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# Structures and stabilities of charged cobalt-doped carbon clusters

Pilar Redondo*, Carmen Barrientos, Antonio Largo

*Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain*

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ABSTRACT

The structure and properties of the different linear, fan and cyclic isomers of $CoC_n^+$ and $CoC_n^-$ ($n = 1–8$) clusters have been calculated using the B3LYP method with the 6–311+G(d) basis set. The stability of clusters as a function of the size has been discussed in terms of the incremental binding energies. Linear, fan and cyclic structures of $CoC_n^+$ clusters show a clear even–odd alternation in stability, $n$-odd members being more stable than the corresponding $n$-even ones. An opposite parity effect is found for linear and fan $CoC_n^-$ clusters, whereas the relative stability of cyclic isomers decrease with $n$. Linear structures are the most stable $CoC_n^+$ and $CoC_n^-$ clusters, with the only exception of $CoC_2^{+/-}$ and $CoC_7^-$ where the fan and cyclic arrangements are slightly lower in energy. The computed ionization potentials for the three structures show a clear even–odd alternation, with higher values for $n$-even clusters than for $n$-odd ones. Electron affinities for $CoC_n$ clusters increase along the series.

## 1. Introduction

In the last years, clusters of carbon doped with transition metal atoms, $MC_n$, are one of the most interesting subjects of theoretical and experimental studies because they present important interest in several fields, such as astrochemistry, modern material science or combustion chemistry. The relevance of transition metals carbides in modern material science is related to the different type of materials that can be formed. 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, whereas some rare-earth elements can be trapped inside fullerenes cages to form endohedral metallofullerenes [9]. It seems that to a great extent the type of structure formed depends essentially on the nature of the interaction between carbon atom and transition metals. Therefore, theoretical studies of small carbon clusters containing transition metals are very useful for understanding the growth mechanisms of the various metal–carbon nanomaterials as well as for obtaining an insight into their physical and chemical properties. Transition metal carbide clusters have quite complicated electronic structures, related with the presence of nd shell in the transition metal, and are also interesting subjects from the perspective of theoretical chemistry.

Small first-row transition metal carbides, with a general formula $MC_n$, have been the subject of several theoretical studies. In particular, different theoretical studies have been devoted to first-row transition metal carbides and dicarbides [10–28]. In the case of $MC_2/MC_2^+$ systems it is found that they prefer a $C_{2v}$-symmetric arrangement [27,28]. Theoretical studies on systems such as $ScC_n$ ($n = 1–10$) [29,30], $TiC_n$ ($n = 1–8$) [31–33], $VC_n$ ($n = 1–8$) [34–36], $CrC_n$ ($n = 1–8$) [37], $FeC_n$ ($n = 1–4$) [38], $NiC_n$ [39–41], and $ZnC_n$ ($n = 1–8$) [42], have shown that when the number of carbon atoms in transition metal carbides increases three geometrical configurations can be reached as the most stable ones: a fan-type structure with the transition metal atom interacting with the whole carbon chain; a linear isomer which has the transition metal atom sited at the end position; a cyclic arrangement with the transition atom bonded to the two terminal carbon atoms of the chain. The stability of the different structures is related to the transition metal atom. On the other hand, photoelectron spectra of first-row transition metal carbides ($MC_2$ and $MC_3$) have been determined experimentally [43,44].

One interesting point is to compare the behavior of the early and late transition metals. It is well known that the formation of stable met-cars is more favorable for early transition metals (Ti or V), while for late transition metals (Co or Ni) these compounds are not formed [4,45]. Various experiments have also shown that for early transition metals both neutral and charged met-cars are stable [5]. Vanadium and Cobalt atoms can be considered as representative of early and late transition metals, respectively. In this way, we have carried out a theoretical study of the $VC_n/VC_n^+/VC_n^-$ ($n = 1–8$) clusters [34–36], and a study of $CoC_n$ ($n = 1–8$) neutral clusters [46],

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* Corresponding author. Fax: +34 983 423013.
*E-mail address:* predondo@qf.uva.es (P. Redondo).

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where a comparison of the stability of vanadium and cobalt-doped clusters has been presented. In order to complete the study on small cobalt-doped carbon clusters, in the present work a theoretical study of $CoC_n^+/CoC_n^-$ ($n = 1–8$) systems will be presented. We analyze the relative stability of the three structures (linear, fan and cyclic) as a function of $n$, and for the most stable isomers we report their equilibrium structures and some spectroscopic data. The knowledge of the cationic and anionic species allows us to estimate properties such as ionization potentials (IPs) and electron affinities (EAs) for $CoC_n$ linear, 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 and compared with that found for $VC_n^+/VC_n^-$ clusters [35,36]. In addition, accurate theoretical information could be useful to interpret future experimental information of this type of systems.

## 2. Computational methods

The same theoretical approach than in our previous studies on doped carbon clusters, and in particular that employed on $CoC_n$ compounds [46] has been employed. Therefore, all our calculations have been made using the density functional theory (DFT), in particular, we selected the B3LYP exchange-correlation functional [47,48] which has been widely applied to the study of many medium-size heteroatom-doped carbon clusters, providing structures in good agreement with experimental results at a relatively low cost in term of computing time [49]. In addition, our recent studies on first-row transition metals dicarbides [27,28] have shown that B3LYP predicted ground states and low-lying excited states in reasonable agreement with multiconfigurational approach and molecular orbital methods, such as QCISD or CCSD(T). B3LYP functional consists of the Lee–Yang–Parr [50] correlation functional in conjunction with a hybrid exchange functional first proposed by Becke [51]. The latter is a linear combination of local density approximation, Becke's gradient correction [52], and the Hartree–Fock exchange energy based on Kohn–Sham orbitals [53]. In B3LYP calculations we have employed the triple split-valence d-polarized basis set denoted as 6-311+G(d). The Wachters [54] and Hay [55] basis set with the scaling factor of Ragavachari and Trucks [56] is used for vanadium and the conventional 6-311G(d) basis set [57] for carbon atoms which also includes diffuse functions.

For each reported structure, harmonic vibrational frequencies were computed using analytical gradient techniques. These frequencies enable us to estimate the zero-point vibrational energy (ZPVE) correction and 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, or rotational constants were also computed.

All calculations reported in this work were carried out with the *Gaussian-98* program package [58].

## 3. Results and discussion

In this study different isomers of $CoC_n^+$ and $CoC_n^-$ ($n = 1–8$) systems, on the singlet, triplet and quintet potential energy surfaces have been searched. We will present the results on each potential energy surface for the three more competitive structures of the small cobalt-doped carbon clusters which have also been considered in our previous works on $VC_n^+/VC_n^-$ [35,36] and $CoC_n$ [46], namely, linear, cyclic and fan. The results for each type of structure will be discussed separately in order to analyze systematic trends, in different properties considered, with the size of the cluster. As in our previous works [34–36,46] the first members of the series $CoC_2^+/CoC_2^-$ are included in fan-type structures, because cobalt in this structure is bonded to the $C_2$ unit (giving rise to a T-shape structure). Other possible structures as an open-chain structure with the cobalt atom located in an intermediate position or a cyclic isomer with an exo-cyclic cobalt atom were also considered but are not shown since they lie much higher in energy, and therefore they will not be competitive. As in the case of neutral systems, $CoC_n$ [46], a structure where the cobalt atom is bonded to the three terminal carbon atoms of the $C_n$ chain, has only been found for $CoC_6^+(^1A')$, $CoC_5^-(^1A', ^3A'', ^5A'')$ and $CoC_6^-(^1A')$. These isomers are located 69.71, 21.91, 14.68, 22.59, and 53.12 kcal/mol above the most stable linear isomers $CoC_6^+(^5\Delta)$, $CoC_5^-(^3\Phi)$ and $CoC_6^-(^6A'')$, respectively. Similar conformations are not true minima for the others members of the series, and therefore they will not be included.

Harmonic vibrational frequencies and rotational constants calculated for each isomer presented in this study, which may be helpful in an experimental search of these species, are provided as Supplementary Tables S1–S6. Harmonic vibrational frequencies reported in this work are unscaled. As can be seen in Supplementary Tables S1–S6 harmonic vibrational frequencies are positive values, and therefore all the structures reported in this study are true minima on their respective potential energy surface. Finally, B3LYP method, as a single-reference based one, provided non-degenerate π-type frequencies for those structures with electronic states of Φ symmetry.

### 3.1. $CoC_n^+$ clusters

In Table 1 we provide the total electronic energies, $S^2$ expectation values, binding (atomization) energies, and relative energies for the different electronic states of linear $CoC_n^+$ structures at the B3LYP/6-311+G(d) level. Analogous information computed for fan and cyclic $CoC_n^+$ compounds are collected in Tables 2 and 3, respectively. The geometries of the predicted lowest lying linear, fan, and cyclic $CoC_n^+$ species are shown in Figs. 1–3, respectively. From Table 2 we can see that for $CoC_6^+$ only a quintet state has been

