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# Cyclic Carbon Cluster Dianions and Their Aromaticity

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**Abstract:** Cyclic carbon cluster dianions $(CC_2)_n^{2-}$ ($n = 3-6$) are investigated by ab initio methods with regard to their geometric properties, electronic stability, and aromaticity. The unique wheel-like structures of these dianions consist of a *n*-membered carbon ring, where a $C_2$ unit is attached to each carbon atom. All investigated dianions represent stable gas-phase dianions. While the smallest member of this family $(CC_2)_3^{2-}$ is clearly aromatic, the aromatic character decreases rapidly with increasing ring size. The geometries and the aromaticity of the cyclic clusters $(CC_2)_n^{2-}$ ($n = 3-6$) can be nicely explained using resonance structure arguments.

## 1. Introduction

Carbon clusters were and still are an intensively studied area. The investigations range from studies on such small clusters as $C_3$, which was detected in a carbon star,[1] to examinations of very big fullerenes, the most prominent of which is represented by the "buckyball" $C_{60}$.[2-5] Although these works were originally inspired by astronomy, the investigations of such clusters cover all fields of chemistry today. The reader is referred to some representative reviews in this field.[6-8] The investigations do not only address neutral clusters—also, positively and negatively charged clusters were examined.[9-11]

Especially the discovered doubly negatively charged carbon clusters are of great interest since they represent the first *small* dianionic species observed in the gas phase.[12] The existence of small isolated dianions is not trivial due to the strong Coulomb repulsion between the excess negative charges. This electrostatic repulsion must be compensated to form an electronically stable gas-phase dianion. Indeed, this is the reason most of the "classical" multiply charged anions (MCA) were found to be unstable with respect to electron emission, e.g., the prominent "textbook" MCAs $CO_3^{2-}$,[13,14] $SO_4^{2-}$,[13,15,16] and $PO_4^{3-}$,[15] which are well known in condensed-phase chemistry. These MCAs have very short lifetimes when they are isolated in the gas phase[17,18] and spontaneously emit one or more electrons without experiencing the stabilizing effects of neighboring atoms or counterions. Thus, they do only exist in solution or solid phase.[19]

Until today, several dianions have been found to be stable in the gas phase, both experimentally and theoretically. Examples are some fluoro or chloro complexes of alkali, earth alkali, and heavy metals $LiF_3^{2-}$,[14] $BeF_4^{2-}$,[20,21] and $PtCl_6^{2-}$ [22] and mixed silicon−carbon and beryllium−carbon clusters $SiC_6^{2-}$ [23,24] and $BeC_4^{2-}$,[25] etc. The research field of MCAs in the gas phase is summarized in several reviews.[26-30]

Here, we focus on the pure carbon clusters dianions $C_n^{2-}$ ($n = 7-28$), which were observed by Schauer et al. in a double-focusing mass spectrometer.[12] They produced these dianions by sputtering a graphite surface with cesium ions. The dianionic carbon clusters were proposed to have a linear structure, which is the most stable geometry for monoanionic carbon clusters.[4,31]

Indeed, the even *n* isomers of the carbon dianions $C_n^{2-}$ do exhibit strictly linear geometries,[31] but in contrast, the odd *n* isomers, first $C_7^{2-}$ and $C_9^{2-}$, possess only branched isomers

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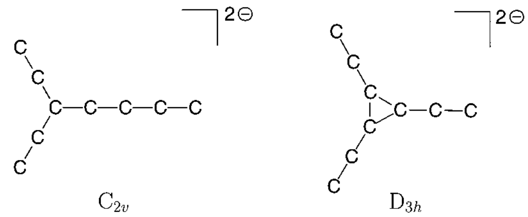

***Figure 1.*** Stable isomers of the carbon cluster dianion $C_9^{2-}$.[33]

that are stable with respect to electron emission.[32,33] The only stable isomer of $C_7^{2-}$ has a starlike $D_{3h}$ symmetric structure and is better referred to as $C(C_2)_3^{2-}$.[32] The dianion $C_9^{2-}$ possesses two electronically stable isomers, the structures of which are displayed in Figure 1. While the $C_{2v}$ symmetric dianion can be formally obtained from the $D_{3h}$ symmetric $C_7^{2-}$ simply by elongation of one of the branches by a further $C_2$ group, the $D_{3h}$ symmetric isomer of $C_9^{2-}$ has some unique properties. Its structure can be regarded as a cyclopropenylium cation whose three hydrogen atoms have been substituted by three acetylide $C_2^-$ groups. Thus, this isomer may have, in analogy to the simple cyclopropenylium cation and according to Hückels $4n + 2\pi$-electron rule, aromatic character.

