuse functions. It is not surprising that the compound with $n = 1$ has a quartet ground state, since the electronic configuration is $\sigma^2\sigma^2\pi^2\sigma^1$ ($^4\Sigma$), which could be represented by the following valence bond structure,



$$:\mathrm{Al}-\overset{\bullet}{\underset{\bullet}{\mathrm{C}}}\bullet$$

and allowing the electrons to be spatially separated. However, it should be noted that Bauschlicher et al.[27] describe this state as having three one-electron bonds. This electronic configuration is favored over $\sigma^2\sigma^2\pi^3$ ($^2\Pi$), which according to Bauschlicher et al.[27] should have a two-electron and a one-electron π bonds.

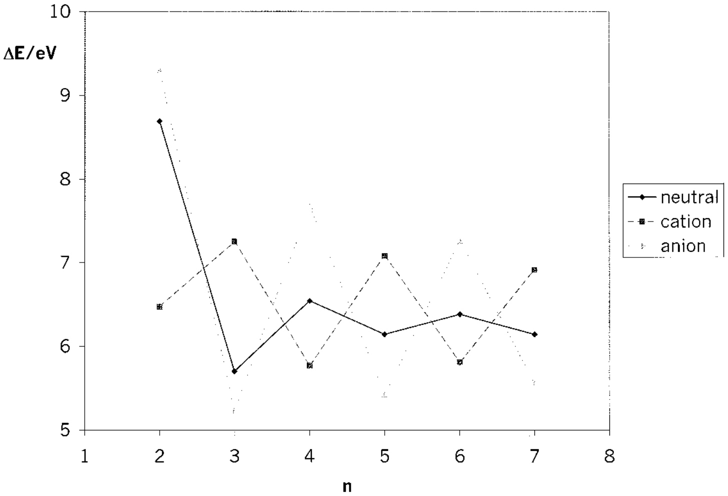
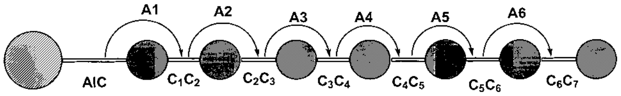


Figure 1. Incremental binding energies (eV) for the AlC_n, AlC_n^+, and AlC_n^- clusters vs the number of carbon atoms.

TABLE 3: Equilibrium Geometries of AlC_n^+ ($n = 1-7$) Clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in Parentheses) Levels of Theory[a]



	AlC	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_7	A1	A2	A3	A4	A5	A6
AlC^+ ($^1\Delta$)	1.997												
	(1.998)												
($^3\Sigma$)	1.977												
	(1.977)												
AlC_2^+ ($^1\Sigma$)	1.842	1.251											
	(1.842)	(1.251)											
($^3\Pi$)	1.949	1.309											
	(1.949)	(1.309)											
AlC_3^+ ($^1\Sigma$)	2.542	1.263	1.316										
	(2.544)	(1.263)	(1.316)										
($^3\Pi$)	1.869	1.256	1.344										
	(1.869)	(1.256)	(1.343)										
AlC_4^+ ($^1A'$)	1.941	1.279	1.298	1.315				171.4	190.3	134.6			
	(1.942)	(1.280)	(1.298)	(1.314)				(172.6)	(190.2)	(134.7)			
($^3A'$)	1.841	1.241	1.328	1.271				179.6	178.7	170.7			
	(1.842)	(1.242)	(1.327)	(1.274)				(179.7)	(178.7)	(171.3)			
AlC_5^+ ($^1\Sigma$,$^1A'$)	2.335	1.250	1.307	1.260	1.310								
	(2.339)	(1.251)	(1.306)	(1.260)	(1.309)			(180.5)	(180.0)	(180.0)	(180.1)		
($^3\Pi$)	1.846	1.245	1.314	1.261	1.321								
	(1.846)	(1.245)	(1.314)	(1.262)	(1.320)								
AlC_6^+ ($^1A'$)	1.990	1.266	1.301	1.269	1.284	1.312		139.4	189.4	180.0	179.8	180.0	
(^3A)	2.023	1.261	1.303	1.267	1.285	1.314		149.3	187.9	181.6	180.9	182.3	
AlC_7^+ ($^1\Sigma$)	2.237	1.246	1.316	1.248	1.294	1.266	1.307						
($^3\Pi$)	1.834	1.244	1.318	1.249	1.299	1.268	1.312						

[a] Distances are given in angstroms and angles in degrees.