**Table 1**
Electronic energies, $<S^2>$ values, binding energies (for the ground states), dipole moments, and relative energies for linear $CoC_n^+$ clusters at the B3LYP/6-311+G(d) level

| Isomer | State | $-E$ (a.u.) | $<S^2>$ | BE (eV) | $\mu$ (D) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $CoC^+$ | $^1\Sigma$ | 1420.378276 | – | 2.68 | 1.54 | 0.00 |
| | $^3\Delta$ | 1420.377025 | 2.2113 | | 1.58 | 0.31 |
| | $^5\Phi$ | 1420.339000 | 6.0224 | | 1.19 | 23.77 |
| $CoC_2^+$ | $^1\Sigma$ | 1458.350609 | – | | 2.44 | 70.65 |
| | $^3A''$ | 1458.454127 | 2.9815 | | 3.32 | 5.78 |
| | $^5A'$ | 1458.461983 | 6.0315 | 8.80 | 3.33 | 0.00 |
| $CoC_3^+$ | $^1\Sigma$ | 1496.520604 | – | | 3.83 | 48.05 |
| | $^3\Delta$ | 1496.597054 | 2.0488 | 16.18 | 4.17 | 0.00 |
| | $^5\Phi$ | 1496.531218 | 6.0599 | | 1.15 | 41.29 |
| $CoC_4^+$ | $^1A'$ | 1534.572172 | – | | 2.92 | 59.29 |
| | $^3A'$ | 1534.649827 | 2.9185 | | 5.37 | 10.86 |
| | $^5\Delta$ | 1534.667866 | 6.0419 | 21.39 | 5.83 | 0.00 |
| $CoC_5^+$ | $^1\Sigma$ | 1572.712367 | – | | 5.24 | 48.17 |
| | $^3\Delta$ | 1572.789010 | 2.0490 | 28.89 | 5.69 | 0.00 |
| | $^5\Phi$ | 1572.730405 | 6.0941 | | 1.81 | 36.37 |
| $CoC_6^+$ | $^1\Sigma$ | 1610.770518 | – | | 3.33 | 58.51 |
| | $^3\Phi$ | 1610.847718 | 2.9600 | | 6.62 | 9.63 |
| | $^5\Delta$ | 1610.863403 | 6.0649 | 34.69 | 7.42 | 0.00 |
| $CoC_7^+$ | $^1\Sigma$ | 1648.900101 | – | | 6.73 | 48.15 |
| | $^3\Delta$ | 1648.976502 | 2.0504 | 41.47 | 7.23 | 0.00 |
| | $^5\Phi$ | 1648.922752 | 6.1224 | | 2.72 | 33.13 |
| $CoC_8^+$ | $^1A'$ | 1686.964350 | – | | 4.62 | 55.68 |
| | $^3A'$ | 1687.039645 | 2.9937 | | 7.99 | 7.72 |
| | $^5A''$ | 1687.053757 | 6.0865 | 47.39 | 9.05 | 0.00 |

**Table 2**
Electronic energies, <$S^2$> values, binding energies (for the ground states), dipole moments, and relative energies for fan $CoC_n^+$ clusters at the B3LYP/6-311+G(d) level

| Isomer | State | −$E$ (a.u.) | <$S^2$> | BE (eV) | $\mu$ (D) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $CoC_2^+$ | $^1A_1$ | 1458.407132 | – | | 1.79 | 39.10 |
| | $^3A''$ | 1458.462272 | 2.8402 | | 2.98 | 4.13 |
| | $^5A_2$ | 1458.469369 | 6.0406 | 8.96 | 2.80 | 0.00 |
| $CoC_3^+$ | $^1A_1$ | 1496.497727 | – | | 1.14 | 41.39 |
| | $^3A_1$ | 1496.562742 | 2.0582 | 15.26 | 1.84 | 0.00 |
| | $^3B_1$ | 1496.561441 | 2.0704 | | 1.85 | 0.85 |
| | $^5A'$ | 1496.506451 | 6.0698 | | 2.77 | 35.04 |
| $CoC_4^+$ | $^1A_1$ | 1534.586167 | – | | 0.49 | 20.59 |
| | $^3A_2$ | 1534.618444 | 2.4728 | 20.52 | 0.71 | 0.00 |
| | $^3B_2$ | 1534.617347 | 2.5007 | | 0.72 | 0.72 |
| | $^5B_1$ | 1534.616524 | 6.0479 | | 1.08 | 0.99 |
| $CoC_5^+$ | $^1A'$ | 1572.652089 | – | | 2.28 | 38.90 |
| | $^3B_2$ | 1572.713368 | 2.0992 | 26.88 | 0.02 | 0.00 |
| | $^5B_1$ | 1572.699962 | 6.0359 | | 0.27 | 8.16 |
| $CoC_6^+$ | $^5A_1$ | 1610.757735 | 6.0452 | 31.83 | 2.38 | 0.00 |
| $CoC_7^+$ | $^1A_1$ | 1648.821888 | – | | 4.35 | 34.00 |
| | $^3A_1$ | 1648.874816 | 2.4000 | 38.77 | 3.32 | 0.00 |
| $CoC_8^+$ | $^1A_1$ | 1686.877130 | – | 42.55 | 4.68 | 0.00 |

**Table 3**
Electronic energies, <$S^2$> values, binding energies (for the ground states), dipole moments, and relative energies for cyclic $CoC_n^+$ clusters at the B3LYP/6-311+G(d) level

| Isomer | State | −$E$ (a.u.) | <$S^2$> | BE (eV) | $\mu$ (D) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $CoC_3^+$ | $^1A_1$ | 1496.515386 | – | | 2.11 | 29.42 |
| | $^3B_2$ | 1496.561674 | 2.5094 | 15.23 | 2.64 | 0.00 |
| | $^5B_2$ | 1496.545934 | 6.0159 | | 3.75 | 9.94 |
| $CoC_4^+$ | $^1A'$ | 1534.556429 | – | | 3.30 | 23.39 |
| | $^3A''$ | 1534.592425 | 3.0216 | 19.86 | 1.89 | 0.00 |
| $CoC_5^+$ | $^1A_1$ | 1572.681739 | – | | 2.08 | 33.43 |
| | $^3B_2$ | 1572.734418 | 2.0700 | 27.40 | 1.70 | 0.00 |
| | $^5A'$ | 1572.691295 | 6.0268 | | 2.89 | 26.11 |
| $CoC_6^+$ | $^1A$ | 1610.765241 | – | | 1.04 | 35.77 |
| | $^3A''$ | 1610.820946 | 2.8706 | | 1.73 | 0.75 |
| | $^5A''$ | 1610.821530 | 6.0433 | 33.54 | 1.72 | 0.00 |
| $CoC_7^+$ | $^1A'$ | 1648.880906 | – | | 1.31 | 44.92 |
| | $^3A_1$ | 1648.951953 | 2.1084 | 40.81 | 0.98 | 0.00 |
| | $^3B_1$ | 1648.951716 | 2.1036 | | 0.89 | 0.31 |
| | $^5A'$ | 1648.918831 | 6.0457 | | 2.03 | 19.67 |
| $CoC_8^+$ | $^1A'$ | 1686.980495 | – | | 1.35 | 27.44 |
| | $^3A$ | 1687.021752 | 2.8048 | | 0.36 | 1.03 |
| | $^5A''$ | 1687.023433 | 6.0443 | 46.53 | 0.79 | 0.00 |

obtained, since all our attempts to obtain a singlet and triplet fan structure collapsed to the cyclic one. The same situation has been found for the quintet state of $CoC_7^+$ and the triplet and quintet ones of $CoC_8^+$ system. On the other hand, in the case of cyclic isomers (Table 3), the optimization of quintet state of $CoC_4^+$ leads to the fan-type structure.

Before discussing our results we will analyze the previous theoretical results available for $CoC_n^+$ isomers. To the best of our knowledge, only for $CoC^+$ [10] and $CoC_2^+$ [28] systems theoretical results can be found. Gutsev et al. [10] in their study of 3d-metal monocarbides using different DFT functionals give results for a $^1\Sigma$ state $CoC^+$. We have also found that the $^1\Sigma$ state is the most stable one but a $^3\Delta$ state is located very close in energy (with an energy difference lower than 1 kcal/mol) and therefore, higher levels of theory should be necessary in order to establish beyond any doubt the ground state for this system. Our calculated value of $D_0$ (2.68 eV) is lower than the available experimental values (3.90 ± 0.30 eV [59], 3.59 ± 0.30 eV [60]). In our theoretical study of $MC_2^+$ ($M$ = Sc–Zn) systems [28] we have shown that in the case

