

Energetics and bonding in small lithiated carbon clusters

Anthony D. Patrick, Andrew Skene, Estela Blaisten-Barojas *

Computational Materials Science Center, College of Science, George Mason University, MSN 6A2, Fairfax, VA 22030, USA

Received 14 October 2006; accepted 14 December 2006

Available online 27 December 2006

Abstract

Small carbon clusters metallized with Li were studied within a hybrid density functional approach with generalized gradient correction. Structures of the ground state and several excited states associated with different isomers and multiplicities were systematically calculated for C_xLi_y , with $x = 1-3$ and $y = 1-5$. The most stable isomers are either linear or planar in the ground state. Three-dimensional structures are only identified for CLi_4 , CLi_5 , and C_3Li_4 . There is important charge transfer in these compounds, showing that ionic bonding is favored as the cluster grows in size. Ionization potentials, electron affinities, and the vibrational analysis of all studied states is provided for all clusters. Structural transitions are predicted for C_2Li_2 at 1400 K and C_2Li_4 at 420 K.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Aerosols; Carbon metallization; Molecular clusters; Density functional theory; Vibrational analysis

1. Introduction

The early metallization of small carbon clusters has an intrinsic interest for the aerosol community. From the perspective of carbon compounds, it is important to understand unusual geometries that macromolecules containing Li and other electropositive elements acquire in the early stages of their formation. It is recognized that small molecular units are the building blocks of complex molecular assemblies and that the characteristics of those building blocks are fundamental in determining the structure of the assembly. For example, boron carbide crystals are known as ceramic materials displaying the antifluorite structure, in which the B atoms lie in tetrahedral coordination and the C atoms in octahedral. However, a few studies of boron molecular compounds show the preference for bridged or planar structures [1,2]. Some poly lithium carbon compounds are predicted to exhibit planar rather than tetrahedral carbon atoms [3,4], while other compounds have electron deficient bridging lithium sites [5,6]. Intercalation compounds such as graphite have layered structures that

allow for insertion of atoms or small clusters between layers. Lithium intercalated graphite is of great interest because of the high charge capacity. Cluster models have been developed to simulate this bulk material [7].

In this work, we perform an exhaustive all-electron study within the density functional theory (DFT) framework and the generalized gradient approximation (GGA) of C_xLi_y clusters containing up to three carbon atoms and five metal atoms. Methods are explained in more detail in Section 2, which includes the results for the CLi molecule. The energetics and vibrational frequencies for the family of five CLi_x clusters are described in Section 3. The next two Sections 4 and 5, contain the results for nine binary clusters C_2Li_x and C_3Li_x , respectively. Concluding remarks are given in Section 6.

2. Methods and the CLi molecule

The Kohn–Sham equations [8] were solved self-consistently within the GGA representation and using Becke's 3-parameter hybrid method which includes a combination of Hartree–Fock (HF) exchange with DFT correlation energies [9]. The Gaussian 03 package [10] was used throughout this work with the adoption of the B3PW91

* Corresponding author.

E-mail address: blaisten@gmu.edu (E. Blaisten-Barojas).

hybrid density functional approach containing the Purdue and Wang local and non-local correlation functionals [11,12]. A triple valence basis set (6-311g) containing 8s, 7p, and 1d gaussians contracted as (62111111,3311111,3) and augmented with one *d* polarization function was used throughout. We found this basis set to be sufficiently large to give good results at a reasonable computational effort. Additional s or p diffuse functions produced insignificant changes in both the energy and bond length of the diatomics, and were not added for the calculations of the larger clusters.

The selection of the density functional is based on a validation done on the ground state and first excited state of CLi compared with full CI, CASSCF and MP2 calculations. For these systems the B3PW91 functional hybrid yielded the best agreement. The basis set superposition error (BSSE) [13] gave corrections on the order of 0.02 eV for calculations with one or two polarization functions. Worth noting is that BSSE is important when the basis set is small, whereas the basis set used in this work is large and small BSSE corrections are expected.