Our computed bond length and relative energy for this $^2\Pi$ state are in reasonable agreement with the values reported by Bauschlicher et al.[27] (1.860 Å and 24.8 kcal/mol, respectively).

In the case of $n = 2$ the electronic configuration is $\sigma^2\sigma^2\sigma^2\pi^4\sigma^1(^2\Sigma)$, and the most important valence structures contributing to its description are

$$:\mathrm{Al{-}C{\equiv}C}\bullet \leftrightarrow \bullet\mathrm{Al{=}C{=}C}:$$

This configuration is predominant over $\sigma^2\sigma^2\sigma^2\pi^3\sigma^2(^2\Pi)$ associated to the valence bond structure:

$$:\mathrm{Al{-}\dot{C}{=}C}:$$

Nevertheless, as n increases, the cumulenic-type structures prevail and $^2\Pi$ states are preferred over $^2\Sigma$ ones.

The dipole moment increases regularly with n going from 1.83 D for AlC to 13.65 D when $n = 7$ [6-311G(d)]. The rotational constant for $n = 1$ is slightly smaller than the experimental one, indicating that the Al−C distance given by this method is overestimated by about 0.003 Å.

The next electronic state in the energy ordering for the linear isomers alternate in a regular manner between $^4\Sigma$ state for odd $n \geq 3$ and $^4\Pi$ for even $n \geq 4$. It is also interesting to note in Table 2 that the doublet−quartet energetic separation for n-odd is always smaller that the corresponding to n-even.

As suggested by Pascoli and Lavendy in their work on C_nP clusters,[12] the relative stability of AlC_n clusters will be discussed in terms of the incremental binding energies,[31] as we have done in a previous work on C_nCl compounds.[32] The incremental binding energy can be defined as the change in energy

TABLE 4: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for AlC$_n^+$ 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})
AlC$^+$	$^1\Delta$	279.986449		552		3.10	15.265	36.02
		279.986476		549		3.16	25.246	35.96
	$^3\Sigma$	280.047139	2.2433	529	0.59	3.00	15.565	0.0
		280.044405	2.2423	528		3.08	15.565	0.0
AlC$_2^+$	$^1\Sigma$	318.134354		129(2)/584/1885		6.26	5.829	5.13
		318.135149		128(2)/583/1883		6.32	5.829	5.40
	$^3\Pi$	318.142422	2.0053	159/400/409/1671	7.06	5.34	5.244	0.0
		318.143532	2.0054	160/342/451/1674		5.46	5.244	0.0
AlC$_3^+$	$^1\Sigma$	356.267829		62(2)/163(2)/178/1239/2178	14.30	4.53	1.905	0.0
		356.269512		69/70/165/173/177/1237/2174		4.62	1.903	0.0
	$^3\Pi$	356.235459	2.0151	118/137/286/383/541/1215/2012		7.87	2.606	21.24
		356.237197	2.0152	120/139/317/385/540/1215/2008		8.00	2.605	21.22
AlC$_4^+$	^{1}A′	394.319499		80/166/200/355/433/554/898/1669/2041		7.71	59.736/1.589/1.548	13.87
		394.321542		81/169/202/356/444/553/987/1669/2048		7.87	61.337/1.585/1.545	13.73
	^{3}A′	394.341047	2.0502	54/102/262/406/486/536/1034/1386/1987	20.07	8.94	611.802/1.495/1.491	0.0
		394.342813	2.0531	52/104/262/411/487/541/1040/1433/1975		9.17	650.569/1.492/1.489	0.0
AlC$_5^+$	$^1\Sigma$	432.463629		37(2)/127(2)/208/263(2)/639(2)/806/1494/2086/2272	27.16	4.87	0.788	0.0
	^{1}A′	432.466136		43/125/140/207/270/281/632/633/897/1495/2087/2274		5.04	241549.055/0.787/0.787	0.0
	$^3\Pi$	432.432763	2.0247	76/81/166/192/324/344/454/464/635/901/1475/2029/2100		11.18	0.905	19.72
		432.435270	2.0248	77/82/170/193/331/347/456/464/640/901/1476/2029/2097		11.37	0.905	19.75
AlC$_6^+$	^{1}A′	470.520240		55/95/114/199/220/336/438/483/537/633/705/1250/1780/1998/2127		8.55	62.578/0.615/0.609	11.00
	^{3}A	470.536654	2.0637	55/77/119/158/191/269/368/439/483/549/685/1242/1783/1966/2093	32.97	7.61	136.428/0.592/0.590	0.0
AlC$_7^+$	$^1\Sigma$	508.654543		24(2)/80(2)/169(2)/225/297(2)/563(2)/605/836(2)/1119/1594/2054/2054/2225/2248	39.88	5.16	0.389	0.0
	$^3\Pi$	508.623410	2.0350	50/52/116/128/199/219/339/354/398/462/572/587/740/728/1156/1577/2009/2085/2139		14.24	0.419	19.40

