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Structures and stabilities of non-linear $VC_n^{+/-}$ ($n = 1$–8) clusters

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Abstract

A theoretical study of the different fan and cyclic isomers of $VC_n^{+/-}$ ($n = 2$–8) clusters has been carried out. Predictions for different molecular properties, such as electronic energies, harmonic vibrational frequencies or rotational constants, have been made using the B3LYP method with different basis set including effective core potentials, ECPs. In general, fan and cyclic structures have been predicted to prefer triplet ground states. The stability of fan and cyclic clusters as a function of the size has been discussed in terms of the incremental binding energies. For cationic systems a clear even–odd alternation in stability is found, n-even clusters being more stable than n-odd ones. This parity effect is also found for the first members of the *fan* isomers of VC_n^-, whereas for cyclic VC_n^- structures the stability decreases along the series. It is also found that VC_n^+ systems with $n < 5$ prefer fan structures over linear ones, whereas for $n = 5$–7 the open-chain isomers are the most stable and for $n = 8$ cluster the cyclic structure is the most stable. Anionic vanadium-doped carbon clusters with $n \leq 5$ prefer fan structures, whereas for $n > 5$ n-even clusters prefer open-chain structures and for VC_7^- the cyclic structure is the most stable.

Keywords: Density functional; Molecular property; Vanadium-doped carbon cluster; Ionization potential; Electron affinity

1. Introduction

In the last years small transition-metal carbides are one of the most interesting subjects of study from structural chemistry as a model system to understand the interaction between metal and carbon atoms. Transition-metal carbides are also relevant in modern material science, where different type of materials can be formed. The growth mechanism of these compounds, and in fact, the type of structure formed depends essentially on the kind of interaction between carbon atom and transition metals. Late transition metals have interesting properties as catalysts for carbon nanotube formation [1], whereas early transition metals (Ti, V or Cr) have been found to form stable gas-phase metal–carbon clusters, known as metallocarbohedrenes, *met-cars*, with a M_8C_{12} stoichiometry [2–7]. Finally, *networked* metallofullerenes [8] can be originated when transition metals are incorporated into the carbon cage.

First-row transition metal monocarbides and dicarbides have been the subject of several theoretical studies [9–22]. Dicarbides systems have been found to prefer a C_{2v}-symmetric arrangement and the main factors governing the competition between linear and cyclic isomers have also been addressed in a recent theoretical work [23]. When the number of carbon atoms increases in transition-metal carbides, it is shown that different geometrical configurations can be reached, as it is shown in the theoretical studies on systems such as CrC_n ($n = 1$–8) [24], TiC_n ($n = 1$–8) [25,26], FeC_n ($n = 1$–4) [27], NiC_n [28–30] and ScC_n ($n = 1$–10) [31,32]. On the other hand, photoelectron spectra of first-row transition-metal carbides (MC_2 and MC_3) have been determined experimentally [33,34]. In a recent study, we have carried out a theoretical study of the VC_n ($n = 1$–8) neutral clusters [35], where it was found that neutral VC_n systems with $n \leq 6$ prefer fan-type structures (with the vanadium atom interacts with the whole carbon chain) over linear and cyclic isomers (which have the vanadium atom sited at the end position, or bonded to the two terminal carbon atoms of the chain, respectively), whereas cyclic ground states are predicted for the clusters with $n > 6$. In addition, as various experiments have shown that both neutral and charged met-car are stable [5], a systematic study has also been reported for linear VC_n^+ and VC_n^- ($n = 1$–8) isomers [36]. In order to complete the study on small vanadium-doped carbon clusters, in the present work a theoretical study of cyclic and fan-type structures of VC_n^+ and VC_n^- ($n = 2$–8) systems will be presented. We analyze the relative stability of the two structures

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as a function of n, and for the most stable isomers we report their equilibrium structures and some spectroscopic data that could be helpful in their experimental search. The knowledge of the cationic and anionic species allows us to estimate properties such as ionization potentials (IPs) and electron affinities (EAs) for VC_n fan and cyclic structures, as well as to discuss their systematic behavior with the size of the cluster. Finally, the competition between the different structures of cationic and anionic systems as a function of the number of carbon atoms will be analyzed.

2. Computational methods

We have employed the same theoretical approach than in our previous studies on transition-metal heteroatom-doped carbon clusters [26,31,32], and in particular that employed on VC_n compounds [35,36]. Therefore, all our calculations have been made using the density functional theory (DFT), in particular, we selected the B3LYP exchange-correlation functional [37,38]. This consists of the Lee–Yang–Parr [39] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke [40]. The latter is a linear combination of local density approximation, Becke's gradient correction [41], and the Hartree–Fock exchange energy based on Kohn–Sham orbitals [42]. In these calculations, we have used two different basis set. First, we employed an all-electron basis set, namely, the triple split-valence d-polarized 6-311+G(d) basis set (the Wachters [43] and Hay [44] basis set with the scaling factor of Ragavachari and Trucks [45] is used for vanadium and the conventional 6-311+G(d) basis set [46] for carbon atoms), which also includes diffuse functions. The use of effective core potential, ECP, for the description of clusters reduces significantly the computational time. Therefore, to check the performance of a basis set containing ECP in these systems we have employed a mixed basis set formed by Los Alamos ECP plus DZ, LanL2DZ [47–49] for vanadium in conjunction with the 6-311+G(d) basis set for carbon atoms. This basis set will be denoted as LAN-6+(d).

As is known, the DFT/B3LYP method has been widely applied to the study of many medium-sized heteroatom-doped carbon clusters, providing structures in good agreement with the experimental results [50]. In addition, our study on first-row transition-metal dicarbides [23] and other studies on vanadium carbides systems, such as the works on VC [12,51] VC^+ [13] and VC_2 [19], have shown that B3LYP method is in reasonable agreement with multiconfigurational approaches and molecular orbital methods, such as QCISD or CCSD(T), predicting similar ground state and lowest-lying excited states. These facts suggest that the B3LYP method can be applied in the study of these compounds.

Harmonic vibrational frequencies were computed for all structures using analytical gradient techniques. These frequencies were employed to estimate the zero-point vibrational energy (ZPVE) correction and enable us to check the nature of stationary points, and therefore to characterize if they are true minima on the respective potential surface. Other properties, such as dipole moments, calculated taking the center of mass as origin, or rotational constants were also computed.

All calculations reported in this work were carried out with the Gaussian-98 program package [52].

3. Results and discussion

In the present work we have searched for different non-open-chain isomers of VC_n^+ and VC_n^- ($n = 2$–8) systems, on the singlet, triplet and quintet potential energy surfaces. We will present the results for the two most stable isomers on each potential surface, which as in the case of neutral VC_n system, are a fan structure, where the vanadium is side-bonded to the entire C_n unit, and a cyclic structure with the vanadium bonded essentially to the two terminal carbon atoms of the C_n unit. Other isomers, such as those in which a carbon or a vanadium atom is in a bridge position outside the ring, were found to lie higher in energy, and consequently these isomers are not relevant for small-size VC_n^+ and VC_n^- clusters. One of the main purposes of this work is to carry out a systematic study of some properties as a function of the size of the clusters, consequently we will analyze the results of each type of structure separately. In the case of $n = 4$, cyclic type structure for both cationic and anionic systems, has not been located; all our attempts to obtain this arrangement collapsed to the fan-type one. Finally, the first members of the series $VC_2^{+/-}$ are considered as fan-type structures, because vanadium in this structure is bonded to the C_2 unit (giving to a T-shape structure).