Our calculations for the lower two states of CLi are in excellent agreement with previous CI results [14,15]. The ground state is a $^4\Sigma^-$ that dissociates into $C(^3P)$ and $Li(^2S)$ states with a dissociation energy $D_e = 2.6733$ eV and constants $R_e = 1.884$ Å, $\omega_e = 693$ cm $^{-1}$, $\omega_{ex_e} = 5.57$ cm $^{-1}$, $B_e = 1.072$ cm $^{-1}$, $\alpha_e = 4.83$ Å 3 , $\mu_e = 6.12$ D and Morse $\beta = 1.204$ Å $^{-1}$. Round-off Mulliken atomic charges on the two atoms are 0.47*e*, carbon been negative. The ionization potential is 7.77 eV and the electron affinity is 0.52 eV. Both of these quantities were calculated as differences between the energy of the ground state of neutral and cation or anion without considering the zero point energy. The ground state of the cation is $^3\Pi$ and that of the anion is a $^3\Sigma^-$.

The first excited state is a $^2\Pi$ that lies 1.512 eV above the ground state with a dissociation energy $D_e = 1.19$ eV and constants $R_e = 2.080$ Å, $\omega_e = 558$ cm $^{-1}$, $\omega_{ex_e} = 9.65$ cm $^{-1}$, $B_e = 0.88$ cm $^{-1}$, $\alpha_e = 9.64$ Å 3 , $\mu_e = 6.11$ D and Morse $\beta = 1.47$ Å $^{-1}$.

The binding energies and dipole moment of the ground and first excited states are reported in Table 1 (structures 1-1a and 1-1b). It is important to note that this is a highly dipolar molecule. The vibrational frequencies are given in Table 2. Results in forthcoming sections do not include the BSSE correction. However, we did test for BSSE with calculations up to CLi $_2$ and found a decrease of 0.03 eV in the total energy for this cluster size.

3. Carbon–lithium $_x$ clusters, $x = 2, 3, 4, 5$

In this section, we describe the energetics for four clusters CLi $_x$, with $x = 2-5$. The larger clusters belong to the hypervalent family and might be considered as metal clusters with a dopant carbon. The CLi bond lengths do not change much along this family of clusters, being close to 2.05 ± 0.05 Å. The binding energy presents a linear depen-

Table 1

Calculated binding energies and dipole moments of CLi $_x$ ($x = 1-5$) for the ground state and various excited states

Species	Cluster	Group	State	E_b (eV)	D (Debye)
CLi	1-1a	$C_{\infty v}$	$^4\Sigma^-$	-2.7019	6.12
	1-1b	$C_{\infty v}$	$^2\Pi$	-1.1907	6.11
CLi $_2$	1-2a	$D_{\infty h}$	$^3\Sigma_g^+$	-4.1565	0
	1-2b	C_{2v}	5A_2	-3.6596	0.19
	1-2c	C_{2v}	1A_1	-2.9657	1.61
	1-2d	$C_{\infty v}$	$^5\Sigma^+$	-2.9250	10.36
CLi $_3$	1-3a	D_{3h}	$^2A''_2$	-5.8961	0
	1-3b	C_{2v}	4B_1	-5.5052	2.21
	1-3c	C_{2v}	4A_2	-5.0274	2.55
	1-3d	$C_{\infty v}$	$^4\Sigma^+$	-4.4710	3.96
	1-3e	C_{2v}	6B_1	-4.030	3.13
	1-3f	$C_{\infty v}$	$^6\Sigma^+$	-3.1429	15.00
CLi $_4$	1-4a	T_d	1A_1	-8.1412	0
	1-4b	D_{2d}	3B_2	-7.6282	0
CLi $_5$	1-5a	C_{4v}	2A_1	-10.0244	0.58
	1-5b	D_{3h}	$^2A'_1$	-10.0207	0

The structure of the clusters is given in Fig. 1.