accompanying the following process:

$$\mathrm{AlC}_n \rightarrow \mathrm{AlC}_{n-1} + \mathrm{C}$$

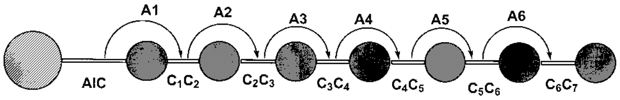
and can be computed as the consecutive binding energy differences between adjacent AlC$_n$ and AlC$_{n-1}$ clusters.

The incremental binding energies against the number of carbon atoms are represented in Figure 1. From this figure it can be observed that a small even−odd alternation in stability exits for AlC$_n$ clusters, the species containing an even number of carbon atoms being more stable then the odd $n-1$ and $n+1$ congeners. In principle it could be expected that the stability of both n-odd and n-even species should not differ much because none of them correspond to a fully occupied HOMO. However, this even−odd effect can be connected to the filling of the last doubly degenerate π level, since doublet AlC$_n$ clusters present $\sigma^2\pi^1$ electronic configuration for odd n and π^3 for even n.

AlC$_n^+$ Clusters. In Table 3 we report the equilibrium geometries for the singlet and triplet states of AlC$_n^+$ clusters, whereas their corresponding properties ($\langle S^2\rangle$, vibrational frequencies, dipole moments, rotational constants, and both binding and relative energies) are shown in Table 4.

From Table 4 it is readily seen that the clusters with n-odd (except $n = 1$, which is a special case as mentioned earlier) have singlet ground states, whereas n-even clusters present triplet ground states. The singlet−triplet energy difference is large enough, except in AlC$_2^+$, to be confident in the state ordering. This behavior can be connected with the electronic configuration for the neutrals. For n-odd neutral clusters the electronic

TABLE 5: Equilibrium Geometries of AlC_n^- ($n = 1-7$) Clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in Parentheses) Levels of Theory[a]



	AlC	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_7	A1	A2	A3	A4	A5	A6
AlC^- ($^1\Sigma$)	1.797												
	(1.803)												
($^3\Pi$)	1.884												
	(1.886)												
AlC_2^- ($^1\Sigma$)	1.868	1.266											
	(1.874)	(1.265)											
($^3\Pi$)	1.892	1.259											
	(1.885)	(1.260)											
AlC_3^- ($^1\Delta$)	1.907	1.304	1.298										
	(1.907)	(1.340)	(1.298)										
($^3\Sigma$)	1.891	1.302	1.303										
	(1.891)	(1.303)	(1.302)										
AlC_4^- ($^1\Sigma$)	1.885	1.251	1.341	1.259									
	(1.889)	(1.250)	(1.343)	(1.257)									
($^3A''$)	1.908	1.260	1.334	1.270				152.7	185.0	179.0			
	(1.888)	(1.257)	(1.337)	(1.266)				(154.2)	(184.4)	(179.0)			
AlC_5^- ($^1\Delta$)	1.907	1.280	1.290	1.306	1.282								
	(1.908)	(1.280)	(1.290)	(1.306)	(1.281)								
($^3\Sigma$)	1.899	1.279	1.293	1.305	1.285								
	(1.901)	(1.279)	(1.293)	(1.306)	(1.283)								
AlC_6^- ($^1\Sigma$)	1.903	1.248	1.333	1.241	1.333	1.261							
($^3\Delta$)	1.939	1.277	1.301	1.276	1.307	1.290							
AlC_7^- ($^1\Delta$)	1.913	1.268	1.303	1.281	1.273	1.311	1.277						
($^3\Sigma$)	1.909	1.267	1.305	1.280	1.275	1.310	1.279						

[a] Distances are given in angstroms and angles in degrees.

configuration is $\sigma^2\pi^1$, and the corresponding cations are σ^2 ($^1\Sigma$), which is preferred over $\sigma^1\pi^1$ ($^3\Pi$), whereas in the case of *n*-even neutral clusters the electronic configuration is $\sigma^2\pi^3$ and the preferred configuration for the corresponding cations is $\sigma^1\pi^3$ ($^3\Pi$ in linear geometries, $^3A'$ in nonlinear geometries).