3.1. VC_n^+: fan and cyclic structures

In Table 1 we present the total electronic energies, S^2 expectation values, binding (atomization) energies, and relative energies for the different electronic states of fan structures at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) levels. Analogous information computed for cyclic compounds are collected in Table 2. The geometries of the predicted lowest-lying fan and cyclic species are shown in Figs. 1 and 2, respectively, and their calculated vibrational frequencies and rotational constants are collected in Table 3. The complete information about vibrational frequencies and rotational constants for all the isomers included in this study is provided as Supplementary Material (Tables S1 and S2). Harmonic vibrational frequencies reported in this work are unscaled. All the structures are true minima on their respective potential energy surface, with the only exception of $^3B_1$ of fan VC_7^+ structure, which has an imaginary frequency at the B3LYP/6-311+G(d) level. When LAN-6+(d) basis set was employed, $^5B_1$ of fan VC_8^+ structure, and the $^5B_2$ and $^1A_1$ states of the cyclic structures of VC_5^+ and VC_3^+, respectively, present also an imaginary frequency. All of our attempts to find non-symmetric minima in these cases failed. However, the most stable structures of both fan and cyclic structures are true minima, as can be seen in Table 3.

To the best of our knowledge, there are only available theoretical results for the first member of the series, VC_2^+ [19]. Majumdar et al. have studied different states of VC_2^+ system in C_{2v} symmetry employing MR SDCI and DFT/B3LYP method with a RECPs basis set. They have predicted a $^3B_1$ as the ground state and the lowest-lying quintet and singlet states ($^5B_1$ and $^1A_1$), are located 20.75 and 32.75 kcal/mol above the $^3B_1$ state,

Table 1
Electronic energies, $\langle S^2\rangle$ values, binding energies (for the ground states), dipole moments, and relative energies (including the ZPVE correction) for fan VC_n^+ clusters with the B3LYP/6-311+G(d) (first line) and B3LYP/LAN-6+(d) (second line) methods

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	BE (eV)	μ (D)	ΔE (kcal/mol)
VC_2^+	$^1\mathrm{A}_1$	1019.693309	–		4.65	23.35
		147.019764	–		4.42	23.53
	$^3\mathrm{B}_1$	1019.729738	2.0484	9.74	5.14	0.00
		147.056527	2.0571	9.49	4.93	0.00
	$^5\mathrm{B}_1$	1019.718479	6.0267		5.13	6.95
		147.047141	6.0280		5.11	5.66
VC_3^+	$^1\mathrm{A}_1$	1057.804959	–		3.94	4.43
		185.127767	–		3.72	5.76
	$^3\mathrm{A}_2$	1057.810423	2.0868	15.68	4.44	0.00
		185.135197	2.0991	15.39	4.33	0.00
	$^5\mathrm{A}_1$	1057.806173	6.0419		4.19	2.52
		185.132706	6.0435		4.18	1.35
VC_4^+	$^1\mathrm{A}_1$	1095.880440	–		2.66	27.12
		223.202394	–		2.46	27.43
	$^3\mathrm{B}_1$	1095.924102	20.501	22.48	2.75	0.00
		223.246393	2.0586	22.12	2.62	0.00
	$^5\mathrm{A}''$	1095.877546	6.0645		3.35	28.20
		223.202703	6.0698		3.30	26.30
VC_5^+	$^1\mathrm{A}'$	1133.964574	–		2.55	13.21
		261.282546	–		2.36	14.30
	$^3\mathrm{B}_1$	1133.983583	2.0823	27.91	1.12	0.00
		261.304163	2.1043	27.47	1.08	0.00
	$^5\mathrm{B}_2$	1133.963535	6.0488		2.86	12.07
		261.291648	6.0505		2.98	6.96
VC_6^+	$^1\mathrm{A}_1$	1172.035474	–		0.86	25.55
		299.352306	–		0.95	25.06
	$^3\mathrm{B}_1$	1172.076715	2.0539	34.12	0.71	0.00
		299.392388	2.0692	33.60	0.79	0.00
	$^5\mathrm{A}''$	1172.046043	6.0634		1.97	17.63
		299.367956	6.0631		1.95	13.75
VC_7^+	$^1\mathrm{A}$	1210.119759	–		3.16	15.60
		337.433365	–		3.26	17.94
	$^3\mathrm{B}_1$	1210.141463	2.0692		2.93	0.85
		337.458974	2.0843		2.83	0.87
	$^5\mathrm{A}_1$	1210.143236	6.1052	39.75	2.21	0.00
		337.460418	6.1087	39.25	2.27	0.00
VC_8^+	$^1\mathrm{A}'$	1248.210016	–		3.86	23.55
		375.526397	–		3.89	23.20
	$^3\mathrm{B}_1$	1248.247889	2.0535	46.30	3.83	0.00
		375.563314	2.0677	45.77	3.88	0.00
	$^5\mathrm{A}$	1248.200115	6.0490		3.19	28.00
	$^5\mathrm{B}_1$	375.521691	6.0429		3.29	23.72

Table 2
Electronic energies, $\langle S^2\rangle$ values, binding energies (for the ground states), dipole moments, and relative energies (including the ZPVE correction) for cyclic VC_n^+ clusters with the B3LYP/6-311+G(d) (first line) and B3LYP/LAN-6+(d) (second line) methods

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	BE (eV)	μ (D)	ΔE (kcal/mol)
VC_3^+	$^1\mathrm{A}_1$	1057.776252	–		6.16	28.71
		185.105319	–		5.93	29.99
	$^3\mathrm{B}_2$	1057.822624	2.7516	16.01	6.20	0.00
		185.153692	2.7622	15.88	6.12	0.00
	$^5\mathrm{B}_2$	1057.815858	6.0229		5.03	4.26
		185.146080	6.0236		5.03	4.74
VC_5^+	$^1\mathrm{A}_1$	1133.929571	–		6.22	22.58
		261.257600	–		5.88	24.19
	$^3\mathrm{A}_2$	1133.964707	2.7381	27.39	5.64	0.00
		261.295208	2.7367	27.25	5.57	0.00
	$^5\mathrm{B}_2$	1133.962660	6.0113		4.49	0.83
		261.293152	6.0105		4.31	0.08
VC_6^+	$^1\mathrm{A}_1$	1172.053098	–		4.61	19.25
		299.380415	–		4.29	19.66
	$^3\mathrm{A}''$	1172.083798	2.2167	34.35	4.83	0.00
		299.411818	2.2650	34.14	4.60	0.00
	$^5\mathrm{A}'$	1172.058422	6.0390		4.44	15.57
		299.388193	6.0389		4.56	14.39
VC_7^+	$^1\mathrm{A}_1$	1210.154522	–		3.28	14.38
		337.478368	–		2.91	16.68
	$^3\mathrm{B}_2$	1210.175505	2.3034	40.62	3.28	0.00
		337.502917	2.3697	40.39	2.99	0.00
	$^3\mathrm{A}_2$	1210.174533	2.3243		3.13	0.61
		337.501795	2.3945		2.82	0.70
	$^5\mathrm{A}_1$	1210.171830	6.0753		1.89	2.00
		337.500249	6.0587		1.73	1.45
VC_8^+	$^1\mathrm{A}_1$	1248.244585	–		1.89	24.46
		375.571786	–		1.63	24.18
	$^3\mathrm{B}_1$	1248.283580	2.1726	47.28	1.60	0.00
		375.610124	2.2171	47.02	1.32	0.00
	$^5\mathrm{A}'$	1248.264717	6.0292		4.69	11.22
		375.596123	6.0281		4.77	8.24

respectively, at the MR SDCI+Q level. As can be seen in Table 1 we have found the same stability order, and the differences in the relative energies can be related, as has been pointed out by Majumdar et al. [19], to the multireference nature of the $^3\mathrm{B}_1$ state.