Enlarging the inner carbon ring by a further carbon atom and adding another $C_2^-$ unit, a similiar cyclic $C_{12}^{2-}$ dianion can be constructed. This system can be seen as a cyclobutadienyl dication with all four hydrogens substituted by acetylide groups. Analogously, this dianion should be aromatic, too. The explained construction principle can be driven further to construct wheel-like mutually aromatic $C_{15}^{2-}$, $C_{18}^{2-}$, etc., dianions, which can be written as the homologous series of cyclic $(CC_2)_n^{2-}$ dianions.

In this report, we address two questions. First, we examine the geometries and the stability with respect to electron emission of the cyclic $(CC_2)_n^{2-}$ ($n = 3-6$) dianions using straightforward quantum chemical techniques (sections 3 and 4). Second, the possible aromaticity of these dianions will be investigated (section 5). For this objective, we use a geometric criterion as well as *nuclear independent chemical shifts* (NICS), which are well established to be a reliable measure for aromaticity. The NICS criterion was employed on such different systems as, for example, five-membered heterocycles,[34] inorganic benzene analogues,[35] the three-membered ring $C_3Li_3^+$,[36] and borane cages.[37] One interesting class of recently investigated compounds is the series of oxocarbon dianions $(CO)_n^{2-}$,[38] the aromatictity of which has been discussed since 1960.[39] These clusters are analogues to our $(CC_2)_n^{2-}$ dianions because they can be obtained from each other by exchanging oxygen atoms with $C_2$ groups and vice versa. Thus, we finally compare our calculated NICS values of the cyclic carbon clusters $(CC_2)_n^{2-}$ with those obtained by Schleyer et al. for the $(CO)_n^{2-}$ clusters.[38] Here we stress that the $(CO)_n^{2-}$ dianions are electronically unstable as free entities while the $(CC_2)_n^{2-}$ clusters are stable dianions.

## 2. Computational Methods

All calculations were done within the framework of the Gaussian 98[40] and ACES II[41] ab initio packages of programs.

Within the calculations, a Cartesian Gaussian-type double-$\zeta$ basis set,[42] representing a contraction of Huzinaga's primitive sets,[43] was employed. Additionally, the set was augmented with a set of d-type polarization functions. This basis set is referred to as DZP and proved to be sufficiently accurate to verify electronic stability in a previous theoretical investigation of $(CC_2)_3^{2-}$,[33] which is the smallest member of the $(CC_2)_n^{2-}$ series. To examine the dependence of the geometrical parameters of the carbon cluster dianions on the basis set, we additionally augmented the DZP basis set with diffuse functions. A set of p-type functions with an exponent of 0.034 and a s-type function with an exponent of 0.0454 were added leading to the DZP(p) and DZP(sp) basis sets. These larger, diffuse basis sets had only negligible effects on the geometric parameters of the smaller $(CC_2)_n^{2-}$ clusters ($n = 3-5$); thus, we decided to use the DZP basis set as standard in geometry optimizations, unless otherwise mentioned. For the calculation of the NICS values, we used both the DZP and DZP(sp) basis sets, and as we will see later, we obtained similar results. To check for contributions of higher angular momentums and to get a feeling for the reliability of the calculated NICS values, we also used the large aug-cc-pVTZ basis set,[44] which includes sets of d- and f-type functions.

Geometry optimizations of the compounds $(CC_2)_n^{2-}$ ($n = 3-6$) were first performed at the independent particle level using the self-consistent field (SCF) restricted Hartree−Fock (RHF) technique. The geometry was further refined using correlated methods, mainly Møller−Plesset pertubation theory of second order (MP2) and for the smaller clusters ($n = 3-5$) coupled cluster singles and doubles (CCSD).[45] The stationary points found on the corresponding potential energy surface (PES) were tested by an analysis of the harmonic vibrational frequencies. By checking for imaginary frequencies, whether the stationary points represent minimums or mere saddle points was tested.