Singlet and triplet states are linear with the exception of the larger *n*-even clusters, $n = 4$ and $n = 6$ (although in the case of triplet AlC_4^+ with bond angles rather close to 180°). The most significant feature of the AlC_n^+ geometries is the larger Al−C bond distances found in general for both singlet and triplet states compared with their neutral counterpart, especially for the singlets. This fact can be mainly attributed to the contribution of the two main valence bond structures that can be proposed for the singlets:

$$:\mathrm{Al}-\overset{+}{\mathrm{C}}(=\mathrm{C})_{n-2}=\mathrm{C}: \leftrightarrow :\overset{+}{\mathrm{Al}} \leftarrow :\mathrm{C}(=\mathrm{C})_{n-2}=\mathrm{C}:$$

Due to the higher electronegativity of carbon the second structure is preferred over the first one, and the Al−C bond is longer than in the neutral molecule and has a high dative character.

On the other hand, the dominant valence bond structure for the triplet states is

$$\bullet\overset{+}{\mathrm{Al}}-\overset{\bullet}{\mathrm{C}}(=\mathrm{C})_{n-2}=\mathrm{C}:$$

which explains why the Al−C bond distance remains closer to the corresponding neutral analogues, since essentially one of the electrons of an aluminum lone-pair has been removed.

The C−C bond distances are typical of cumulene-type structures; that is ≈1.23−1.34 Å, although some polyacetylenic character appears in *n*-odd clusters especially in $n = 5$ and $n = 7$.

In Figure 1 the incremental binding energies for the cations are also represented. In each case we have taken the lowest lying state (singlet for *n*-odd, triplet for *n*-even). As can be seen *n*-odd clusters are more stable than *n*-even ones, and it is also apparent that in this case the incremental binding energies change more drastically between consecutive members in the series than do in their neutral counterpart. This behavior again can be attributed to electronic structure considerations, since a ground state corresponding to a fully occupied set of π orbitals (singlet state) is energetically much more favorable than a half-fillled set of π orbitals (triplet states), and AlC_n^+ ground states are either linear or slightly nonlinear with ground states derived from $^1\Sigma$ or $^3\Pi$. This behavior was also found for the C_nCl^+ clusters.[32]

AlC_n^- Clusters. The geometrical parameters for the singlet and triplet lowest lying states of AlC_n^- anions and their corresponding properties are shown in Tables 5 and 6, respectively. From our calculations we can conclude that AlC_n^- clusters adopt linear structures for the lowest lying geometry. Electronic ground states alternate between triplet for *n*-odd AlC_n^- clusters and singlet for *n*-even ones. This can be rationalized considering the respective electronic configurations. *n*-odd AlC_n^- clusters have $\pi^4\sigma^2\sigma^2\pi^2$ electronic configuration, and therefore $^3\Sigma$ states are preferred over $^1\Delta$ ones. On the other hand the $\pi^4\sigma^2\sigma^2\pi^3$ configuration of *n*-even neutrals gives rise to $\pi^4\sigma^2\sigma^2\pi^4$ configuration, with full occupation of the highest lying p-bonding set, and therefore $^1\Sigma$ states are preferred over any triplet arrangement.

The Al−C distance in AlC^-($^1\Sigma$) is 1.803 Å [B3LYP/6-311+G(d) level] in good agreement with previous calculation by Gutsev et al.[30](1.7961 Å). For AlC^-($^3\Pi$), our computed value is 1.886 Å [B3LYP/6-311+G(d) level], again very closed to other theoretical computations 1.89 Å[28] and 1.8708 Å.[30] In general a noticeable shortening of Al−C bonds relative to their neutral ground states is observed, mainly as a consequence of the enhanced possibility of π donation from C to Al when a π electron is added. It is also worth noting that inclusion of diffuse functions does not change significantly the geometrical parameters.