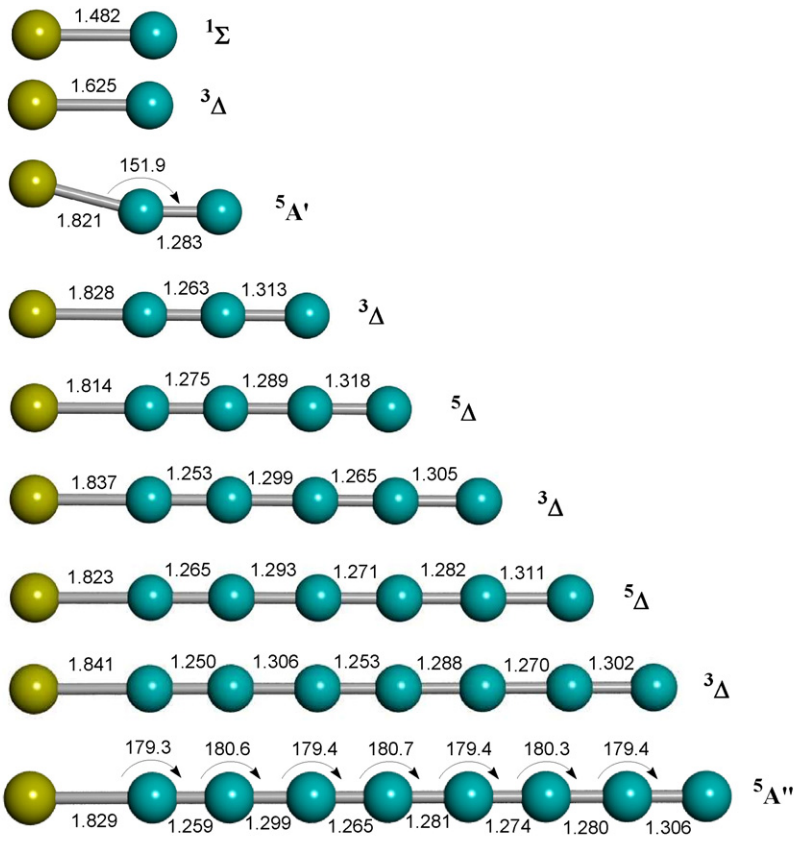


**Fig. 1.** Equilibrium geometries of linear $CoC_n^+$ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

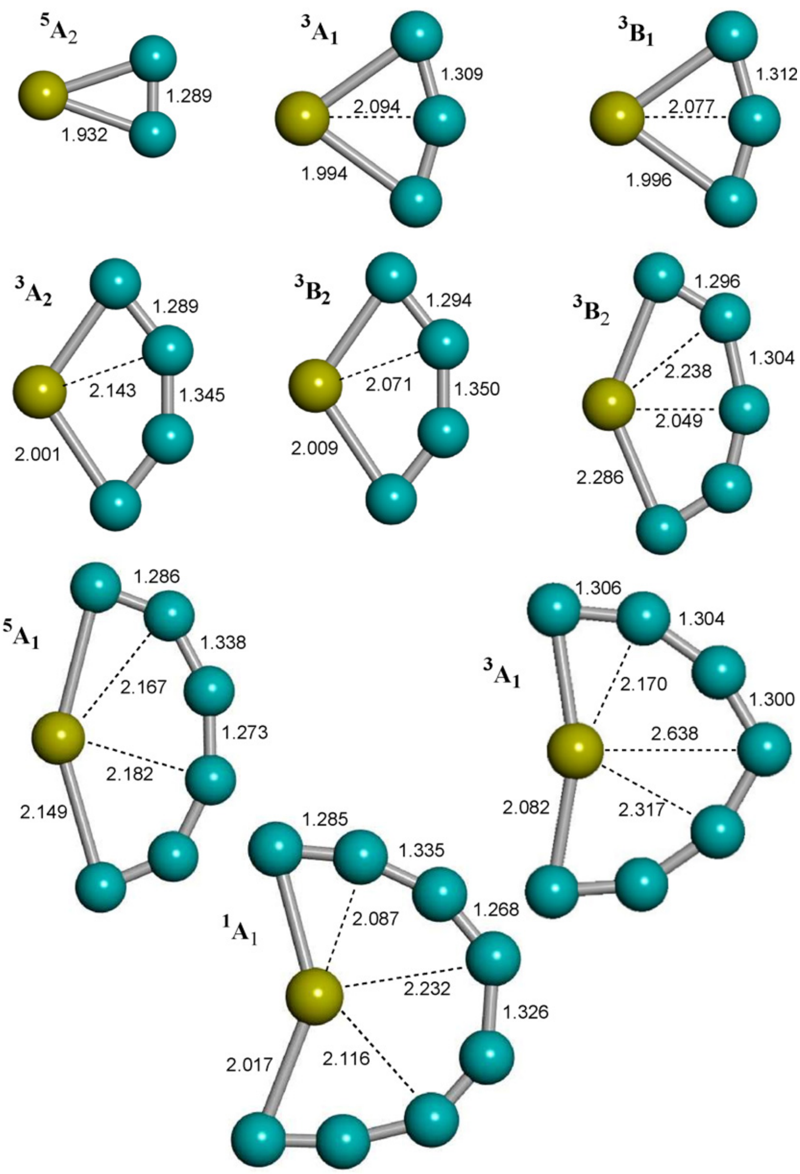


**Fig. 2.** Equilibrium geometries of fan $\mathrm{CoC}_n{}^+$ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms.

of $\mathrm{CoC}_2{}^+$, B3LYP predicts the same ground states than the MCSCF approach and molecular orbital methods, such as QCISD or CCSD(T) for both linear and $\mathrm{C}_{2\mathrm{v}}$ structures, namely ${}^5\prod({}^5\mathrm{A}')$ and ${}^5\mathrm{A}_2$, respectively. All the employed methods found the ${}^5\mathrm{A}_2$ state as the most stable one. A reasonable agreement between the B3LYP and QCISD computed bond distances was also shown [28].

As can be seen from Table 1, linear $\mathrm{CoC}_n{}^+$ isomers with $n$-even carbon atoms have a quintet ground state, ${}^5\Delta({}^5\mathrm{A}',{}^5\mathrm{A}'')$ symmetry. The corresponding triplet states are located about 5.00–10.00 kcal/mol above the quintet ones, whereas the singlet states are very high in energy. In the case of $n$-odd linear $\mathrm{CoC}_n{}^+$ clusters, with the only exception of the $\mathrm{CoC}^+$ system, where the carbon is only bonded to cobalt and we found two states nearly isoenergetic (${}^1\Sigma$ and ${}^3\Delta$), the ground state corresponds to a ${}^3\Delta$ symmetry and the singlet and quintet states are located relatively high in energy. Therefore, we can conclude that linear $\mathrm{CoC}_n{}^+$ species show a clear alternation in stability between quintet and triplet states. The electronic configurations of triplet and quintet states might help to understand this alternation. Cationic cobalt-doped carbon clusters have $4n+8$ valence electrons, and the corresponding valence configurations of the respective ground states can be generalized as

$$\{\mathrm{core}\}1\sigma^2\ldots1\pi^4\ldots(n+2)\sigma^1\left(\frac{n+2}{2}\right)\pi^2 1\delta^3 \quad n-\mathrm{even}$$

$$\{core\}1\sigma^2\ldots1\pi^4\ldots(n+2)\sigma^1\left(\frac{n+1}{2}\right)\pi^4 1\delta^3 \quad n-\mathrm{odd}$$

except for the first element of the series ($\mathrm{CoC}^+$: $1\sigma^2 1\pi^4 2\sigma^2 1\delta^4$). Linear $n$-even and $n$-odd $\mathrm{CoC}_n{}^+$ isomers have been obtained from the corresponding $\mathrm{CoC}_n$ neutral ones [46] removing an $((n+2)/2)\pi^3$ or $(n+2)\sigma^2$ electron, respectively. In the case of $n$-even linear $\mathrm{CoC}_n{}^+$ clusters the lowest lying triplet state, which is located relatively close to the quintet one, is obtained from ${}^5\Delta$ electronic configuration upon a $((n+2)/2)\pi \rightarrow (n+2)\sigma$ promotion. Both orbitals are mainly located at the cobalt atom, and therefore they present similar energy. The dipole moments of the lowest lying linear isomers shown in Table 1 are relatively high and increase along the series.

Concerning the geometrical parameters of the lowest lying linear structures, given in Fig. 1, it can be seen that Co–C bond distances for linear $\mathrm{CoC}_n{}^+$ isomers are very similar for the different structures (within the range 1.814–1.841 Å) with the only exception

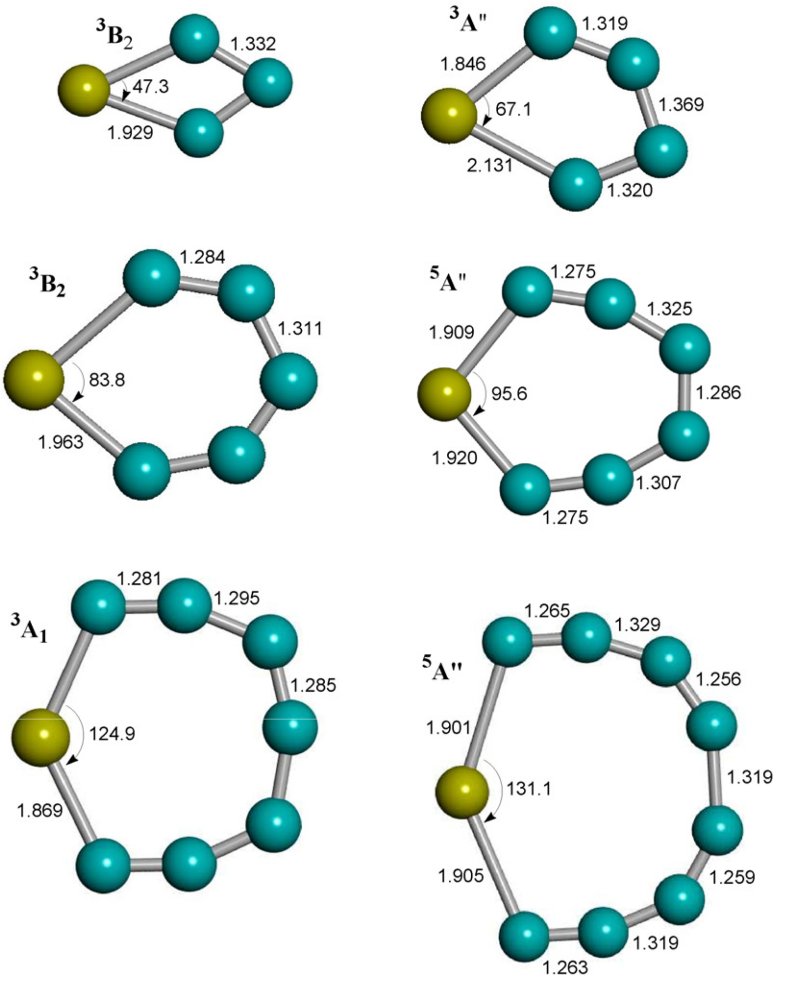
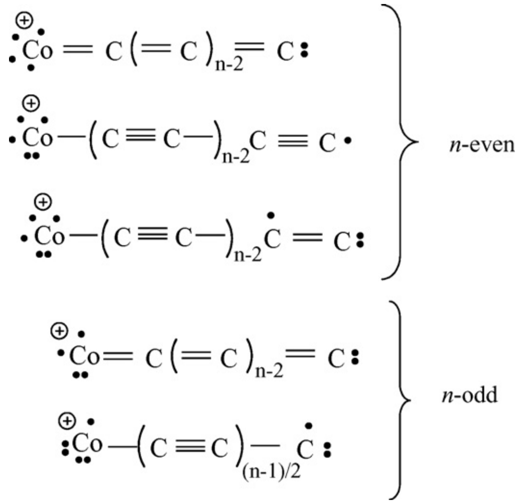