Our results for fan VC_n^+ structures in Table 1 show that all isomers have a triplet ground state. We must point out that for VC_7^+ isomer the triplet and quintet states are located very close in energy. The energy difference between both states, is less than 1 kcal/mol, therefore, in the case of VC_7^+ no definitive conclusion about the lowest-lying fan structure can be drawn, and higher level calculations should be required. With the only exception of VC_3^+ all triplet ground states correspond to a $^3\mathrm{B}_1$ symmetry. In general, n-odd members have singlet and quintet states located closer to the triplet than in the case of n-even ones, especially in the case of $n = 3$.

By looking at Table 2, it can be seen that all cyclic VC_n^+ structures also have a triplet ground state. The triplet–quintet energy difference is larger for n-even clusters, whereas for n-odd cyclic structures the triplet state lies only slightly below the quintet one, especially for VC_5^+. In the case of $n = 7$, we have found two triplet states ($^3\mathrm{B}_2$ and $^3\mathrm{A}_2$) with similar energy and located slightly below the $^5\mathrm{A}_1$ state. In all the cyclic VC_n^+ structures singlet states are clearly the less stable one. In general, it can be seen that comparing with the results obtained for open-chain VC_n^+ systems [36], for the fan and cyclic structures there is a stabilization of singlet and triplet states respect to the quintet ones.

It can also be seen, that dipole moments for cyclic and fan VC_n^+ structures shown in Tables 1 and 2, are always lower than those found for the open-chain isomers [36]. The general trend

Table 3
Vibrational frequencies and rotational constants for the most stable fan and cyclic VC_n^+ and VC_n^- isomers at the B3LYP/6-311+G(d) level

VC_n^+	Isomer	State	Vibrational frequencies (cm^{-1})	Rotational constants (GHz)	VC_n^-	Isomer	State	Vibrational frequencies (cm^{-1})	Rotational constants (GHz)
VC_2^+	Fan	$^3B_1$	398/634/1598	48.794/10.300/8.504	VC_2^-	Fan	$^5B_1$	369/487/1762	51.603/8.205/7.079
VC_3^+	Fan	$^3A_2$	271/341/460/734/1303/1657	13.936/8.065/5.108	VC_3^-	Fan	$^3B_1$	334/476/486/800/1271/1507	13.865/8.438/5.246
	Cyclic	$^3B_2$	296/423/476/952/1158/1565	39.641/4.298/3.877		Cyclic	$^5B_2$	284/356/473/886/1054/1460	40.787/4.143/3.761
VC_4^+	Fan	$^3B_1$	292/459/474/479/562/649/1158/1744/1871	7.049/6.994/3.511	VC_4^-	Fan	$^5B_2$	203/232/272/436/449/578/964/1830/ 1983	6.212/5.583/2.940
VC_5^+	Fan	$^3B_1$	88/228/254/347/424/437/543/576/1008/1391/1770/1845	7.057/3.630/2.397	VC_5^-	Fan	$^3A'$	233/267/349/432/470/598/619/752/959/1123/1640/1717	6.211/4.171/2.696
	Cyclic	$^3A_2$	229/234/268/284/361/398/430/550/1183/1560/1719/1749	6.175/2.709/1.883		Cyclic	$^3A_2$	263/402/409/434/447/469/554/568/1039/1059/1347/1608	7.483/2.620/1.940
VC_6^+	Fan	$^3B_1$	125/220/354/383/414/425/461/528/583/664/925/1280/1826/1951/2045	5.436/2.754/1.828	VC_6^-	Fan	$^3B_1$	82/230/257/260/403/435/453/472/576/611/869/1106/1649/1779/1881	6.316/2.454/1.767
	Cyclic	$^3A''$	113/185/271/332/369/402/459/473/489/528/1184/1396/1740/1832/1867	5.002/1.907/1.381		Cyclic	$^5A''$	133/189/219/394/404/453/500/590/592/872/911/1006/1639/1860/2121	3.311/3.257/1.667
VC_7^+	Fan	$^5A_1$	100/169/284/298/360/367/393/395/399/505/577/601/919/1182/1543/1594/1820/1858	4.142/2.126/1.405	VC_7^-	Fan	^3A	89/177/262/321/366/380/404/408/519/573/592/676/879/1054/1309/1740/1801/1895	4.204/2.152/1.478
	Cyclic	$^3B_2$	134/159/203/243/279/378/383/448/463/529/543/589/1006/1178/1502/1685/1881/1893	2.943/1.706/1.080		Cyclic	$^3B_1$	138/145/189/219/420/467/476/490/495/551/597/604/971/1119/1395/1635/1844/1874	2.762/1.937/1.138
VC_8^+	Fan	$^3B_1$	103/148/258/273/304/339/357/385/420/440/464/510/593/606/870/1091/1362/1825/1842/1998/2044	3.039/1.835/1.144	VC_8^-	Fan	$^3A''$	115/171/172/258/312/337/398/407/422/464/467/480/603/634/833/930/1189/1606/1798/1832/1938	3.387/1.558/1.067
	Cyclic	$^3B_1$	73/139/172/172/246/331/335/367/426/452/462/512/592/596/923/1095/1406/1881/1887/1995/2060	2.160/1.318/0.819		Cyclic	$^3A''$	70/134/150/186/291/308/388/432/447/507/521/527/555/573/846/957/1255/1623/1828/1939/1979	2.051/1.730/0.939