TABLE 6: Electronic Energies, $\langle S^2 \rangle$ Values, Vibrational Frequencies, Binding Energies (for the ground states), Dipole Moments, Rotational Constants, and Relative Energies for AlC$_n^-$ 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})
AlC$^-$	$^1\Sigma$	280.364608		828		2.18	18.849	21.65
		280.369341		813		3.28	18.717	23.72
	$^3\Pi$	280.398878	2.0737	726	3.99	0.95	17.149	0.0
		280.406937	2.0724	721		1.93	17.108	0.0
AlC$_2^-$	$^1\Sigma$	318.600575		98(2)/624/1925	13.28	3.07	5.675	0.0
		318.610939		114(2)/615/1921		4.19	5.654	0.0
	$^3\Pi$	318.520524	2.0077	151/219/524/1853		2.78	5.575	50.34
		318.531988	2.0072	158/191/544/1868		3.24	5.624	49.54
AlC$_3^-$	$^1\Delta$	356.628769		119/155/329/504/495/1292/1886		2.17	2.534	15.71
		356.638752		126/142/342/493/496/1293/1871		3.20	2.534	15.84
	$^3\Sigma$	356.653694	2.0264	136(2)/431(2)/510/1288/1802	18.51	2.99	2.553	0.0
		356.663901	2.0282	129/132/431/436/509/1289/1794		4.00	2.552	0.0
AlC$_4^-$	$^1\Sigma$	394.797777		84/257/472/585/1043/1945/2138	26.19	5.38	1.443	0.0
		394.808353		81/257/466/580/1037/1946/2133		6.49	1.441	0.0
	^{3}A”	394.711553	2.0252	95/243(2)/398/539/573/988/1830/1976		4.21	174.510/1.488/1.476	53.30
		394.721868	2.0188	90/247/302/406/534/229i/995/1854/2000		5.57	194.656/1.495/1.484	
AlC$_5^-$	$^1\Delta$	432.835610		71/74/180/186/353/418/445/508/701/875/1524/1948/1983		3.85	0.880	13.45
		432.845288		65/70/161/187/354/414/416/492/679/874/1522/1944/1971		4.98	0.880	13.58
	$^3\Sigma$	432.856661	2.0475	74(2)/196(2)/405(2)/423/564(2)/878/1513/1892/1915	31.60	4.91	0.882	0.0
		432.866541	2.0493	72/73/190/193/398(2)/420/533(2)/875/1512/1872/1908		6.04	0.881	0.0
AlC$_6^-$	$^1\Sigma$	470.986527		56(2)/146(2)/281/282/392/536(2)/720(2)/772/1268/1947/2123/2202	38.87	7.60	0.588	0.0
	$^3\Delta$	470.914131	2.0094	59/61/147/150/283/306/364/385/525/607/717/731/1268/1741/1902/1982		3.22	0.579	44.06
AlC$_7^-$	$^1\Delta$	509.031927		47/48/117/125/208/228/363/367/434/522/632/684/725/905/1133/1636/1898/2004/2080		5.67	0.409	12.14
	$^3\Sigma$	508.050616	2.0698	49(2)/121(2)/232(2)/365/399(2)/547(2)/686/775/1130/1626/1805/1972/2036	44.42	6.95	0.409	0.0

C−C bond lengths for n-odd clusters are ≈1.28−1.31 Å, typical of cumulenic structures. By contrast, there exists a weak alternation in the C−C bond length for n-even species: for example, evaluated from aluminun in AlC$_6^-$ these distances are 1.248, 1.333, 1.241, 1.333, and 1.261 Å; consequently, this fact confers to the latter ones some acetylenic character. This behavior was also observed in the isoelectronic system C$_n$P^{+12}. The linear geometries of n-even clusters are related with their higher polyacetylenic character as reflected in the alternance of C−C bond distances.

As can be seen in Table 6, the dipole moments increase with n as we consider the lowest lying singlets and triplets separately. Thus, for the lowest lying singlet, dipole moments running from 3.07 D for $n = 2$ to 7.60 D for $n = 6$, and for the triplets ones the values varying from 0.95 D for $n = 1$ to 6.95 D for $n = 7$ [B3LYP/6-311G(d) level]. It is worth noting that inclusion of diffuse functions has a significant effect on the dipole moment which is modified in about 1 D for most AlC$_n^-$ clusters.