After having established the equilibrium geometries, we turned to the investigation of the electronic stability of the dianionic carbon clusters at the calculated respective geometries. The stability with respect to electron emission was checked by direct as well as by indirect methods. First, one can determine the binding energy of the excess electron, equivalent to the electron detachment energy (EDE), by employing Koopman's theorem (KT), which relates the EDE to the negative of the orbital energy of a RHF calculation. Another possibility to calculate the EDE directly is given by the outer-valence Green's function (OVGF) approach.[46,47] This method includes electron correla-

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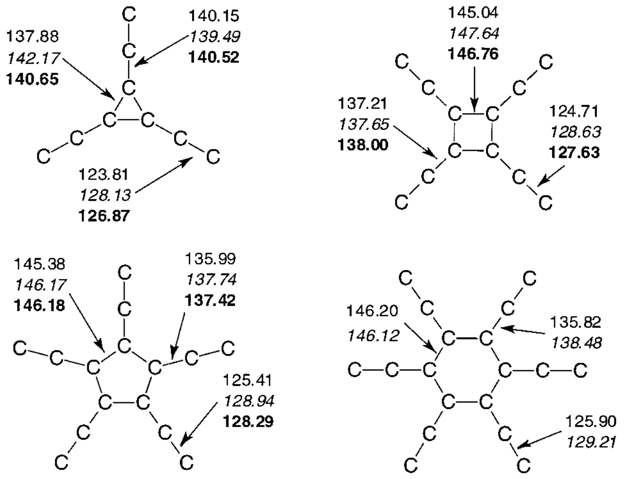

***Figure 2.*** Optimized bond lengths (pm) of the $(CC_2)_n^{2-}$ ($n = 3-6$) clusters at $D_{nh}$ symmetry obtained at the SCF (plain text), MP2 (italics), and CCSD (bold) levels of theory using the DZP basis set. Note that the $D_{6h}$ symmetric isomer of $(CC_2)_6^{2-}$ does not correspond to a minimum on the PES but to a saddle point with three imaginary frequencies at the RHF level of theory.

tion and orbital relaxation effects; hence, it yields improved orbital energies compared to KT. Second, indirect methods were used to determine the EDE. This is done by calculating the difference of the total energies of the monoanion and the dianion; thus, they are referred to as Δ methods. We have employed different levels of theory, leading to ΔSCF , ΔMP2, and ΔCCSD values. Note that a positive value of the EDE corresponds to a stable dianion with respect to electron autodetachment, in the sense that energy has to be applied to detach an electron.

The NICS values were computed using the gauge-including atomic orbital (GIAO) method at the RHF level of theory. The nuclear magnetic resonance (NMR) parameters are calculated for a ghost atom in the framework of the Gaussian 98 package of programs. The NICS is defined as the negative of the isotropic magnetic shielding constant of this ghost atom. Aromaticity of a ring or cage system can be investigated by computing the NICS for a ghost atom placed in the center of the ring (NICS(0)) or 1 Å above the center (NICS(1)). If the corresponding NICS has a clearly negative value, aromaticity is given.[34,35]

## 3. Geometries and Energetics

The geometries of the $(CC_2)_n^{2-}$ clusters were optimized at the RHF level and at the correlated MP2 and CCSD levels of theory using the DZP basis set. Figure 2 summarizes the optimized bond lengths at $D_{nh}$ geometry of the $(CC_2)_n^{2-}$ clusters. The smaller investigated $(CC_2)_n^{2-}$ clusters ($n = 3-5$) favor this highly symmetric minimum structure where they possess only real frequencies. Thus, they are planar and no bond alternation does occur, which is a geometrical criterion for Hückel-type aromatics, discussed further below (section 5). Analysis of the harmonic frequencies of the $(CC_2)_6^{2-}$ dianion gives three imaginary values and consequently the $D_{6h}$ symmetric structure does not represent a local minimum on the PES. The geometry of $(CC_2)_6^{2-}$ is investigated separately in detail below, since it is a difficult task to definitely establish its ground-state structure.

The obtained lengths for the C−C bonds within the ring of 141 pm for $(CC_2)_3^{2-}$ and ∼146 pm for the larger carbon clusters lie between the standard values of 154 pm for a single and 132 pm for a double carbon−carbon bond. Values of 141 pm for $(CC_2)_3^{2-}$ and ∼138 pm for $(CC_2)_{4-6}^{2-}$ are calculated for the distances between the $C_2$ groups and the ring, also indicating an intermediate between a single and a double bond, whereas the bond lengths within the $C_2$ groups are found to vary between 127 and 129 pm, which is in the range between a double and a triple bond (121 pm). These general trends can be explained in the framework of a simple model. If one looks at the Lewis structure of the $(CC_2)_n^{2-}$ clusters, one can always draw $n$ allenic resonance structures, omitting structures with bonds across the ring, and one aromatic structure. These resonance structures are shown in Figure 3 for the smallest dianionic cluster $(CC_2)_3^{2-}$. From this picture, it is clear that the bonds within the ring and between the $C_2$ groups and the ring range between a single and a double bond. Furthermore, the bond within the $C_2$ groups is partly a double and partly a triple bond. The simple Lewis resonance structures thus explain the observed bond lengths quite nicely.