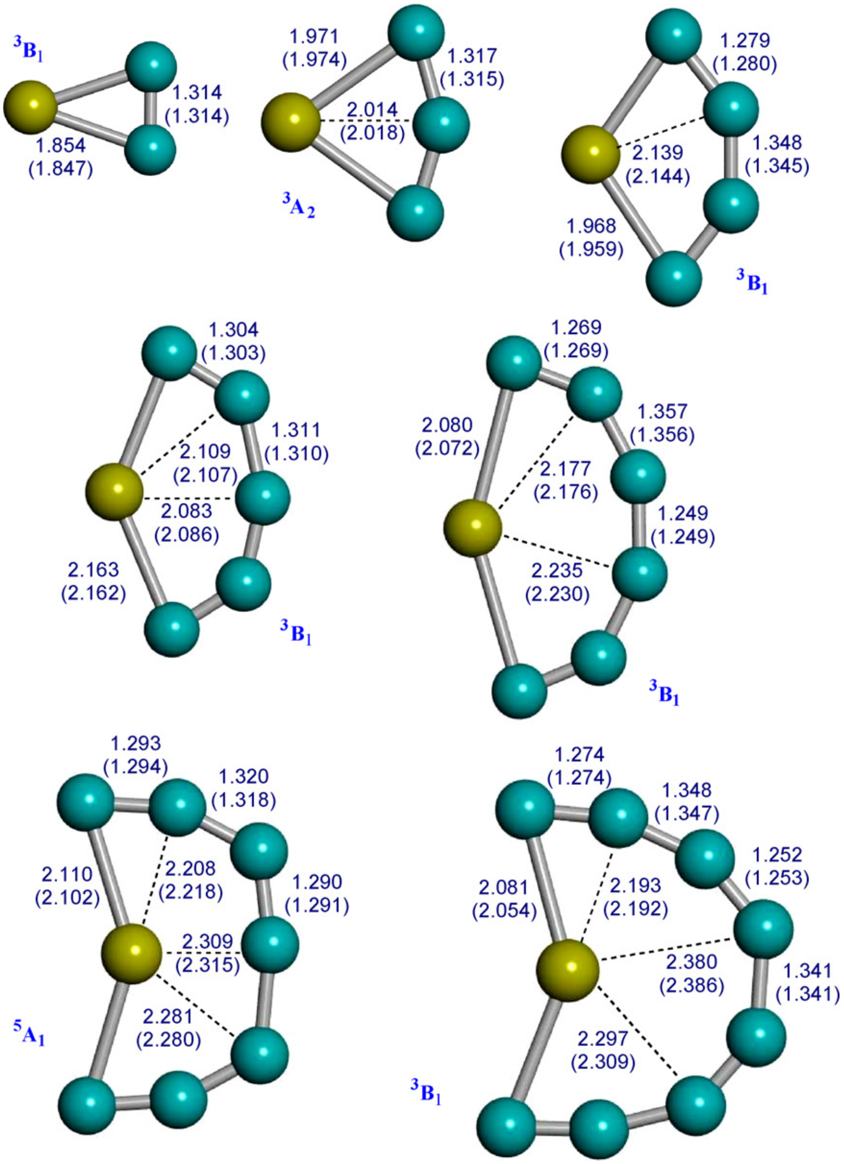

Fig. 1. Equilibrium geometries of fan VC_n^+ clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in Å.

is to decrease as the number of carbon atoms increases, but in the case of fan structures an inversion of this trend is observed from $n = 6$. This change, similar to that found for neutral systems [35], can be related to the fact that the vanadium atom tends to be included into the C_n unit for larger fan structures, see Fig. 1.

The geometrical parameters for fan VC_n^+ clusters (Fig. 1) show that in this type of structures there is a similar interaction (π-type) between the vanadium atom and each of the carbon atoms of the C_n unit, reflected in the fact that all V–C bond distances are very close. In general, it can be seen that the V–C bond distances with the two terminal carbon of C_n unit, are higher for n-even clusters, as in the case of neutral fan structures [35]. The ionization of fan structures causes a shortening of the V–C bond distances, mainly in n-even clusters. On the other hand, V–C bond distances in fan structures are longer than for open-chain VC_n^+ isomers [36]. Concerning the geometrical parameters of cyclic VC_n^+ structures, it can be seen in Fig. 2, that as in the case of neutral systems [35], V–C bond distances in cyclic systems are between those found for linear and fan isomers, according to the fact that the vanadium atom is bonded to the two terminal carbon atoms. In contrast with fan VC_n^+ structures, V–C bond distances in cyclic isomers are higher for n-odd clusters. It can be seen in Figs. 1 and 2, that in both types of structures, fan and cyclic, all C–C bond distances are in the range 1.25–1.36 Å, following in general the same pattern observed in the case of open-chain isomers [36], with a clear alternation of C–C distances (C_{odd}–C_{even} distances considerably shorter than C_{even}–C_{odd} ones). This alternation effect, related to the extent of polyacetylenic character, is more important for n-even isomers.

3.2. VC_n^-: fan and cyclic structures

Absolute energies, S^2 expectation values, dipole moments and binding and relative energies for the lowest-lying singlet, triplet and quintet states of fan VC_n^- clusters are given in Table 4, whereas the geometries for the ground states are shown

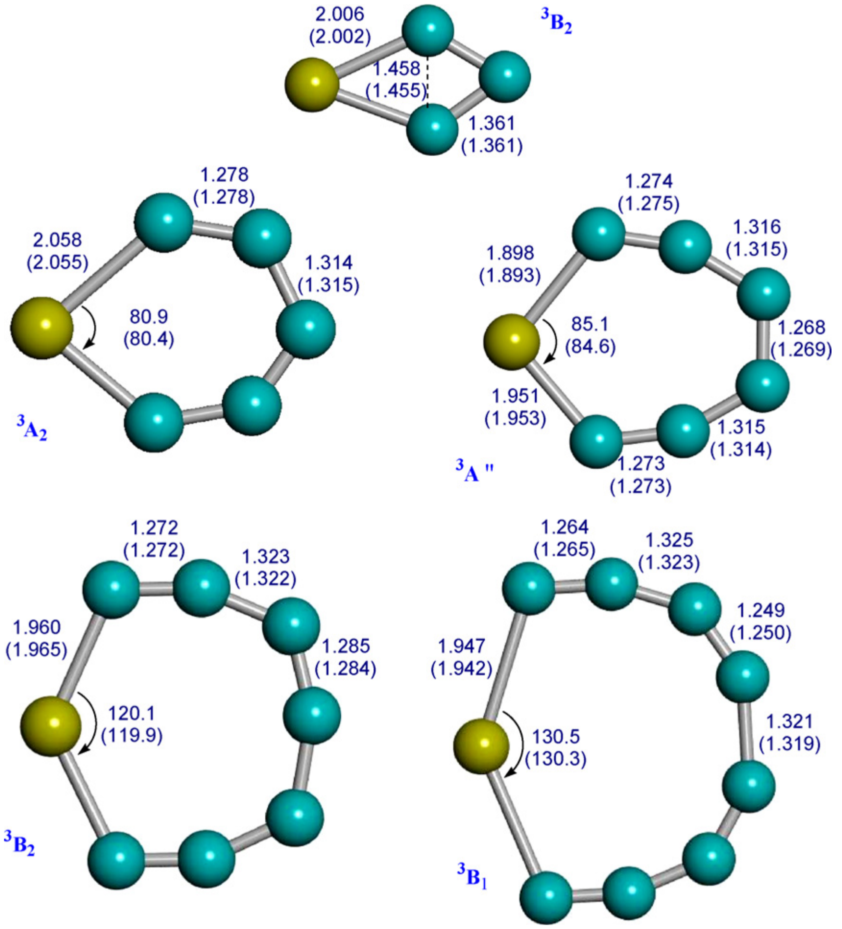

Fig. 2. Equilibrium geometries of cyclic VC_n^+ clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in Å and angles in degrees (°).

in Fig. 3. Table 5 and Fig. 4 report the corresponding results obtained for cyclic VC_n^- structures. Vibrational frequencies and rotational constants for the ground states of fan and cyclic VC_n^- isomers are shown in Table 3. The corresponding values for all the isomers included in Tables 4 and 5 are provided as Supplementary Material (Tables S3 and S4 for fan and cyclic structures, respectively). All reported fan and cyclic structures for the anionic system are true minima on their respective potential energy surface, with the only exception of $^5B_1$ state of cyclic VC_5^-. All our attempts to locate a true minimum on C_s symmetry collapse into the corresponding fan-type structure.

As in the case of VC_n^+ systems the only study devoted to VC_n^- clusters are that by Majumdar et al. [19] on VC_2^- isomer. They found for the VC_2^- system a $^5B_1$ ground state, whereas the lowest-lying triplet ($^3B_1$) and singlet ($^1A_1$) states lie 14.53 and 57.65 kcal/mol, respectively, above the ground state at the MR SDCI+Q level. Majumdar et al. have also shown that, for VC_2^- system, DFT/B3LYP, MR SDCI and MR SDCI+Q levels predict the same ground state and also a similar trend in energy separations of the various excited states. Our B3LYP results computed with the 6-311+G(d) and LAN-6+(d) basis sets also give the same stability order (see Table 4).