**Fig. 3.** Equilibrium geometries of cyclic $CoC_n^+$ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

of $CoC^+$, which is a special case. Comparing with neutral structures [46], we can observe a similar behaviour with the exception of $n$-odd clusters ($n = 3$ and 5, which have a $^2\Delta$ ground state) where there is a lengthening of Co–C bond distance. The C–C bond distances are all within the range 1.250–1.318 Å, corresponding to moderately strong double bonds, and they show a certain alternation in the C–C bond lengths, in general with $C_{odd}$–$C_{even}$ distances being shorter than $C_{odd}$–$C_{even}$ ones. Taking into account these facts and the results of charge distribution and spin densities, the most relevant valence structures for these clusters are:



The results of fan $CoC_n^+$ clusters collected in Table 2, show that $n$-odd clusters present triplet ground states, so ionization takes place in a single-filled orbital, except for $CoC_3$ [46]. In the case of $n$-even clusters, we have found a quintet ground state ($^5A_2$) as the lowest lying for $CoC_2^+$, whereas two triplet ($^3A_2$, $^3B_2$) and one quintet ($^5B_1$) states are nearly isoenergetic for $CoC_4^+$, they are located within an interval of 1.00 kcal/mol, and therefore, no definitive conclusion about the lowest lying state can be drawn, and high level calculations should be required. For larger $n$-even fan clusters ($n = 6,8$) no comparison is possible because in this system only one stable minimum has been reached ($^5A_1$ and $^1A_1$, for $CoC_6^+$ and $CoC_8^+$, respectively). Concerning the geometrical parameters shown in Fig. 2, the Co–C bond distances are larger for the fan structures than for their linear counterparts, whereas they are similar to those found for neutral isomers [46], although there are some oscillations in this similarity. On the other hand, the C–C bond distances show an alternation, with $C_{odd}$–$C_{even}$ bond distances shorter than $C_{even}$–$C_{odd}$ ones, mainly for $n$-even fan structures.

It can be seen from Table 3, that cyclic $CoC_n^+$ clusters with $n$-odd carbon atoms present a triplet ground state. In the case of $CoC_7^+$ two triplet states are included because they are nearly isoenergetic. Whereas, with the only exception of $CoC_4^+$ (where the quintet state is not a true minimum for this type of structure), triplet and quintet states are found to be very close in energy for $n$-even clusters, with the quintet state slightly lower in energy. Therefore, high-level calculations should be necessary in order to establish the lowest lying state. In general it can been seen from Tables 1–3, that with the only exception of $CoC^+$, for the different structures of $CoC_n^+$ studied in this work singlet states are higher in energy than the corresponding triplet and quintet ones. The geometrical parameters of cyclic $CoC_n^+$ clusters given in Fig. 3, show that in general Co–C bond distances increase along the series and are intermediate between those found for linear and fan structures. Concerning C–C bond distances, the same alternation for cyclic structures than for linear and fan ones is found, $C_{odd}$–$C_{even}$ distances being shorter than $C_{even}$–$C_{odd}$ ones.

Finally, the dipole moments of fan and cyclic $CoC_n^+$ isomers collected in Tables 2 and 3, are always lower than those computed for linear species.

### 3.2. $CoC_n^-$ clusters

In Table 4 we have reported absolute energies, $S^2$ expectation values, dipole moments and binding and relative energies for the lowest lying singlet, triplet and quintet states of linear $CoC_n^-$ clusters. The geometries of the predicted lowest lying linear isomers are shown in Fig. 4. Tables 5 and 6 also collect the main properties for fan and cyclic structures, whereas the corresponding geometries for the respective lowest lying states are given in Figs. 5 and 6, respectively. As it has been indicated in the case of neutral and cationic clusters, some fan and cyclic structures are not located on their respective potential energy surface. In particular no true minima are found for cyclic $CoC_4^-$ clusters and only a singlet state has been reached for fan $CoC_8^-$ structure.

To the best of our knowledge for anionic $CoC_n^-$ clusters previous results are only available for the first member of the series, $CoC^-$. Gutsev et al. [10] in their study of 3d-metal monocarbides predicted for $CoC^-$ a $^1\Sigma$ ground state at the BPW91 level. In this work employing the B3LYP approach we have found a $^3\Phi$ state as

**Table 4**
Electronic energies, $<S^2>$ values, binding energies (for the ground states), dipole moments, and relative energies for linear $CoC_n^-$ clusters at the B3LYP/6-311+G(d) level

| Isomer | State | $-E$ (a.u.) | $<S^2>$ | BE (eV) | $\mu$ (D) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $CoC^-$ | $^1\Sigma$ | 1420.717139 | – | | 0.08 | 3.46 |
| | $^3\Phi$ | 1420.721946 | 2.3019 | 3.31 | 1.89 | 0.00 |
| | $^5\Delta$ | 1420.705457 | 6.0631 | | 3.55 | 10.18 |
| $CoC_2^-$ | $^1A'$ | 1458.796639 | – | | 7.51 | 47.95 |
| | $^3\Phi$ | 1458.873608 | 2.1100 | 11.20 | 9.15 | 0.00 |
| | $^5\Delta$ | 1458.858422 | 6.0287 | | 5.27 | 9.63 |
| $CoC_3^-$ | $^1\Sigma$ | 1496.917409 | – | | 8.05 | 17.14 |
| | $^3\Delta$ | 1496.943075 | 2.9908 | 16.87 | 3.92 | 0.00 |
| | $^5A'$ | 1496.934307 | 6.0510 | | 5.56 | 5.31 |
| $CoC_4^-$ | $^1\Delta$ | 1534.997048 | – | | 10.83 | 46.72 |
| | $^3A''$ | 1535.071173 | 2.1794 | 24.08 | 14.55 | 0.00 |
| | $^5\Delta$ | 1535.056786 | 6.0446 | | 8.12 | 9.12 |
| $CoC_5^-$ | $^1\Sigma$ | 1573.109295 | – | | 11.51 | 20.57 |
| | $^3\Phi$ | 1573.140050 | 2.6781 | 29.73 | 8.83 | 0.00 |
| | $^5A'$ | 1573.135766 | 6.1459 | | 10.15 | 2.57 |
| $CoC_6^-$ | $^1A'$ | 1611.191714 | – | | 14.73 | 45.50 |
| | $^3A''$ | 1611.264067 | 2.1372 | 36.82 | 18.67 | 0.00 |
| | $^5\Phi$ | 1611.247080 | 6.0330 | | 11.26 | 10.74 |
| $CoC_7^-$ | $^1\Sigma$ | 1649.296696 | – | | 14.49 | 24.11 |
| | $^3A''$ | 1649.332071 | 2.6963 | 42.45 | 11.64 | 0.00 |
| | $^5A'$ | 1649.329842 | 6.0711 | | 14.40 | 1.00 |
| $CoC_8^-$ | $^1\Delta$ | 1687.376225 | – | | 16.41 | 48.37 |
| | $^3A$ | 1687.453303 | 2.1131 | 49.51 | 22.44 | 0.00 |
| | $^5\Phi$ | 1687.433886 | 6.0402 | | 13.46 | 11.96 |

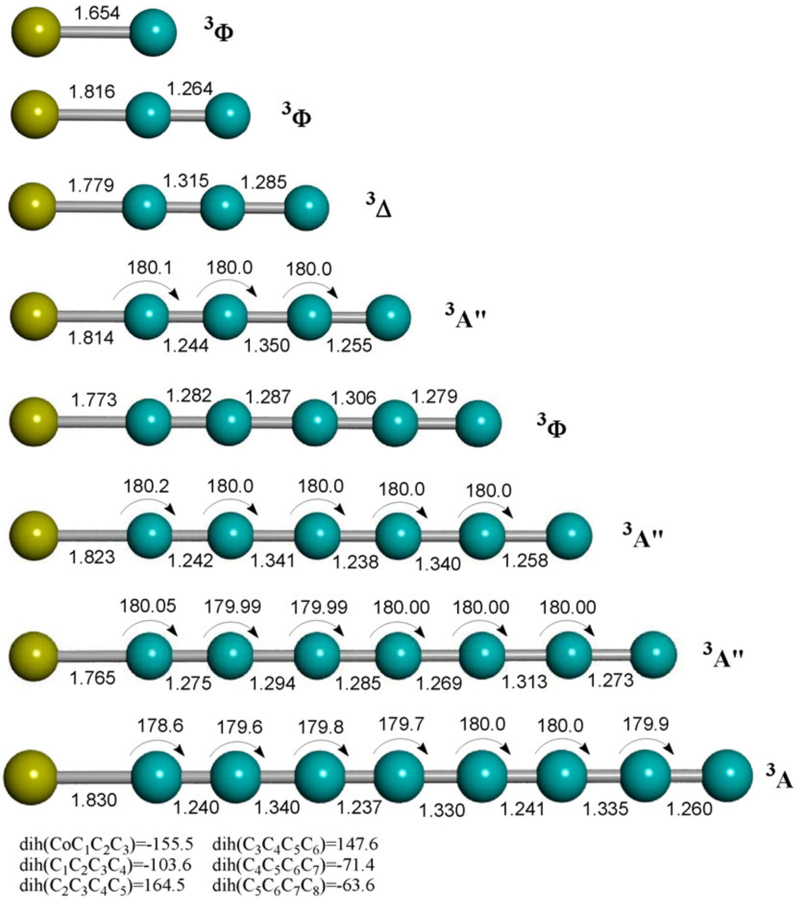


**Fig. 4.** Equilibrium geometries of linear $CoC_n^-$ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

**Table 5**
Electronic energies, <$S^2$> values, binding energies (for the ground states), dipole moments, and relative energies for fan $CoC_n^-$ clusters at the B3LYP/6-311+G(d) level