Comparing the bond lengths of the $D_{nh}$ symmetric dianionic clusters, some trends can be seen. The distance of two carbon atoms within the rings increases with increasing ring size, indicating that the ring bonds gradually lose double and gain single bond character. This corresponds to the fact that in all allenic resonance structures only one double bond can be assigned to the ring. For example, in the four-membered ring, there are one double and three single bonds within the ring, resulting in a formal bond order of $1^1/_4$ for each bond. The same argumentation leads to a bond order of $1^1/_5$ for the ring bonds of the five-membered ring and so on. Hence, the double bond character of this bond decreases and the increase of the carbon ring bond lengths is explained by this simple picture.

The bond lengths between the ring and the $C_2$ groups and within the $C_2$ groups remain essentially constant and only a weak trend toward bond length equilibration can be observed with cluster size. This is interpreted as follows. As the cluster size increases, the acetylenic structure of the $C_2$ groups becomes more and more allenic in character, being consistent with the decreasing negative partial charge on the outer carbon atom of the $C_2$ groups shown in Table 1. Using the same resonance structure argument discussed above, the structure in which a particular $C_2$ group is acetylenic becomes gradually less important, while the number of the other resonance structures, which all include an allenic structure for this $C_2$ group, increases. The observed bond length equilibration is thus also easily explained within the resonance structure model.

Regarding the stability of the calculated structures above, one point to note is that all investigated $(CC_2)_n^{2-}$ cluster dianions are stable with respect to fragmentation. This is due to the fact that the clusters are covalently bound and thus high energies are necessary to break any bond.

As mentioned above, the geometry of the largest investigated carbon cluster dianion $(CC_2)_6^{2-}$ appears to be more complicated than those of the smaller ones. The three imaginary frequencies of the $D_{6h}$ symmetric structure indicate a high-order saddle point on the PES. To obtain the minimum geometry of the $(CC_2)_6^{2-}$ cluster, various isomers ($D_{3d}$, $D_2$, $C_{2v}$, and $C_s$ symmetric ones) were suggested and their geometries independently optimized at the RHF as well as at the MP2 level of theory. The differences in energy and numbers of imaginary frequencies of these geometries are given in Table 2. At the RHF level of theory, a $C_s$ symmetric minimum is found by employing the DZP basis set. Structures of this symmetry are also found to lie low in

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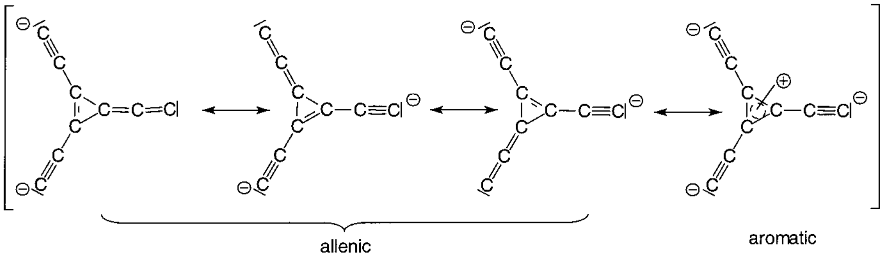

***Figure 3.*** Resonance structures for the $(CC_2)_3^{2-}$ cluster. One aromatic and three allenic resonance structures can be drawn.

***Table 1.*** Mulliken Charge Distribution of the $(CC_2)_n^{2-}$ Dianions ($n$ = 3−6) Using the Nondiffuse DZP Basis Set[a]

| ring size | symmetry | opt. with | $C_{ring}$ | $C_{inner(C2)}$ | $C_{outer(C2)}$ |
|---|---|---|---|---|---|
| 3 | $D_{3h}$ | CCSD | 0.163 | −0.575 | −0.255 |
| 4 | $D_{4h}$ | CCSD | 0.211 | −0.502 | −0.209 |
| 5 | $D_{5h}$ | CCSD | 0.231 | −0.432 | −0.199 |
| 6 | $D_{6h}/D_{3d}$ | MP2 | 0.209 | −0.393 | −0.149 |

[a] For $(CC_2)_6^{2-}$, essentially the same charge distribution was found at both the $D_{6h}$ and $D_{3d}$ symmetric geometries.