It is readily seen in Table 4, that fan VC_n^- n-odd clusters have triplet ground states, and the lowest-lying quintet states are lying relatively close in energy (the energy difference is within the range 3.16–5.44 kcal/mol at the B3LYP/6-311+G(d) level). For VC_3^- and VC_5^- we have included two triplet states because both are below the lowest-lying quintet ones. In the case of n-even clusters triplet and quintet states are also more stable than singlet states and there is a stabilization of triplet states respect to the quintet ones along the series, given a quintet ground state for VC_2^- and VC_4^- structures whereas for the last members of the series, VC_6^- and VC_8^-, the ground state corresponds to a triplet state. In the anionic fan structures singlet states are lying above the triplet and quintet ones. Comparing with the results that were found for open-chain VC_n^- systems [36], both n-even and n-odd fan clusters show a destabilization of singlet states respect to the linear systems. As in the case of fan VC_n^- isomers, triplet and quintet states are more stable than the corresponding lowest-lying singlet ones for cyclic VC_n^- structures. As can be seen in Table 5, cyclic VC_5^- and VC_8^- have a triplet ground state, whereas for VC_3^- and VC_6^- the ground state is a quintet. In the case of VC_7^- we have found two triplet and a quintet states ($^3B_1$, $^3A_1$ and $^5B_2$) within an energy range of 1.0 kcal/mol, and therefore in this case high-level calculations should be required in order to establish a definitive conclusion about the lowest-lying state.

As expected, dipole moments for fan and cyclic structures in anionic clusters are always lower than those found for the open-chain isomers [36]. The behavior of the dipole moment with

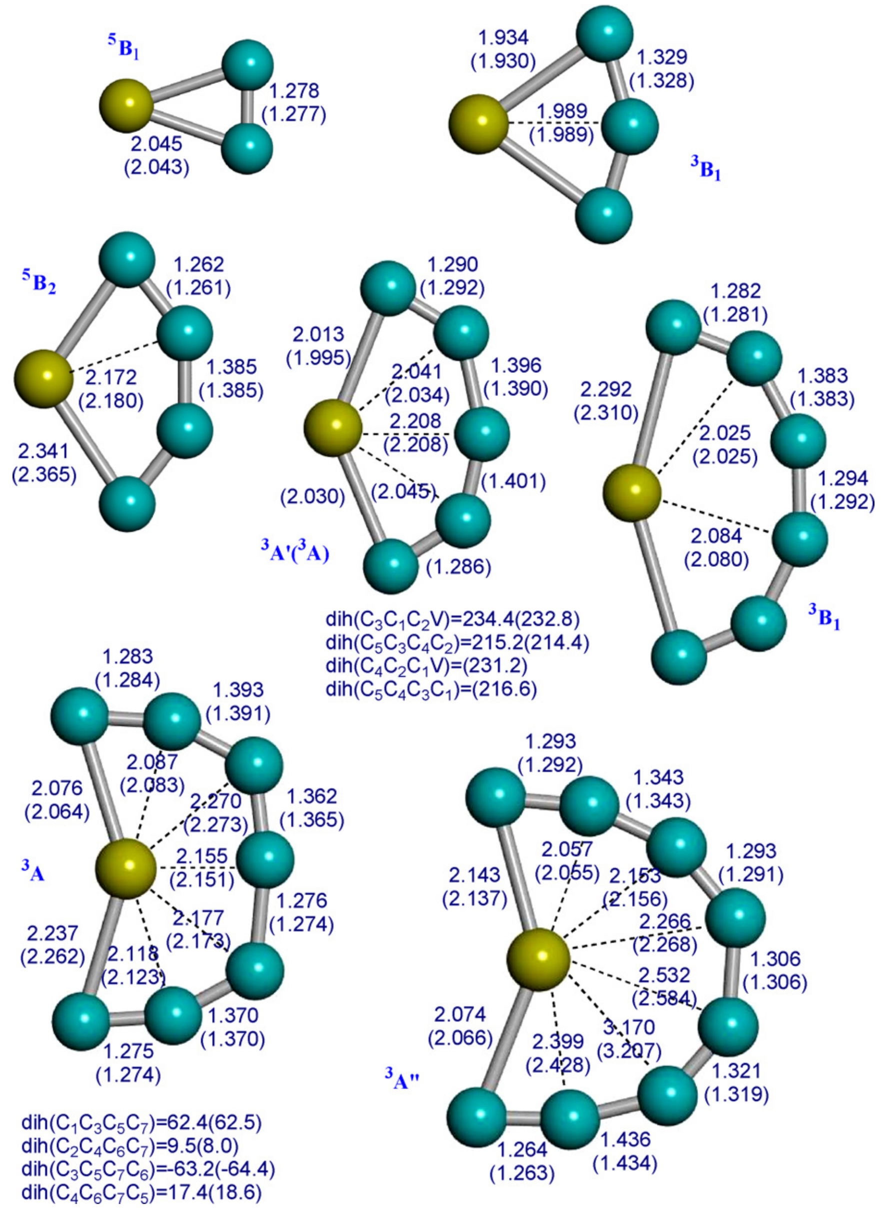

Fig. 3. Equilibrium geometries of fan VC_n^- clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in Å.

the number of carbon atoms is similar to that found for cationic systems in the previous section.

The geometrical parameters of fan and cyclic VC_n^- structures are presented in Figs. 3 and 4, respectively. Concerning the V–C bond distances it can be seen that they are larger for fan structures than for the corresponding cyclic ones (excepting VC_3^-), and in both cases are larger than the previously reported V–C bon distances for the open-chain VC_n^- isomers [36]. This fact, as in the case of neutral and cationic systems, is related to the type of interaction between the vanadium atom and the C_n unit. No significant changes can be noticed when comparing V–C bond distances of anionic with those of the neutral species [35]. On the other hand, the C–C distances in fan and cyclic structures follow the same pattern observed for the cations, with values close to typical cummulenic structures with some acetylene character, which is reflected in the alternation of C–C bond distances.

Finally, looking at the results presented for fan and cyclic $VC_n^{+/-}$ systems, it can be concluded that, for describing these systems the employment of effective core potentials, in particular LanL2DZ, for the vanadium atom gives similar results to those obtained with the 6-311+G(d) basis set. This fact can be useful for the study of larger systems, since the use of effective core potentials might reduce the computational cost without losing quality in the results. In the following sections we will only report the results obtained with the 6-311+G(d) basis set, because the general conclusions are similar with both basis sets.