| Isomer | State | −$E$ (a.u.) | <$S^2$> | BE (eV) | $\mu$ (D) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $CoC_2^-$ | $^1A_1$ | 1458.813026 | – | | 4.64 | 38.28 |
| | $^3B_1$ | 1458.873795 | 2.1537 | 11.23 | 7.05 | 0.00 |
| | $^5B_1$ | 1458.862147 | 6.0131 | | 2.42 | 7.62 |
| $CoC_3^-$ | $^1A_1$ | 1496.918215 | – | | 4.14 | 7.27 |
| | $^3B_1$ | 1496.928461 | 2.6829 | 16.48 | 0.24 | 0.00 |
| | $^5A''$ | 1496.913572 | 6.1209 | | 1.03 | 9.13 |
| $CoC_4^-$ | $^1A_1$ | 1534.997722 | – | | 2.93 | 33.38 |
| | $^3B_1$ | 1535.051235 | 2.1253 | 23.54 | 4.41 | 0.00 |
| | $^5A_1$ | 1535.040078 | 6.0098 | | 1.22 | 6.63 |
| $CoC_5^-$ | $^1A'$ | 1573.075608 | – | | 2.62 | 27.44 |
| | $^3B_2$ | 1573.117881 | 2.0252 | 29.16 | 3.47 | 0.00 |
| | $^5A_2$ | 1573.114086 | 6.0605 | | 1.92 | 2.68 |
| | $^5A_1$ | 1573.114105 | 6.0655 | | 1.61 | 3.02 |
| $CoC_6^-$ | $^1A$ | 1611.175582 | – | | 1.95 | 33.05 |
| | $^3A_2$ | 1611.228030 | 2.0415 | 35.89 | 1.84 | 0.00 |
| $CoC_7^-$ | $^1A_1$ | 1649.284055 | – | | 0.38 | 5.19 |
| | $^3A_2$ | 1649.278736 | 2.4655 | | 0.86 | 6.87 |
| | $^5A''$ | 1649.289949 | 6.0803 | 41.35 | 2.60 | 0.00 |
| $CoC_8^-$ | $^1A$ | 1687.318358 | – | 45.88 | 0.03 | 0.00 |

**Table 6**
Electronic energies, <$S^2$> values, binding energies (for the ground states), dipole moments, and relative energies for cyclic $CoC_n^-$ clusters at the B3LYP/6-311+G(d) level

| Isomer | State | −$E$ (a.u.) | <$S^2$> | BE (eV) | $\mu$ (D) | $\Delta E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $CoC_3^-$ | $^1A'$ | 1496.873365 | – | | 5.26 | 27.98 |
| | $^3B_2$ | 1496.913516 | 2.8032 | | 3.12 | 2.47 |
| | $^5B_2$ | 1496.917945 | 6.0174 | 16.19 | 2.72 | 0.00 |
| $CoC_5^-$ | $^1A_1$ | 1573.054457 | – | | 3.47 | 7.80 |
| | $^3B_1$ | 1573.066084 | 2.1675 | 27.73 | 4.23 | 0.00 |
| | $^3A''$ | 1573.065328 | 2.1168 | | 3.71 | 0.09 |
| $CoC_6^-$ | $^1A'$ | 1611.182764 | – | | 2.86 | 34.87 |
| | $^3A''$ | 1611.237767 | 2.0273 | 36.11 | 3.61 | 0.00 |
| $CoC_7^-$ | $^1A_1$ | 1649.301804 | – | | 0.27 | 29.54 |
| | $^3B_2$ | 1649.348223 | 2.1866 | 42.82 | 1.27 | 0.00 |
| | $^5B_1$ | 1649.318203 | 6.0617 | | 3.63 | 18.22 |
| $CoC_8^-$ | $^1A'$ | 1687.362051 | – | | 2.93 | 41.87 |
| | $^3A''$ | 1687.428648 | 2.0480 | 48.82 | 2.58 | 0.00 |
| | $^5A''$ | 1687.414170 | 6.0333 | | 1.69 | 8.86 |

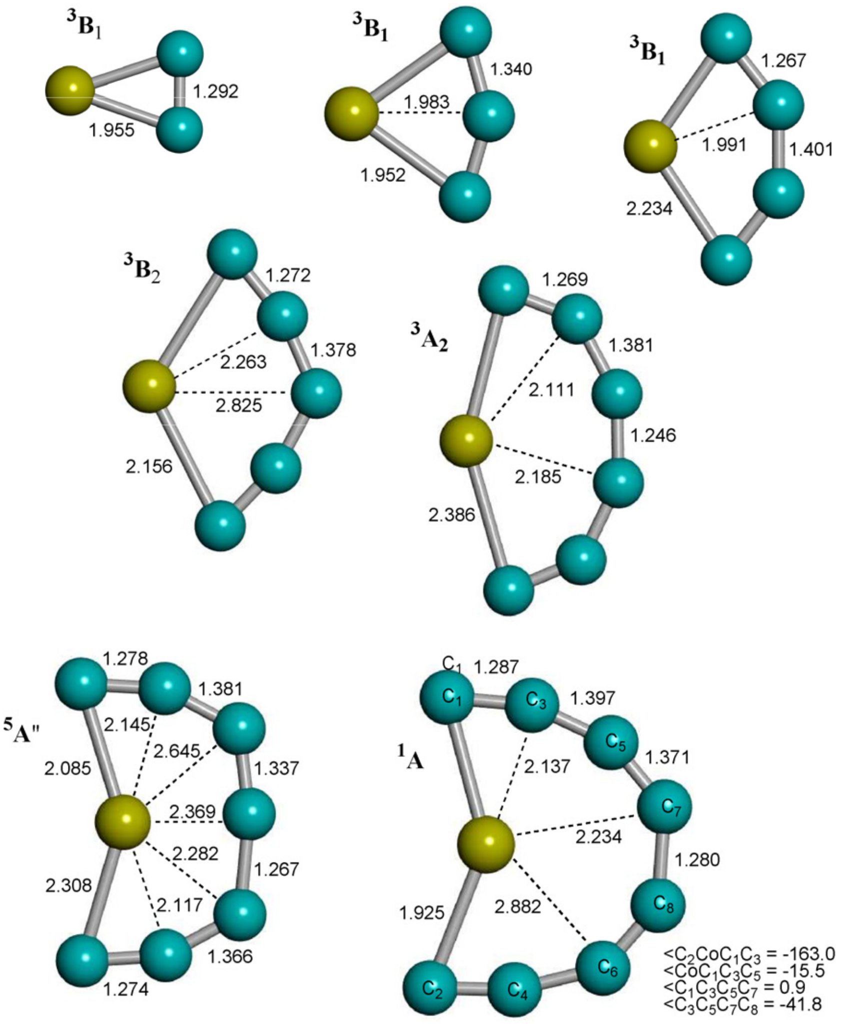


**Fig. 5.** Equilibrium geometries of fan $CoC_n^-$ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms.

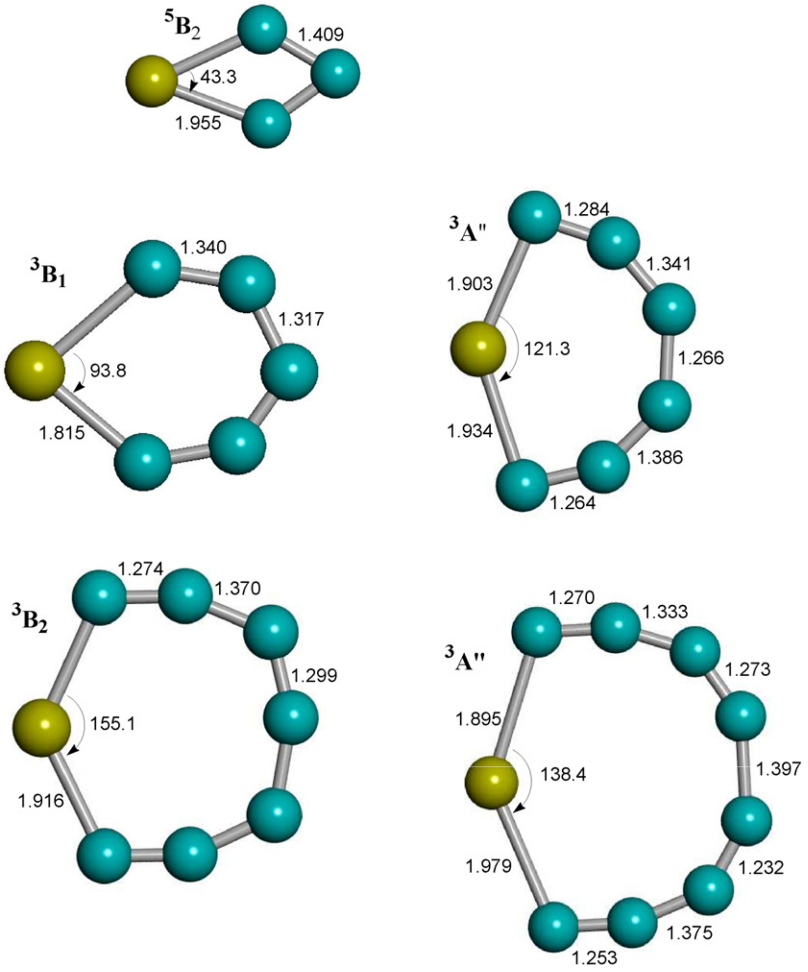


**Fig. 6.** Equilibrium geometries of cyclic $CoC_n^-$ clusters at the B3LYP/6-311+G(d) level of theory. Distances are given in angstroms and angles in degrees.

the lowest lying state, which is located about 3.46 kcal/mol lower in energy than the $^1\Sigma$ one. Quintet states are found to be higher in energy than triplet and singlet ones.