***Table 2.*** Energy Differences between Various Stationary Points of the $(CC_2)_6^{2-}$ Dianion at the SCF as Well as the MP2 Level of Theory[a]

| symmetry | $E_{rel}^{SCF}$ (kJ/mol) | $E_{rel}^{MP2}$ (kJ/mol) |
|---|---|---|
| $D_{6h}$ | 0 (3) | 0 |
| $D_{3d}$ | −0.42 (2) | −2.44 |
| $D_2$ | −1.667 (2) | $\rightarrow D_{6h}$ |
| $C_{2v}$ | −1.673 (1) | $\rightarrow D_{6h}$ |
| $C_s$ | −1.742 (0) | $\rightarrow D_{3d}$ |

[a] At the SCF level of theory, the number of imaginary frequencies is given in parentheses behind the energy difference. Note that the $C_s$ symmetric structure is the minimum at the SCF level, but starting at this structure converges to a $D_{3d}$ symmetric geometry at the MP2 level of theory.

energy with the larger basis sets DZP(p) and DZP(sp). Employing the DZP(p) basis set, the minimum structure is found to favor $D_2$ symmetry, and employing the DZP(sp) basis set, it is totally asymmetric. On the MP2 level of theory, the results are more consistent. Starting the search for the minimum at the above symmetries, only two structures remain. Optimization of the structure with the DZP basis set ends in all cases at $D_{6h}$ or $D_{3d}$ symmetry.

Starting with structures of $D_2$ and $C_{2v}$ symmetry, we obtained the $D_{6h}$ optimized structure, whereas starting with $C_s$ symmetry, we obtained the $D_{3d}$ optimized structure. Note that $D_2$ and $C_{2v}$ are subgroups of $D_{6h}$, but not of $D_{3d}$. The contrary applies to $C_s$, which is a subgroup of both $D_{6h}$ and $D_{3d}$. Furthermore, using the larger DZP(p) basis set, the optimization at the MP2 level of theory did not converge for any other than $D_{6h}$ and $D_{3d}$ symmetric structures. The energy difference between the $D_{6h}$ and the $D_{3d}$ symmetric structures has a value of −2.44 kJ/mol at the MP2 level of theory using the DZP basis set. Using the larger DZP(p) basis set, the energy difference increases to −12.0 kJ/mol; i.e., the $D_{3d}$ symmetric structure is further favored by a lower energy. These values indicate that the $D_{3d}$ symmetric structure is the equilibrium geometry of $(CC_2)_6^{2-}$, although we were not able to obtain the harmonic frequencies or to carry out the optimization using even larger basis sets to establish this conclusion beyond doubt.

One further aspect is that all stationary points of $(CC_2)_6^{2-}$ lie close in energy and the lowest eigenfrequencies are very small at the RHF level of theory, suggesting a shallow PES. It remains a difficult task to conclude which is the true minimum geometry, and high-level theoretical methods have to be employed. Arguing from an electrostatic point of view, the most probable structures are those where the negatively polarized $C_2$ groups can arrange themselves most distantly. Since only $D_{6h}$ and $D_{3d}$ symmetric structures were found at the MP2 level of theory, this geometric criterion can be easily applied. The $D_{3d}$ symmetric structure corresponds to a chairlike geometry of the ring and thus allows for a greater distance between the $C_2$ groups than the $D_{6h}$ symmetric structure does. This supports the MP2 computational findings discussed above that the $D_{3d}$ symmetric structure is the most probable minimum geometry. We shall use the geometry obtained at the MP2 level of theory (DZP basis set) for the investigation of the aromaticity in section 5. This geometry is pictured in Figure 4.

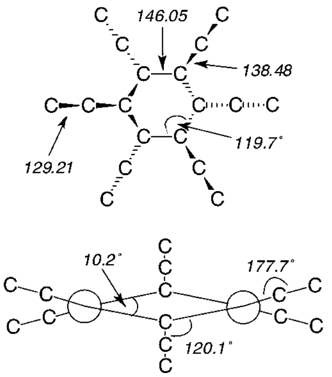

***Figure 4.*** Equilibirum geometry of $(CC_2)_6^{2-}$ with $D_{3d}$ symmetry as concluded in section 3. The geometrical parameters were obtained using the DZP basis sets at the MP2 level of theory. The molecule is shown in top view (upper part) and in front view in a quasi Newman projection along two parallel C−C bonds (lower part).

## 4. Electronic Stability

The vertical electronic stability of the carbon cluster dianions has been investigated by employing KT, OVGF, ΔSCF, ΔMP2, and ΔCCSD using the DZP basis set. One point to note is that vertical EDEs were calculated, which reflect the stability of the dianion at its equilibrium geometry at the corresponding level of theory. These EDEs take account for electron loss of the dianion without allowing for relaxation of the geometry of the created monoanion. The obtained EDEs are given in Table 3.