3.3. Relative stability of VC_n^+ and VC_n^- systems

The relative stability of the fan and cyclic $VC_n^{+/-}$ clusters along the series will be analyzed in term of the incremental binding energies [53]. This concept has been shown by Pascoli and Lavendy [54] to be useful in the study of heteroatom-doped

Table 4
Electronic energies, $\langle S^2\rangle$ values, binding energies (for the ground states), dipole moments, and relative energies (including the ZPVE correction) for fan VC_n^- clusters with the B3LYP/6-311+G(d) (first line) and B3LYP/LAN-6+(d) (second line) methods

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	BE (eV)	μ (D)	ΔE (kcal/mol)
VC_2^-	$^1A_1$	1020.036556	–		3.33	34.55
		147.364839	–		3.74	34.13
	$^3B_1$	1020.087309	2.9151		1.06	2.83
		147.415511	2.9232		1.27	2.36
	$^5B_1$	1020.092310	6.0233	12.18	2.13	0.00
		147.419830	6.0260	12.51	2.31	0.00
VC_3^-	$^1A_1$	1058.143480	–		0.60	14.36
		185.467322	–		0.97	15.13
	$^3B_1$	1058.165485	2.3725	17.92	2.41	0.00
		185.490488	2.4091	18.18	2.62	0.00
	$^3A_1$	1058.161116	2.3304		0.41	2.74
		185.485013	2.3971		0.36	3.30
	$^5B_2$	1058.156121	6.0681		1.72	5.44
		185.482330	6.0794		1.90	4.65
VC_4^-	$^1A_1$	1096.254928	–		2.44	18.88
		223.581117	–		2.72	19.63
	$^3B_1$	1096.274757	2.0393		3.71	6.19
		223.600186	2.0438		3.93	7.37
	$^5B_2$	1096.284588	6.0161	24.91	2.54	0.00
		223.611797	6.0162	25.24	2.89	0.00
VC_5^-	$^1A'$	1134.338079	–		1.47	18.25
		261.661525	–		1.58	18.23
	$^3A'$	1134.366884	2.0704	30.90	3.07	0.00
	^3A	261.690127	2.0851	31.12	3.25	0.00
	$^3A''$	1134.364657	2.1553		3.54	1.35
		261.689275	2.1663		3.72	0.60
	$^5A''$	1134.354811	6.0445		2.85	4.05
		261.680237	6.0488		3.12	5.78
VC_6^-	$^1A_1$	1172.440963	–		1.88	14.53
		299.765183	–		1.89	14.46
	$^3B_1$	1172.463617	2.1555	37.30	1.00	0.00
		299.787664	2.1787	37.54	0.95	0.00
	$^5A_1$	1172.457812	6.0231		1.00	3.50
		299.784968	6.0206		0.67	1.51
VC_7^-	^1A	1210.527778	–		2.93	19.05
		337.847810	–		2.41	19.86
	^3A	1210.558044	2.0930	43.60	2.30	0.00
		337.879430	2.1204	43.77	2.28	0.00
	$^5A'$	1210.551742	6.0435		1.34	3.16
		337.877216	6.0436		1.34	0.65
VC_8^-	^1A	1284.620883	–		1.98	19.04
	$^1A'$	375.946686	–		1.24	17.05
	$^3A''$	1248.650471	2.1175	49.88	3.03	0.00
		375.972837	2.1614	50.08	3.02	0.00
	$^5A_2$	1248.634050	6.0432		1.62	9.99
		375.961182	6.0461		1.52	7.18

carbon clusters. The incremental binding energy can be defined as the change in energy accompanying the process:

$$VC_n{}^{+/-} \rightarrow VC_{n-1}{}^{+/-} + C \tag{1}$$

and it can be computed as the consecutive binding energy differences between adjacent $VC_n{}^{+/-}$ and $VC_{n-1}{}^{+/-}$ clusters. In order to obtain meaningful results we must compare clusters of different size but corresponding to the same type of structure.

Table 5
Electronic energies, $\langle S^2\rangle$ values, binding energies (for the ground states), dipole moments, and relative energies (including the ZPVE correction) for cyclic VC_n^- clusters with the B3LYP/6-311+G(d) (first line) and B3LYP/LAN-6+(d) (second line) methods

Isomer	State	$-E$ (a.u.)	$\langle S^2\rangle$	BE (eV)	μ (D)	ΔE (kcal/mol)
VC_3^-	$^1A'$	1058.091099	–		0.76	38.02
		185.417343	–		1.23	39.99
	$^3B_2$	1085.143162	2.9599		0.96	5.92
		185.472165	3.0005		1.15	6.10
	$^5B_2$	1058.152348	6.0538	17.58	2.97	0.00
		185.481635	6.0591	17.96	3.06	0.00
VC_5^-	$^1A_1$	1134.267226	–		2.60	15.55
		261.593945	–		2.90	17.04
	$^3A_2$	1134.290856	2.5812	28.87	3.72	0.00
		261.619867	2.6669	29.24	3.74	0.00
	$^5B_1$	1134.280321	6.3854		1.40	5.15
		261.610242	6.4295		1.39	4.62
VC_6^-	^1A	1172.391186	–		3.48	36.16
		299.749599	–		3.73	35.49
	$^3B_1$	1172.422342	3.0314		3.13	16.53
		299.750373	3.0034		0.64	15.78
	$^5A''$	1172.451266	6.0333	36.91	2.94	0.00
		299.776820	3.0369	37.23	2.97	0.00
VC_7^-	$^1A_1$	1210.513768	–		2.36	31.75
		337.840265	–		2.62	32.32
	$^3B_1$	1210.564523	2.4152	43.77	2.70	0.00
		337.891932	2.4474	44.10	2.74	0.00
	$^3A_1$	1210.563051	2.3987		2.76	0.91
		337.890236	2.4565		2.76	1.06
	$^5B_2$	1210.563596	6.0408		2.14	0.04
		337.891643	6.0415		2.24	−0.22
VC_8^-	^1A	1248.620883	–		1.98	21.26
	$^1A'$	375.946686	–		1.24	22.51
	$^3A''$	1248.654342	2.4795	49.98	1.00	0.00
		375.982307	2.4895	50.32	1.00	0.00
	$^5A''$	1248.644418	6.0331		0.96	5.93
		375.972458	6.0337		0.94	5.81

In Fig. 5 the incremental binding energies for fan and cyclic $VC_n{}^{+/-}$ clusters are shown as a function of the number of carbon atoms. We must point out that for cyclic systems, due to the fact that the cyclic structure of $VC_4{}^{+/-}$ cannot be obtained, we have only computed incremental binding energies for the last members of the series.

For fan structures, it can be observed in Fig. 5a, that there is a clear even–odd alternation for cationic isomers, with n-even species being comparatively more stable than n-odd ones. In the case of anionic fan structures the same even–odd alternation is generally found, although the two last members do not exhibit a strict parity alternation effect, since their values are nearly constants (see Fig. 5b). A similar parity effect was found for the fan structures of neutral VC_n clusters [35], and therefore, attachment or detachment of an electron does not change significantly the relative stability of these species, especially for the first members of the series. In the case of cyclic isomers (Fig. 5a), incremental binding energies for cationic $VC_n{}^+$ systems show the same behavior that fan structures with a preference for n-even clusters. However, for anionic cyclic clusters a clear decrease of the