The energy difference between singlet and triplet states for n-odd clusters is smaller than for n-even ones, and is even reduced as n increases.

In Figure 1 we displayed the incremental binding energies for the anionic clusters. It can be observed a higher stability of n-even AlC$_n^-$ clusters than that for n-odd ones. This behavior is a consequence of the fact that for n-even clusters their ground states are derived from an electronic configuration with a fully occupied set of π orbitals (π^4), and in the case of n-odd clusters are derived from a configuration with half-filled π orbitals (π^2). It is also worth noting that the incremental binding energies change drastically between consecutive members in the series (specially for n low), as in the case of cationic clusters, compared with the smooth variations observed for the neutrals.

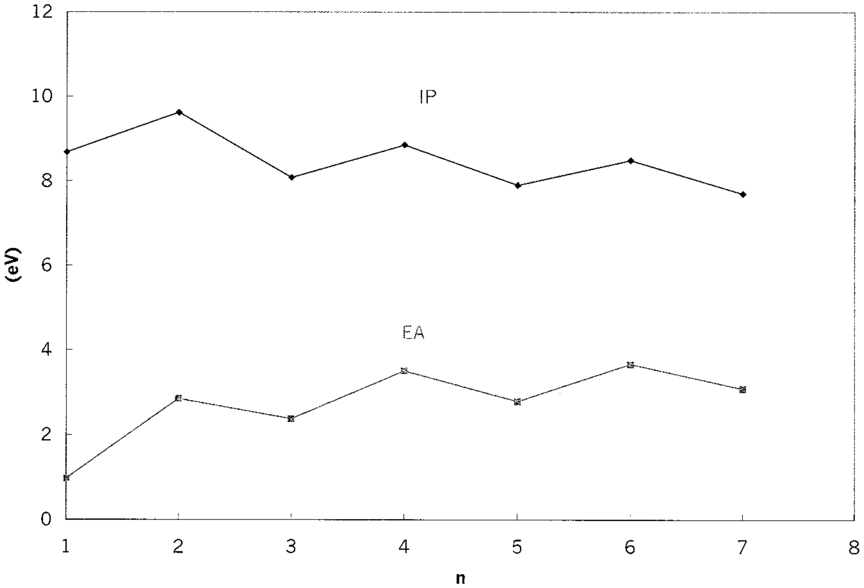


Figure 2. Ionization potentials (IP) and electron affinities (EA), in eV, of AlC_n clusters vs the number of carbon atoms.

In addition, we also estimated the ionization potentials (IP) and the electronic affinities (EA) of the different AlC_n clusters in order to check the relative stability found from the incremental binding energy values of the species studied. The IPs and EAs were computed as the total energy difference between the neutral and positively and negative charged clusters, respectively. In Figure 2 we show these values as function of the number of carbon atoms in the cluster. From this figure it can be concluded that a small odd−even parity effect in cluster stability is apparent in both the ionization potential and electron affinity curves, *n*-even clusters having both higher IP and EA than *n*-odd ones. This behavior is related to the higher stability of *n*-even AlC_n clusters than the *n*-odd ones.

Conclusions

Density functional theory calculations have been carried out for AlC_n, AlC_n^+, and AlC_n^- ($n = 1-7$) clusters by the employment of the B3LYP method with the 6-311G(d) and 6-311+G(d) basis sets. The lowest lying geometry was found to be an open-chain, linear or quasi-linear structure, with aluminun located at the end of the carbon chain.

For the AlC_n clusters the ground state was found to be a doublet with the lowest lying quartet state quite high in energy, with the exception of $n = 1$. In the case of both cationic and anionic species we have found an odd−even alternation, *n*-odd clusters presenting singlet ground states, and *n*-even ones having triplet ones in the AlC_n^+ clusters, and the reverse in the AlC_n^- species.

The relative stability of the different clusters was estimated in terms of both the incremental binding energies and the ionization potential and electron affinity curves. In both cases is quite clear an odd−even parity effect in cluster stability. For both neutral and anionic species *n*-even clusters are more stable than *n*-odd ones, whereas in the AlC_n^+ clusters the alternation in stability is reversed. In the neutral species this effect presents a smooth variation and in the charged systems the alternation in stability is much more pronounced. The ionization potentials and the electron affinities also exhibit an odd−even effect, with *n*-odd clusters having both smaller IP and EA than *n*-even ones.

Prediction for several molecular properties 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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