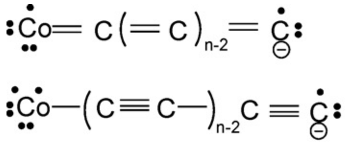
From the results shown in Table 4, we can see that with the only exception of $CoC_3^-$, where the lowest lying state is $^3\Delta$, linear $CoC_n^-$ systems have a $^3\Phi$ ($^3A$) ground state corresponding with to following electronic configuration:

$$\{\text{core}\}1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2 \left(\frac{n+2}{2}\right)\pi^3\delta^3 \quad n-\text{even}$$

$$\{\text{core}\}1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2 \left(\frac{n+3}{2}\right)\pi^1 1\delta^3 \quad n-\text{odd}$$

The $^3\Delta$ state of $n$-odd $CoC_n^-$ clusters is obtained from $^3\Phi$ upon $((n+3)/2)\pi \rightarrow (n+3)\sigma$ promotion. In the case of $CoC_3^-$ system the $^3\Phi$ state is located 1.96 kcal/mol above the $^3\Delta$ one. In addition, $^3\Phi$ presents a $\pi$-type imaginary frequency and all our attempts to obtain a true minimum on $C_s$ symmetry collapsed to the $^3\Delta$ state. For $CoC_n^-$ clusters with $n = 5$–$7$ the $^3\Delta$ state is located higher in energy than the $^3\Phi$ state (2.01 and 4.23 kcal/mol, respectively). The lowest lying quintet state for $n$-odd $CoC_n^-$ clusters is $^5\Phi(^5A')$ and can be obtained from $^3\Phi$ state upon a $(n+2)\sigma \rightarrow (n+3)\sigma$ promotion. The energy difference respect to the triplet ground state decreases with $n$, being only 1.00 kcal/mol for $CoC_7^-$. On the other hand, for $n$-even $CoC_n^-$ clusters $^5\Delta$ and $^5\Phi$ states are located as the lowest lying quintet states (the $^5\Delta$ state is the most stable for small clusters whereas for larger clusters the $^5\Phi$ state is found lower in energy). They are obtained from $^3\Phi$ upon $((n+2)/2)\pi \rightarrow (n+3)\sigma$ or $(n+2)\sigma \rightarrow (n+3)\sigma$ promotions, respectively. With the only exception of $CoC^-$, which is an especial case since the cobalt atom is only bonded to carbon, singlet states are located above their respective triplet and quintet ones and are relatively more stable for $n$-odd clusters than for $n$-even ones. This stability can be related to their corresponding electronic configurations ($\ldots\sigma^2\pi^4\delta^4$ and $\ldots\sigma^2\pi^2\delta^4$, for $n$-odd and $n$-even clusters, respectively). Triplet states of $CoC_n^-$, especially those with $n$-odd number of carbon atoms, have a relatively high spin contamination that could be related to the presence of a quintet state which is located close in energy. Therefore, in these cases the results given for triplet states must be considered with caution. Dipole moments of linear $CoC_n^-$ systems, shown in Table 4, are relatively high and increase along the series with larger values for $n$-even clusters.

The geometrical parameters of the lowest lying linear $CoC_n^-$ systems are given in Fig. 4. We can see that Co–C bond distances follow a similar behaviour to that reported for the neutral systems [46]. Co–C bond lengths are shorter for $n$-odd clusters than for $n$-even ones. The C–C bond distances are all within the range 1.24–1.35 Å and can be assigned to moderately strong double bonds, characteristic of a cummulenic-type structure. In the case of $n$-even species a clear alternation in the C–C bond lengths is found, with $C_{odd}$–$C_{even}$ distances being shorter than $C_{even}$–$C_{odd}$ ones. This fact suggests that $n$-even linear $CoC_n^-$ clusters have a significant polyacetylenic character. Taking into account these facts and considering that the population analysis shows that for linear $CoC_n^-$ clusters the negative charge is located at the $C_n$ unit, the most contributing valence bond structures of these clusters can be summarized as:



*n*-even

From the results obtained for fan structures, shown in Table 5, it seems that small fan $CoC_n^-$ clusters, where minima have been located on the three energy surfaces considered, have a triplet ground state. For $n = 5$ we have found two quintet states that are nearly isoenergetic, and are located about 3 kcal/mol above the triplet ground state. In the case of $n = 7$ the ground state corresponds to a $^5A''$ symmetry. However, for large *n*-even clusters ($n = 6$, 8) fan structures are not located on the quintet potential energy surface, and for $CoC_8^-$ the fan structure has only been located on the singlet surface. On the other hand, triplet states are also the lowest lying for the located cyclic structures as can be seen in Table 6. For $CoC_3^-$ the quintet state is located below the triplet. This cyclic structure is a singular case because it can be seen as a bicyclic arrangement where the transannular C–C bond length is 1.443 Å. With the only exception of the $CoC_5^-$ system the singlet states for cyclic isomers are relatively high in energy. In addition, for this system we have found two triplet states almost isoenergetic, and high level calculation must be necessary in order to establish the symmetry of the ground state. From Tables 5 and 6 we can also see that the dipole moments for fan and cyclic $CoC_n^-$ structures decrease along the series and in both cases are smaller than those corresponding to linear structures.

The most relevant results of the geometrical parameters of fan and cyclic $CoC_n^-$ structures will be briefly discussed. As can be seen from Figs. 5 and 6, Co–C bond distances are longer for the fan structures than for the cyclic ones. This behaviour is related to the type of interactions in these structures. In fan structures the cobalt atom is bonded to the entire $C_n$ unit, whereas in the case of cyclic structures the cobalt is bonded to the two terminal carbon atoms. As in the case of $CoC_n^+$ structures, Co–C bond distances are larger than those corresponding to linear isomers. In general, fan and cyclic Co–C bond lengths are longer for anionic species than for the corresponding cationic ones. On the other hand, the C–C bond distances calculated for these structures show a similar alternation to that found for cationic isomers.

### 3.3. *Relative stability of $CoC_n^+$ and $CoC_n^-$ systems*

Firstly we will analyze the relative stability of the different structures of $CoC_n^{+/-}$ clusters with different sizes in terms of the incremental binding energies [61]. This concept has been shown to be useful in the study of heteroatom-doped carbon clusters [62]. In the present cases, the incremental binding energy is defined as the change in energy accompanying the process:

$$CoC_n^{+/-} \rightarrow CoC_{n-1}^{+/-} + C \qquad (1)$$

and it can be computed as the consecutive binding energy differences between adjacent $CoC_n^{+/-}$ and $CoC_{n-1}^{+/-}$ clusters. In order to obtain meaningful results we must compare clusters of different size but corresponding to the same type of structure. In Fig. 7 the incremental binding energies for linear, fan and cyclic $CoC_n^{+/-}$ clusters are shown as a function of the number of carbon atoms.

From Fig. 7a, we can see that for the linear, fan and cyclic $CoC_n^+$ isomers a clear even–odd alternation in stability is found (fan $CoC_2^+$ slightly deviates for this behavior). In the three structures *n*-odd members are more stable than the corresponding even $n - 1$ and $n + 1$ ones. It is interesting to point out that the incremental binding energies for linear and cyclic isomers vary smoothly as the number of carbon atom increases. However, fan isomers exhibit the opposite trend. In the case of linear structures this parity effect indicates that triplet states found for *n*-odd clusters are relatively more stable than quintet ones (*n*-even species). The relatively low values of incremental binding energies found for cyclic $CoC_4^+$ and fan $CoC_8^+$ isomers suggest a low relative stability of these structures. On the other hand, linear and fan $CoC_n^-$ clusters also shown a clear even–odd parity effect, but in this case *n*-even members are more stable than *n*-odd ones (see Fig. 7b). The parity effect is very close for the two structures with the only exception of the last member of the series, $n = 8$, where the low value found for fan structure, as in the case of cationic system, is related to a low relative stability of fan $CoC_8^-$ isomer. In the case of the linear isomers the parity effect reflects that a $\pi^3\delta^3$ electronic configuration corresponding to the ground state of *n*-even clusters is relatively more stable than a $\pi^1\delta^3$ one found for *n*-odd linear isomers. Finally, the available data of cyclic $CoC_n^-$ show that relative stability of cyclic isomers decreases with *n*.

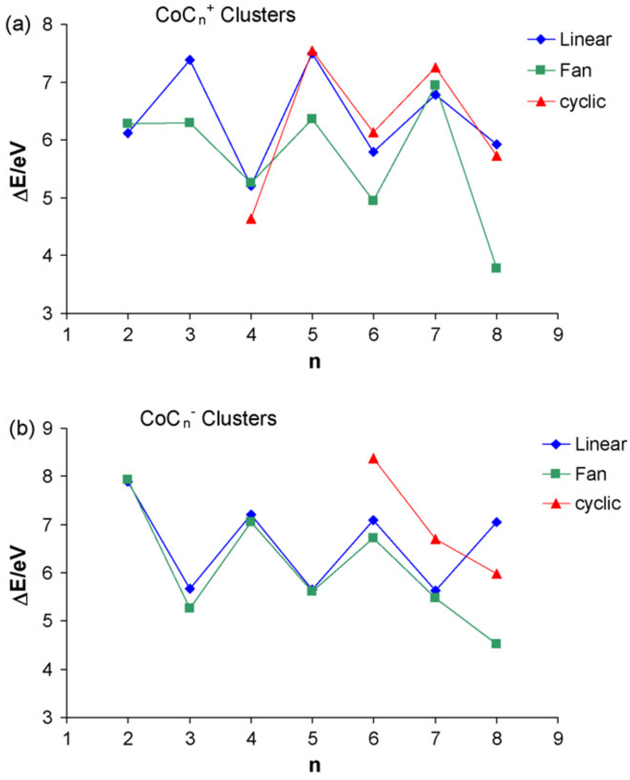


**Fig. 7.** Incremental binding energies (eV) for the $CoC_n^+/CoC_n^-$ linear, fan, and cyclic clusters vs the number of carbon atoms at the B3LYP/6-311+G(d) level.