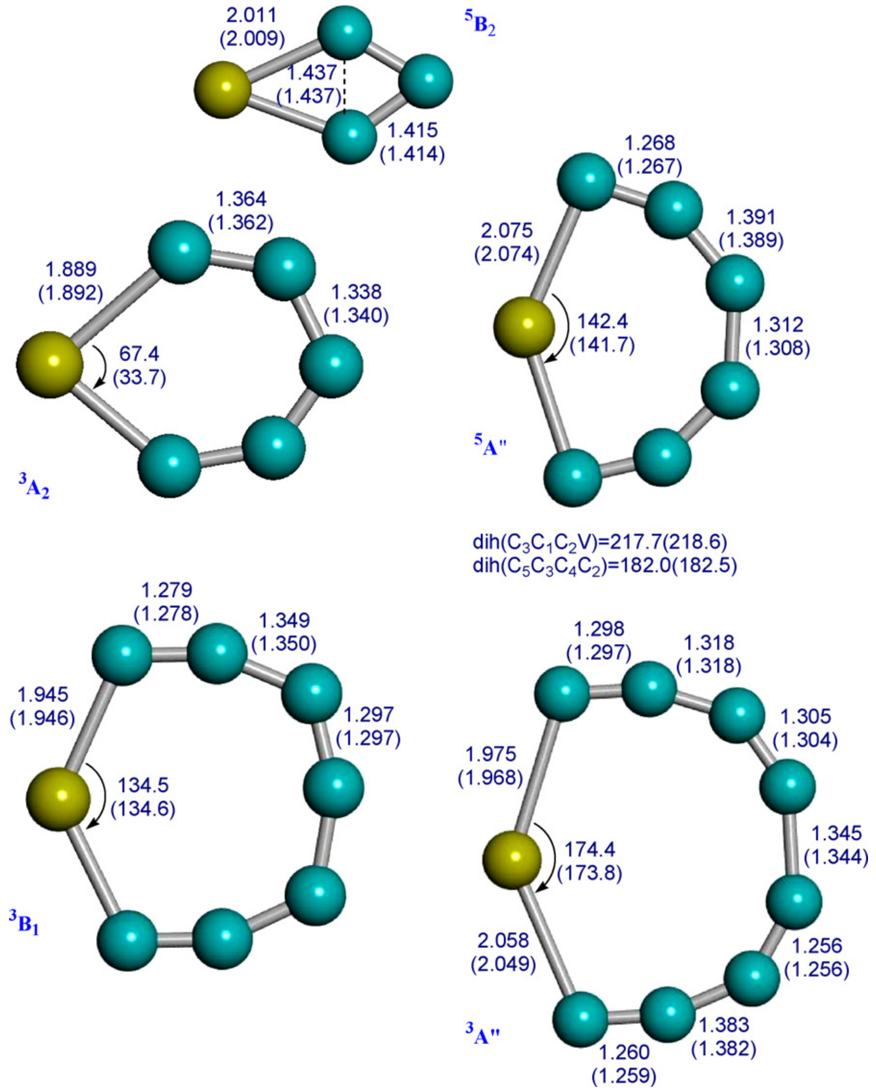

Fig. 4. Equilibrium geometries of cyclic VC_n^- clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in Å and angles in degrees (°).

relative stabilities along the series is found. The relatively large incremental binding energies found for $n = 6$ are related to the fact that cyclic $VC_5^{+/-}$ structures are very unstable (see results of the relative stability for the different structures in Fig. 6).

The energy differences between fan, cyclic and open-chain $VC_n^{+/-}$ species as a function of the number of carbon atom are shown in Fig. 6. We have taken as reference the energy of the open-chain isomers, and therefore, a positive value indicates that the linear isomer is more stable than the fan or cyclic isomer. From Fig. 6a, it can be seen that for cationic systems the open-chain isomers are the most stable ones for $n = 5$–7, whereas for small VC_n^+ clusters fan structures are favored respect to open-chain for n-even clusters. The cyclic structure is the most stable one in the cases of VC_3^+ and VC_8^+. A clear even–odd parity effect is found for the relative energies between fan and open-chain structures, n-even fan structures being relatively more stable than n-odd ones. This parity effect is related to the opposite stability of fan and open-chain systems. Fan structures with an even number of carbon atoms are more stable than n-odd ones, whereas for open-chain isomers the n-odd systems are the most stable ones. It is also shown, in Fig. 6 that the stability of fan structures respect to open-chain isomers decreases along the series. A similar parity effect is found in the relative energies between cyclic and open-chain isomers. In this case, the relative stability of cyclic respect to open-chain structures increases along the series, and the cyclic structure is the most stable one for VC_8^+. However, also for $n = 3$ the cyclic structure is the most stable one. This anomalous stability might be related to the fact that in this structure the transannular C–C bond distance is 1.437, and can be considered as a bicyclic structure. Finally, the most stable non-linear structure corresponds to a *fan* structure for small clusters (with the exception of VC_3^+) and a cyclic structure for $n \geq 6$.

The results for VC_n^- (Fig. 6b) show that anionic vanadium-doped carbon clusters with $n \leq 5$ prefer fan structures, whereas for $n > 5$ n-even clusters generally prefer open-chain structures,

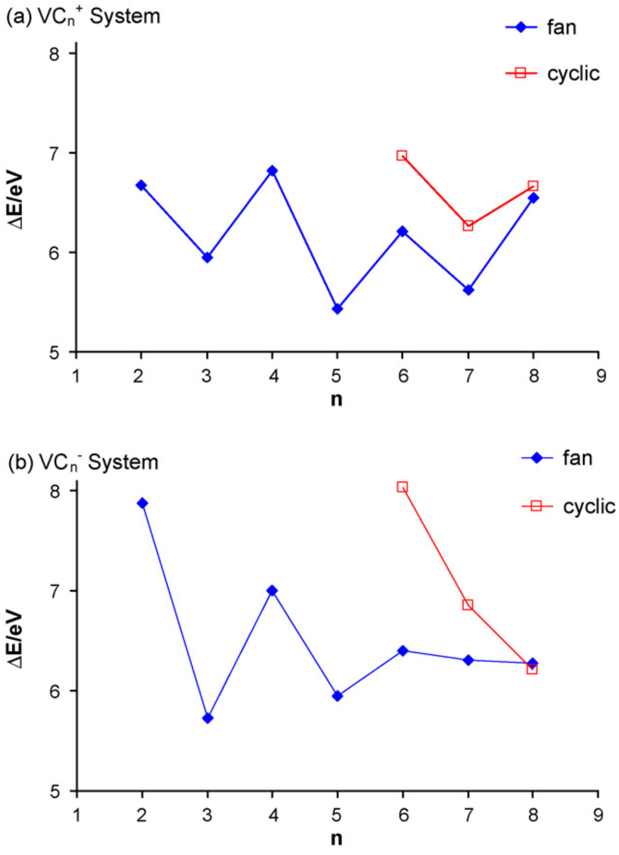

Fig. 5. Incremental binding energies (eV) for the $VC_n^{+/-}$ fan, and cyclic clusters vs. the number of carbon atoms at the B3LYP/6-311+G(d) level.

although for VC_7^- the cyclic structure is slightly more stable. In cationic clusters cyclic structures become more stable than fan ones for $n > 6$, however for larger anionic clusters cyclic and fan structures have a similar stability. There is a clear even–odd parity effect in the relative stability of fan and open-chain anionic structures, with n-odd fan structures being comparatively more stable than n-even ones. This effect is related to the large parity effect that has been found for open-chain VC_n^- systems [36], where n-even clusters are more stable than the corresponding $n+1$ and $n-1$ ones. Comparing with the cationic systems there is only a slight destabilization of fan structures respect to open-chain ones along the series. For clusters with $n < 7$ the cyclic structures are the least stable ones, but, as in the case of cationic systems cyclic VC_3^- is an exception due to its characteristic structure.

The most important difference between the relative stabilities of the different types of neutral VC_n clusters [35] and those found in this study for cationic and anionic systems is the relative stabilization of open-chain structures respect to fan and cyclic ones. This stabilization is larger for the cationic system. Finally we will compare our results on cationic and anionic vanadium-doped carbon clusters with that previously reported for scandium systems [32]. In the case of scandium systems fan (small clusters) and cyclic (larger clusters) structures are always more stable than open-chain ones. Substitution of scandium atom for vanadium gives a relative stabilization of open-chain structures.