At the level of KT, all investigated dianions are electronically stable. However, it is a well-known fact that KT tends to overestimate the binding energy of the excess electron,[24,32,33] since orbital relaxation is excluded. Taking only this relaxation effect into account by a ΔSCF calculation, the monoanion is stabilized in comparison to the dianion and the EDEs are observed to decrease, e.g., for $(CC_2)_4^{2-}$ from 124 kJ/mol at KT to 67 kJ/mol at ΔSCF. Including also electron correlation effects

***Table 3.*** Vertical EDEs (kJ/mol) of the $(CC_2)_n^{2-}$ Dianions ($n$ = 3−6), Which Have Been Calculated Using the DZP Basis Set[a]

| ring size | KT | OVGF | ΔSCF | ΔMP2 | ΔCCSD |
|---|---|---|---|---|---|
| 3 | 110 | 82.1 | 50.7 | 72.9 | 65.0 |
| 4 | 124 | 120 | 67.2 | 140 | 92.8 |
| 5 | 119 | 152 | 70.2 | 210 | |
| 6 ($D_{6h}$) | 117 | - | 76.2 | - | |
| 6 ($D_{3d}$) | 112 | - | 70.4 | 248 | |

[a] 96.49 kJ/mol = 1 eV × $N_A$.

by using the ΔMP2, ΔCCSD, and OVGF methods, the EDE increases again, for example, to 140, 93, and 121 kJ/mol, respectively, for the $(CC_2)_4^{2-}$ dianion. This is due to the fact that the correlation energy of a $N$ electron system (dianion) is expected to be larger than that of a $N - 1$ electron system (monoanion). A similar trend is also observed for the other $(CC_2)_n^{2-}$ dianionic clusters.

In general, it is possible to take the relaxation of the geometry of the monoanion into account by calculating the total energy of the monoanion at its separately optimized geometry. So-called adiabatic EDEs are obtained by calculating the difference between the energies of the optimized monoanion and the optimized dianion. The $C_9^{2-}$ cluster dianion, the smallest member of the $(CC_2)_n^{2-}$ series, already has been proven to be stable both vertically and adiabatically.[33] Since the larger clusters are vertically more stable than $C_9^{2-}$, it is thus not necessary to compute the adiabatic EDEs for the larger clusters (with $n$ = 4−6) to establish overall electronic stability.

When comparing the calculated EDEs of the $(CC_2)_n^{2-}$ clusters with different $n$, one notices that the cluster dianions become gradually more stable with increasing $n$. At the ΔSCF level of theory, the increase of stability with size is much more moderate than that reflected by the available data computed using more advanced methods. As seen in Table 3, electron correlation plays an essential role in stabilizing the excess electron. The rather slow increase in stability with size found at the ΔSCF level may be anticipated from electrostatic considerations. Electrostatically, the increase in stability is subject to two opposing effects: Due to the decreasing bond angle between the ring and the $C_2$ groups with increasing $n$, the distance between the negatively polarized $C_2$ groups becomes smaller, thus increasing the Coulomb repulsion between these units. This just runs oppositely to the stabilizing effect caused by charge delocalization: the excess negative charge becomes more and more delocalized because of the enlarged ring and the growing number of $C_2$ groups.

The observed stability of the $(CC_2)_n^{2-}$ clusters is in contrast to the analogue oxocarbon dianions $(CO)_n^{2-}$ examined theoretically by Schleyer et al.,[38] which are all clearly unstable with respect to electron emission already at the theoretical level of KT. A general trend can be established based on these results: By exchanging oxygen atoms in an unstable dianion by $C_2$ groups, one gets an enormous amount of stabilization energy regarding electron loss. As already observed in the case of the $D_{3h}$ symmetric systems $CO_3^{2-}$ and $C_7^{2-}$,[32] respectively, this trend is easily explained by comparing the electron affinities (EA) of the groups. Oxygen atoms have an EA of 210 kJ/mol, whereas the $C_2$ group has an EA of 310 kJ/mol,[48,49] providing a much better ability to stabilize excessive negative charge. A second stabilizing effect is simply that this formal exchange yields spatially more extended molecules, making a better delocalization of the excess negative charges and thus a smaller Coulomb repulsion possible.