It is also interesting to compare the stability of the three types of structures reported in this study. The energy differences between linear, fan and cyclic structures as a function of the number of carbon atoms are given in Fig. 8 (Fig. 8a contains results for $CoC_n^+$ clusters and Fig. 8b shows those corresponding to $CoC_n^-$). We have taken as reference the energy of linear isomers, and therefore, a positive value indicates that the linear isomer is more stable than the fan or cyclic one. For $CoC_n^+$ clusters we can see in Fig. 8a that the linear structures are the most stable, only in the case of $CoC_2^+$ the $C_{2v}$ structure is located slightly lower in energy than the linear one (about 3.76 kcal/mol). The stability of fan structures respect to the linear ones decreases along the series. However, the opposite trend is found for cyclic structures, since larger systems are relatively more stable, although for $CoC_n^+$ clusters with $n \leq 8$, they are always higher in energy than the corresponding linear isomers. Finally, we can also see that for $n > 5$ cyclic structures are more stable

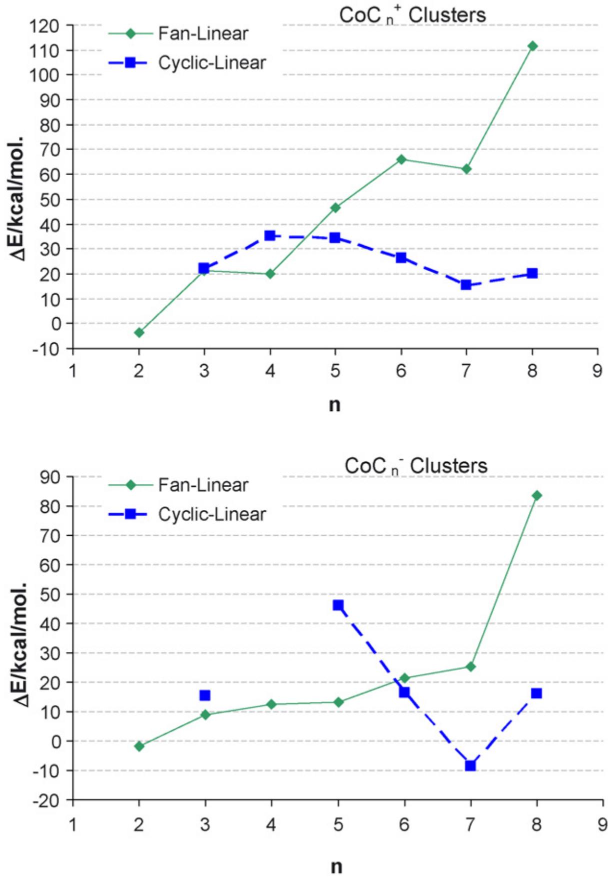


**Fig. 8.** Relative energies (kcal/mol) of linear, fan, and cyclic $CoC_n^+/CoC_n^-$ clusters vs. the number of carbon atoms.

than fan isomers for $CoC_n^+$ clusters. Concerning the relative stability of the different $CoC_n^-$ structures shown in Fig. 8b, in general linear structures are also the most stable, with the exception of $CoC_2^-$ and $CoC_7^-$ isomers where the fan and the cyclic structures, respectively, are the most stable ones. The stability of cyclic $CoC_7^-$ can be related to the behavior found for the incremental binding energies of linear and cyclic isomers (Fig. 7b). The relative stability of fan structures respect to linear ones decreases along the series, mainly for $n = 8$, and fan structures are more stable than cyclic for $n < 6$. In addition, in both systems the cyclic structure for $n = 3$ is anomalously stable, with an energy separation respect to the fan structure relatively low. This fact could be related to the particular structure of this system, which could be viewed as a bicyclic isomer.

The stability found for neutral $CoC_n$ structures [46] is similar to that found for cationic and anionic clusters, in general linear structures are the most stable ones, and the fan structures are more favorable than cyclic ones for the first members of the series. Photoelectron spectroscopy of mono-niobium carbide clusters $NbC_n^-$ ($n = 2$–7) [63], shown that as in the case of $CoC_n^-$ system, a cyclic to linear transition is observed from $n = 3$–4. However, in the case of niobium cyclic isomers for $n > 5$ are not reported. On the other hand, if we compare with the results obtained for $VC_n^+/VC_n^-$ clusters [36], we found a relative stabilization of linear structures respect to fan ones similar to that found for neutral systems [46]. As we have pointed out in the case of neutral systems [46], the stability of fan structures can be related to the number of 3d electrons in the transition metal. A π-donation from the $C_n$ chain to the transition metal in these structures is more favorable for the first members of the series. Similar trend can be also observed in our previous studies on neutral and ionic scandium and titanium-doped carbon clusters [30,32,33], where we have also found that fan-type structures are the most stable for small clusters, however in the case of neutral zinc-doped carbon clusters linear structures are found to be the most stable (with the only exception of $ZnC_2$ [42], where linear and fan structures are similar energy).

### 3.4. Ionization potentials and electron affinities of $CoC_n$ clusters

The results that have been obtained for $CoC_n^{+/-}$ structures allow an estimation of the ionization potentials (IPs) and electron affinities (EAs) of the different $CoC_n$ structures [46]. These magnitudes were computed as the energy difference between the charged and neutral species (including zero-point vibrational energies) at their respective optimized geometries, and therefore, the values correspond to adiabatic IP and EA. The IPs and EAs as functions

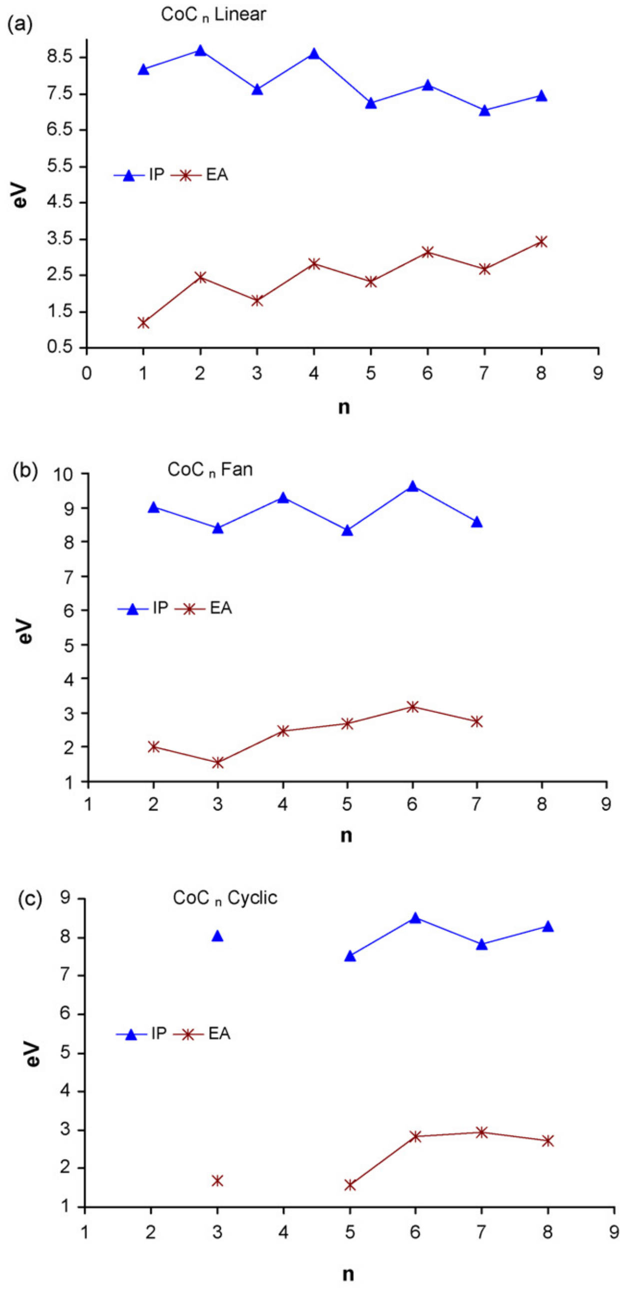


**Fig. 9.** Ionization potential (IP) and electron affinities (EA), in eV, of $CoC_n$ linear, fan and cyclic clusters vs. the number of carbon atoms.

of the number of carbon atoms are shown in Fig. 9 (in Fig. 9a results for linear $CoC_n$ are shown whereas the results corresponding to fan and cyclic $CoC_n$ structures are collected in Fig. 9b and c, respectively).

As can be seen in Fig. 9, the values of the IPs calculated for linear, fan and cyclic $CoC_n$ clusters present a clear even–odd parity effect, with higher values for $n$-even clusters than for $n$-odd ones. This effect is attenuated along the series in the case of linear and cyclic structures whereas for fan isomers is increased. This parity effect is directly related to the behavior found in the relative stability of $CoC_n^+/CoC_n$, since no clear parity effect are found for linear and cyclic neutral clusters. Therefore, the IPs follow a trend similar to that found for cationic clusters, in the case of fan structures cationic and neutral systems have an opposite parity effect, that is summarized. For the different structures the ionization involves an electron located essentially at the cobalt atom, and therefore similar values to that of the cobalt atom, namely 7.90 eV, are estimated. Concerning the EAs, a clear even–odd parity effect is found for linear isomers, with higher values for $n$-even clusters than for $n$-odd. The EAs calculated for fan $CoC_n$ clusters only show a slight parity effect and in the case of cyclic structures no parity effect is found. As in the case of IPs, the behavior of EAs is directly related to the relative stability of $CoC_n/CoC_n^-$ systems. Finally, we can observe from Fig. 9 that in all cases the values computed for EAs tend to increase with $n$.

Experimental values of the EAs for $CoC_2$ and $CoC_3$ have been estimated using photoelectron spectroscopy as 1.70 ± 0.07 eV [43] and 1.55 ± 0.06 eV [44], respectively. Our results calculated at the B3LYP/6-311+G(d) level for the most stable structures, fan $CoC_2$ and linear $CoC_3$ (2.01 and 1.80 eV, respectively), are in reasonable good agreement with the experimental EAs values.