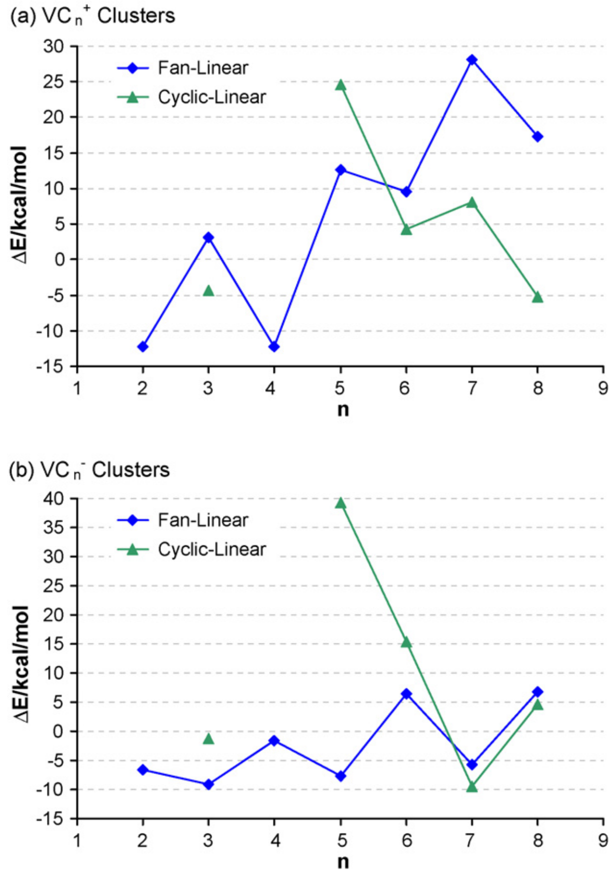

Fig. 6. Relative energies (kcal/mol) of linear, fan, and cyclic $VC_n^{+/-}$ clusters vs. the number of carbon atoms.

3.4. *Ionization potentials and electron affinities of fan and cyclic VC_n clusters*

The results that have been presented in this work for $VC_n^{+/-}$ structures allow an estimation of the ionization potentials (IPs) and electron affinities (EAs) of the different VC_n fan and cyclic structures [35]. The IPs and EAs as functions of the number of carbon atoms are shown in Fig. 7. Since these magnitudes were computed as the energy difference between the charged and neutral species (including zero-point vibrational energies)

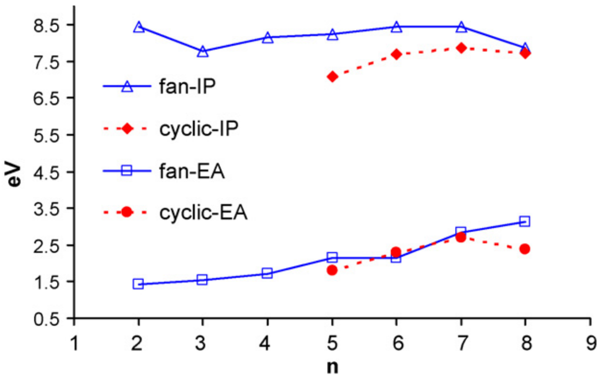

Fig. 7. Ionization potential (IP) and electron affinities (EA), in eV, of VC_n fan and cyclic clusters vs. the number of carbon atoms.

at their respective optimized geometries, the values correspond to adiabatic IP and EA.

It can be readily seen in Fig. 7 that fan VC_n clusters have IPs which exhibit only smooth variations along the series. There is a slight increase from VC_3 to VC_7 (8.13 and 8.45 eV for VC_3 and VC_7, respectively). These results can be related to the stability of fan VC_n/VC_n^+ clusters, since incremental binding energies for both systems have a similar behavior. For cyclic VC_n structures, IPs are smaller than those found for the fan structures and increase along the series having for cyclic VC_8 a similar value to that found for fan structure. The small changes observed for the IP values along the series can be related to the fact that ionization involves an electron located essentially at the vanadium atom, and therefore the values are similar to that found for vanadium atom, namely 6.74 eV. Similar values of IPs are found for open-chain systems [36].

From Fig. 7, it can be observed that EAs for fan VC_n clusters increase along the series (EA takes values from 1.43 to 3.10 eV), and show a slight even–odd alternation for larger members of the series. This alternation is related to the relative stability of fan VC_n/VC_n^- clusters. Values of EA for cyclic isomers are similar to those of fan structures, with the only exception of cyclic VC_8.

For the first members of the series there are experimental values of the EAs in the literature [33,34]. The EAs of VC_2 and VC_3 have been estimated using photoelectron spectroscopy as 1.42 eV [33] and 1.47 eV [34], respectively. At the B3LYP/6-311+G(d) level we obtain a reasonable agreement of the EAs values (1.43 and 1.55 eV for VC_2 and VC_3, respectively).

4. Conclusions

A theoretical study using the B3LYP method with the 6-311+G(d) and LAN-6+(d) basis sets has been carried out for the most stable fan and cyclic isomers of $VC_n^{+/-}$ ($n = 1–8$) clusters. Predictions for their geometrical parameters, vibrational frequencies and other molecular properties that could be useful for an eventual experimental characterization have been provided.

According to our results, all fan VC_n^+ clusters have a $^3B_1$ ground state, with the only exception of VC_3^+ that has a $^3A_2$. In the case of VC_7^+ the $^5A_1$ state is close in energy to the $^3B_1$. The five cyclic VC_n^+ clusters characterized also have triplet lowest-lying states. Fan structures corresponding to anionic VC_n^- systems also have triplet ground states, with the exceptions of VC_2^- and VC_4^-, which have quintet ground states. In the cyclic VC_n^- systems, triplet and quintet states are the most stable, resulting in a triplet ground state for VC_5^- and VC_8^- and a quintet one for VC_3^- and VC_6^-. Both states, $^3B_1$ and $^5B_2$, are similar in energy for *cyclic* VC_7^- isomer. Concerning the geometrical parameters in $VC_n^{+/-}$ systems, fan structures have V–C bond distances that are larger than those of cyclic ones, and in both cases are larger than the corresponding V–C distances in open-chain $VC_n^{+/-}$ structures.

The stability of fan and cyclic clusters as a function of the size has been discussed in terms of the incremental binding energies. For cationic systems both fan and cyclic structures show a clear even–odd alternation in stability, *n*-even clusters being more stable than *n*-odd ones. This parity effect is also found for the first members of the fan isomers of VC_n^-, whereas for cyclic VC_n^- structures the stability decreases along the series. The computed IPs and EAs exhibit only smooth variations along the series. It is also shown that electron affinities for fan VC_n clusters increase along the series.

One of the most interesting results of the present work, related to possible experimental work on these systems, concerns the competition between open-chain, fan and cyclic structures. Our results for VC_n^+ systems suggest that for $n < 5$ there is a preference for fan structures over linear ones, whereas for $n = 5–7$ the open-chain isomers are the most stable and for $n = 8$ cluster the cyclic structure is the most stable one. Anionic vanadium-doped carbon clusters with $n \leq 5$ prefer fan structures, whereas for $n > 5$ *n*-even clusters prefer open-chain structures and for VC_7^- the cyclic structure is the most stable one. A parity effect is also observed in the relative energies between cyclic and open-chain structures, fan isomers being more stable for *n*-even clusters for cationic systems, whereas in the case of anionic clusters the effect is the opposite.

Finally, the results obtained with both basis sets, 6-311+G(d) and LAN-6+(d), for the descriptions of geometrical parameters, energies and other properties are very close. Therefore, the employment of effective core potentials for the description of vanadium atom can be useful in the study of large ionic vanadium–carbon clusters.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2007.01.006.

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