## 5. Aromaticity

Traditionally, a geometrical criterion for aromaticity is that no bond alternation in the investigated ring occurs. Another maybe more stringent criterion for aromaticity often used recently is provided by negative NICS values. Interestingly, the geometric criterion is not a necessary one, as one might by tempted to expect. Choi and Kertesz observed negative NICS values, i.e., aromaticity, in large annulenes with $4n + 2\pi$-electrons despite the appearance of bond alternation.[50] Nevertheless, in most cases, the non-bond-alternation criterion corresponds well to aromaticity and we will discuss it in our treatment of the $(CC_2)_n^{2-}$ clusters as well.

As shown above, the small $(CC_2)_n^{2-}$ clusters (with $n = 3-5$) exhibit a $D_{nh}$ symmetric geometry. This implicitly requires that all bonds within the ring possess the same length. Following the non-bond-alternation criterion, this provides evidence for their aromaticity. Although the largest investigated cluster $(CC_2)_6^{2-}$ probably does not possess a $D_{6h}$ symmetric structure, it is almost planar, as indicated by the small dihedral angle of 10.2° within the ring. Additionally, no bond alternation occurs according to its most likely $D_{3h}$ symmetric structure. Thus, it is still likely that this dianionic cluster has some aromatic character.

To further establish the degree of aromaticity of these compounds, we employed a magnetic criterion which mirrors the ring current. We calculated *nuclear independent chemical shifts*, a criterion that is well known under the abbrevation NICS and is efficiently and easily computed as the negative of the magnetic shielding at the center of ring systems or at other distinctive points. Large negative values correspond to dominating diatropic ring currents; hence, aromaticity, positive values indicate dominating paratropic ring currents, hence antiaromaticity. The NICS values have been shown to agree well with energetic, geometric, and other magnetic criteria of aromaticity, especially in five-membered heterocycles.[34] The NICS(0), meaning the value at the geometrical center of the ring, however, is influenced by effects from the $\sigma$-bonds. Thus, it is better to calculate also the nuclear independent chemical shift 1 Å above the ring plane, because this NICS(1) is mainly effected by contributions of the $\pi$-bonds. It provides a more reasonable estimate of the ring current and the aromaticity of the molecule.[35]

The computed NICS values for the $(CC_2)_n^{2-}$ dianions are collected in Table 4, as well as values for the $(CO)_n^{2-}$ clusters investigated by Schleyer et al.[38] (see section 1). For comparison, we include NICS values for their systems that we recalculated with the DZP and DZP(sp) basis set, because they used the 6-31+G* basis set,[51,52] and unfortunately, severe linear dependencies in the 6-31+G* basis set were detected when they were employed for our $(CC_2)_n^{2-}$ clusters with $n$ = 4,5. No convergence of the RHF equations has been achieved and thus no NICS values are available employing the 6-31+G* basis set for these two systems. But these missing values are not particularly

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***Table 4.*** Comparison of NICS Values (ppm) of $(CC_2)_n^{2-}$ and $(CO)_n^{2-}$ Obtained with Different Basis Sets at $D_{nh}$ Geometry for $n = 3-5$, $D_{3d}$ Geometry for $(CC_2)_6^{2-}$, and $D_2$ Geometry for $(CO)_6^{2-a}$

| system ring size | basis | $(CC_2)_n^{2-}$ NICS(0) | $(CC_2)_n^{2-}$ NICS(1) | $(CO)_n^{2-}$ NICS(0) | $(CO)_n^{2-}$ NICS(1) |
|---|---|---|---|---|---|
| 3 | DZP | −31.6 | −13.0 | −34.9 | −11.1 |
| | DZP(sp) | −30.8 | −12.5 | −35.6 | −10.9 |
| | 6-31+G* | −31.6 | −13.1 | *−36.2* | *−11.0* |
| | aug-cc-pVTZ | −32.5 | −12.5 | | |
| 4 | DZP | +6.7 | −6.1 | −4.5 | −8.5 |
| | DZP(sp) | +8.2 | −4.7 | −5.8 | −8.8 |
| | 6-31+G* | | | *−5.0* | *−8.6* |
| | aug-cc-pVTZ | +6.8 | −5.0 | −7.3 | −8.2 |
| 5 | DZP | +8.5 | −4.1 | +3.3 | −6.0 |
| | DZP(sp) | +10.8 | −1.6 | +2.6 | −6.4 |
| | 6-31+G* | | | *+3.9* | *−5.8* |
| 6 | DZP | +9.6 | −1.1 | 2.9 | −4.5 |
| | DZP(sp) | +10.7 | −0.1 | 2.8 | 4.7 |
| | 6-31+G* | | | +3.1[b] | *−4.3* |

[a] Values in italics are taken from ref 38. No convergence of the RHF procedure was achieved for $(CC_2)_n^{2-}$ ($n = 4-6$) using the 6-31+G* basis set. [b] Recalculated by us; original value of 7.9 is misprinted.

relevant as all other NICS values obtained with different basis sets are consistent with each other for a specific cluster.