## 4. Conclusions

A theoretical study at the B3LYP/6-311+G(d) level has been carried out for the most stable linear, fan and cyclic isomers of $CoC_n^+$ and $CoC_n^-$ ($n$ = 1–8) clusters on the singlet triplet and quintet potential energy surface.

According to our results, linear $CoC_n^+$ clusters present an alternation in stability between triplet and quintet states: $n$-odd $CoC_n^+$ clusters have $^3\Delta$ ground states whereas $n$-even members have $^5\Delta$ ones, except for the first member of the series. Fan and cyclic $CoC_n^+$ clusters with $n$-odd carbon atoms present triplet ground states, whereas in the case of $n$-even systems in general, triplet and quintet states have similar energies. With the only exception of $CoC_3^-$, which has a $^3\Delta$ ground state, a $^3\Phi$ has been found as the lowest lying state for linear $CoC_n^-$ clusters. In general triplet states are also the most stable ones for fan and cyclic $CoC_n^-$ isomers. We can observe that for $CoC_n^+$ and $CoC_n^-$ clusters, the largest Co–C bond lengths are found for fan structures, whereas the shortest ones correspond to linear geometries. The C–C bond distances reported in this work show a similar behavior, $C_{odd}$–$C_{even}$ distances being shorter than $C_{even}$–$C_{odd}$ ones.

The stability of clusters as a function of the size has been discussed in terms of the incremental binding energies. For cationic systems linear, fan and cyclic structures show a clear even–odd alternation in stability, $n$-odd members being more stable than the corresponding $n$-even ones. Linear and fan $CoC_n^-$ clusters also show an even–odd parity effect, but in this case $n$-even members are more stable than $n$-odd, whereas the available results for relative stability of cyclic isomers decrease with $n$.

The relative stability of linear, fan and cyclic structures show that in the case of $CoC_n^+$ clusters, with the only exception of $CoC_2^+$ (the $C_{2v}$ structure is located about 3.76 kcal/mol lower in energy than the linear one), linear structures are the most stable ones. For anionic clusters the linear structures are in general the most stable ones. However, in this case the fan and cyclic structures are slightly lower for $CoC_2^-$ and $CoC_7^-$ clusters, respectively.

Finally, the computed IPs for the three types of structures show a clear even–odd alternation, $n$-even clusters being higher than $n$-odd ones. The same parity effect is found for EAs corresponding to linear clusters, whereas EAs for fan structures exhibit only smooth variations along the series, and no regularities are found for cyclic EAs. It is also shown that in all cases electron affinities for $CoC_n$ clusters increase along the series.

The competitions between linear, fan and cyclic structures, as well as the predictions for their geometrical parameters, vibrational frequencies and other molecular properties that could be useful for an eventual experimental characterization, have been reported.

## Supporting information available

Vibrational frequencies and rotational constants for linear, fan and cyclic $CoC_n^+$ and $CoC_n^-$ clusters are given in Supplementary Tables S1–S6.

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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.2008.02.003.

## References

[1] S. Iijima, T. Ichihashi, Nature 363 (1993) 603.
[2] S. Wei, B.C. Guo, J. Purnell, S. Buzza, A.W. Castleman, Science 256 (1992) 818.
[3] S. Wei, B.C. Guo, J. Purnell, S. Buzza, A.W. Castleman, J. Phys. Chem. 96 (1992) 4166.
[4] J.S. Pilgrim, M.A. Duncan, J. Am. Chem. Soc. 115 (1993) 6958.
[5] M.M. Rohmer, M. Benard, J.M. Poblet, Chem. Rev. 100 (2000) 495.
[6] B.C. Guo, K.P. Kearns, A.W. Castleman, Science 225 (1992) 1411.
[7] B.C. Guo, S. Wei, J. Purnell, S. Buzza, A.W. Castleman, Science 256 (1992) 515.
[8] D.E. Clemmer, J.M. Hunter, K.B. Shelomov, M.F. Jarrold, Nature 372 (1994) 248.
[9] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, R.E. Smalley, J. Phys. Chem. 95 (1991) 7564.
[10] G.L. Gutsev, L. Andrews, C.W. Bauschlicher Jr., Theor. Chem. Acc. 109 (2003) 298.
[11] A. Kalemos, A. Mavridis, J.F. Harrison, J. Phys. Chem. A 105 (2001) 755.
[12] M. Tomonari, K. Tanaka, Mol. Phys. 101 (2003) 111.
[13] A. Kalemos, T.H. Dunning, A. Mavridis, J. Chem. Phys. 123 (2005) 14301.
[14] I.S.K. Kerkines, A. Mavridis, Mol. Phys. 102 (2004) 2451.
[15] A.C. Borin, J.P. Gobbo, B.O. Ross, Chem. Phys. Lett. 418 (2006) 311.
[16] D. Tzeli, A. Mavridis, J. Phys. Chem. A 110 (2006) 8952.
[17] A. Tsouloucha, I.S.K. Kerkines, A. Mavridis, J. Phys. Chem. A 107 (2003) 6062.
[18] S. Roszak, K. Balasubramanian, J. Chem. Phys. A 101 (1997) 2666.
[19] P. Jackson, G.E. Gadd, D.W. Mackey, H. van der Wall, G.D. Willett, J. Phys. Chem. A 102 (1998) 8941.
[20] M. Hendrickx, S. Clima, Chem. Phys. Lett. 388 (2004) 284.
[21] D. Majumdar, S. Roszak, K. Balasubramanian, J. Chem. Phys. 118 (2003) 130.
[22] A.V. Arbuznikov, M. Hendrickx, L.G. Vanquickenborne, Chem. Phys. Lett. 310 (1999) 515.
[23] B.K. Nash, B.K. Rao, P. Jena, J. Chem. Phys. 105 (1996) 11020.
[24] M.V. Ryzhkov, A.L. Ivanovskii, B.T. Delley, Chem. Phys. Lett. 404 (2005) 400.
[25] M. Hendrickx, S. Clima, Chem. Phys. Lett. 388 (2004) 290.
[26] A.V. Arbuznikov, M. Hendrickx, Chem. Phys. Lett. 320 (2000) 575.
[27] V.M. Rayón, P. Redondo, C. Barrientos, A. Largo, Chem. Eur. J. 12 (2006) 6963.
[28] V.M. Rayón, P. Redondo, C. Barrientos, A. Largo, J. Phys. Chem. A 111 (2007) 6345.
[29] P. Redondo, C. Barrientos, A. Largo, J. Phys. Chem. A 109 (2005) 8594.
[30] P. Redondo, C. Barrientos, A. Largo, J. Phys. Chem. A 110 (2006) 4057.
[31] R. Sumathi, M. Hendrickx, J. Phys. Chem. A 102 (1998) 4883.
[32] L. Largo, A. Cimas, P. Redondo, V.M. Rayón, C. Barrientos, Chem. Phys. 330 (2006) 431.
[33] L. Largo, A. Cimas, P. Redondo, V.M. Rayón, C. Barrientos, Int. J. Mass Spectrom. 266 (2007) 50.
[34] P. Redondo, C. Barrientos, A. Largo, J. Chem. Theory Comput. 2 (2006) 885.
[35] P. Redondo, C. Barrientos, A. Largo, J. Mol. Struct. (Theochem.) 769 (2006) 225.
[36] P. Redondo, C. Barrientos, A. Largo, Int. J. Mass Spectrom. 263 (2007) 101.

[37] H.J. Zhai, L.S. Wang, P. Jena, G.L. Gutsev, C.W. Bauschlicher Jr., J. Chem. Phys. 120 (2004) 8996.
[38] E.G. Noya, R.C. Longo, L.J. Gallego, J. Chem. Phys. 119 (2003) 11130.
[39] G.E. Froudakis, M. Muhlhauser, A.N. Andriotis, M. Menon, Phys. Rev. B 64 (2001) 241401-1.
[40] G. Grey, M.M.G. Alemany, O. Dieguez, L.G. Gallego, Phys. Rev. B 62 (2000) 12640.
[41] R.C. Longo, M.M.G. Alemany, B. Fernandez, L.J. Gallego, Phys. Rev. B 68 (2003) 167401-1.
[42] C. Barrientos, P. Redondo, A. Largo, J. Chem. Theory Comput. 3 (2007) 657.
[43] X. Li, L.-S. Wang, J. Chem. Phys. 111 (1999) 8389.
[44] L.S. Wang, X. Li, J. Chem. Phys. 112 (2000) 3602.
[45] B.V. Reddy, S.N. Khanna, Chem. Phys. Lett. 209 (1993) 104.
[46] P. Redondo, C. Barrientos, A. Largo, Int. J. Quantum Chem. (2008), doi:10.1002/qua.21582.
[47] A.D. Becke, J. Chem. Phys. 84 (1986) 4524.
[48] A.D. Becke, J. Chem. Phys. 88 (1988) 2547.
[49] G. Pascoli, H. Lavendy, Int. J. Mass Spectrom. 181 (1998) 11.
[50] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[51] A.D. Becke, J. Chem. Phys. 88 (1988) 1053.
[52] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[53] W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1133.
[54] A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033.
[55] P.J. Hay, J. Chem. Phys. 66 (1977) 4377.
[56] K. Ragavachari, G.W. Trucks, J. Chem. Phys. 91 (1989) 1062.
[57] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
[58] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millan, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelly, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Gaussian Inc., Pittsburgh, PA, 1998.
[59] C.L. Haynes, Y.M. Chen, P.B. Armentrout, J. Phys. Chem. 99 (1995) 9110.
[60] R.L. Hettich, B.S. Freiser, J. Am. Chem. Soc. 108 (1986) 2537.
[61] K. Raghavachari, J.S. Binkley, J. Chem. Phys. 87 (1987) 2191.
[62] G. Pascoli, H. Lavendy, J. Phys. Chem. A 103 (1999) 3518.
[63] H.J. Zhai, S.R. Liu, X. Li, L.S. Wang, J. Chem. Phys. 115 (2001) 5170.