Taking diffuse functions into account does not alter the NICS values substantially. Since we are mainly interested in investigating trends, the calculated values are sufficiently reliable. This is supported by the calculation of the NICS values with the large basis set aug-cc-pVTZ for $(CC_2)_3^{2-}$ and $(CC_2)_4^{2-}$, yielding values that agree quite well with those obtained by employing the smaller basis sets (see Table 4). To consistently compare all clusters studied, the values computed with the DZP(sp) basis set are used in the following.

Since the NICS(1) value increases from −12.5 for $(CC_2)_3^{2-}$ to −4.7 for $(CC_2)_4^{2-}$, −1.6 for $(CC_2)_5^{2-}$, and −0.1 for $(CC_2)_6^{2-}$, the aromaticity decreases with increasing ring size. Although $(CC_2)_3^{2-}$ is approximately as aromatic as benzene, which has a NICS(1) value of −9.7,[34] the next two of the series are only slightly aromatic and the largest investigated cluster has essentially no aromaticity. This trend can again be explained with the help of the resonance structures described above: For each carbon cluster dianion, only one aromatic resonance structure can be drawn, whereas there are always $n$ allenic resonance structures. Thus, with increasing $n$, the aromatic resonance structure becomes less and less important, consequently leading to a decrease in the aromatic character of the clusters.

Comparing our carbon cluster dianions $(CC_2)_n^{2-}$ with the mixed oxocarbon clusters investigated by Schleyer et al., one observes that only the NICS(1) value of the smallest carbon cluster dianion, $(CC_2)_3^{2-}$, is more negative than that of the corresponding oxocarbon dianion $(CO)_3^{2-}$. For the larger cluster dianions on the other hand, the NICS(1) values of the pure carbon clusters are clearly less negative than those of the oxocarbon clusters, indicating less aromaticity of these pure carbon dianions.

## 6. Summary and Conclusion

In this paper, the cyclic carbon cluster dianions $(CC_2)_n^{2-}$ ($n = 3-6$) were investigated. Their geometry was optimized at the independent particle level and at correlated levels of theory. For the smaller cluster dianions with $n = 3-5$, a symmetric, planar $D_{nh}$ minimum structure was found. The largest investigated cluster $(CC_2)_6^{2-}$ has a shallow potential energy surface, and thus, it is a difficult task to establish its ground-state structure with certainty. From the results at the MP2 level of theory and based on electrostatic arguments, it was concluded that this cluster does not possess a $D_{6h}$ symmetric, but probably a chairlike $D_{3d}$ equilibrium geometry.

The stability of the cyclic $(CC_2)_n^{2-}$ dianions with respect to electron autodetachment was investigated at different levels of theory. All yielded clearly positive values for the EDE, and an increasing electronic stability with increasing cluster size was observed. Since fragmentation can be excluded for the covalent carbon cluster dianions, all examined $(CC_2)_n^{2-}$ dianions represent stable compounds and are predicted to be observable in the gas phase.

The aromaticity of the cluster dianions $(CC_2)_n^{2-}$ decreases with increasing $n$. This behavior is manifested in the calculated NICS values, which gradually become less negative when going from $(CC_2)_3^{2-}$ to $(CC_2)_6^{2-}$. Also, the fact that the $(CC_2)_6^{2-}$ cluster seems to possess a nonplanar $D_{3d}$ symmetric ground-state structure supports this tendency.

The computed quantities exhibit systematic trends as a function of the systems size. A simple resonance structure model considering the interplay of allenic and aromatic structures explains nicely the observed trends and provides chemical insight into the results.

Finally, we stress that aromaticity is not a useful property for a dianion to stabilize the excess negative charges. Of course, the examined dianions are stable with respect to electron emission and have aromatic character, but the electronic stability increases as the aromatic character decreases. In a recent combined experimental and theoretical work on the electronic stability of the dianionic species succinate and acetylene dicarboxylate, hints are given that delocalization of both charges in one $\pi$-system is very unfavorable to stabilize the excess negative charges.[53] This also is well in agreement with our findings. Furthermore, very recent calculations on the aromatic cyclooctatetraene dianion $C_8H_8^{2-}$ has clearly shown that this system is highly unstable with respect to electron emission and does not show enhanced stability.[54]

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