Table 2

Calculated normal mode vibrational frequencies of CLi $_x$ ($x = 1-5$) corresponding to the states reported in Table 1

Species	Cluster	Frequencies (cm $^{-1}$)
CLi	1-1a	693
	1-1b	558
CLi $_2$	1-2a	126(2),542,731
	1-2b	265,436,521
	1-2c	28,558,777
	1-2d	41(2),149,665
CLi $_3$	1-3a	113(2),146,544,743(2)
	1-3b	65,127,185,478,589,649
	1-3c	125,183,232,322,434,528
	1-3d	29(2),85(2),180,469,680
	1-3e	49,153,240,280,378,440
	1-3f	24(2),80(2),104,212,649
CLi $_4$	1-4a	165(3),176(2),552,733(3)
	1-4b	96,149,178(2),192,506,558,652(2)
CLi $_5$	1-5a	43,205(2),220,265(2),286,486,509,630,667(2)
	1-5b	44(2),245(2),261,273(2),481,506,643,672(2)

dence with the number of metal atoms with an average gain of 1.9 eV per addition of one Li atom.

The normal mode frequencies of vibration were calculated for all the isomers of each cluster size. Additionally, these frequencies were used in the harmonic calculation of the Helmholtz free energy as a function of temperature. This thermodynamics calculation allows to determine if the ground state isomer continues to be the most stable isomer at finite temperatures up to about 1000 K or if a solid-like structural transition to one of the excited isomers is apparent at a characteristic transition temperature. In this family of clusters, the ground state isomer continues to be the most stable with the lowest free energy up to temperatures of about 1500 K.

3.1. CLi_2

There are four states studied for this cluster size, all of them belonging to isomers with different geometries. The symmetry and state identifications are shown in Fig. 1, isomers 1-2a, b, c, d, and Table 1. The ground state is a linear ${}^3\Sigma_g^+$ with a binding energy of -4.156 eV, zero point energy of 0.094 eV, $-0.64e$ charge on the carbon, ionization potential of 4.86 eV and electron affinity of 0.46 eV. Ionization potential (IP) and electron affinity were calculated with respect to the ground states of the cation and anion clusters, which are relaxed $D_{\infty h}$ linear structures: CLi_2^+ in the ${}^4\Sigma_g^-$ state and CLi_2^- in the ${}^2\Sigma_g^+$, respectively. The IP is in good agreement with the experimental result of 4.55 ± 0.20 eV [16]. The bond length for the ground state is given in structure 1-2a of Fig. 1 and the binding energy is reported in Table 1.

Our findings for the ground state are in disagreement with a previous calculation [16] that identifies the ground state as a triplet in the C_{2v} triangular structure. In our calculation the triangular structure is not stable in the triplet state. The triplet in the linear $D_{\infty h}$ structure is also a saddle of the potential energy surface and is not a stable structure. Nonetheless, the first and second excited states are a quintet and a singlet with this symmetry, the 5A_2 and 1A_1 states that lie 0.497 and 1.191 eV above the ground state, respectively. An even higher excited state was located at about 1.2 eV above the ground state corresponding to a quintet

in the $C_{\infty v}$ linear structure. The bond lengths are reported in Fig. 1 (1-2a through 1-2d) and Table 1 summarizes the binding energy and dipole moment for each state. Normal mode vibrational frequencies for these four states are given in Table 2 along with vibrational frequencies for larger clusters. The most intense IR active mode at 126 cm^{-1} corresponds to the bending mode where the lithium atoms move perpendicular to the molecular axis and opposite to the carbon atom motion. Normal mode vibrations for the three excited states are reported in Table 2.

3.2. CLi_3

There are six states discovered for this cluster. The ground state and the five excited states have different structures as shown in Fig. 1, 1-3a through 1-3f. The ground state structure is a planar equilateral triangle D_{3h} shown in Fig. 1 (1-3a), which is in agreement with previous calculations [16]. The state is ${}^2A_2''$ with a binding energy of -5.896 eV, zero point energy of 0.149 eV, zero dipole moment, and $-0.48e$ charge on the carbon atom. The bond lengths are reported in Fig. 1, the binding energy is included in Table 1 and the normal mode vibrational frequencies are given in Table 2. The ionization potential of 4.93 eV, calculated from energies of the ground state of both neutral and cation (${}^1A_1'$, D_{3h}) clusters, is higher than the experimental value of 4.22 ± 0.30 eV [16]. A Jahn–Teller distortion in the cation ground state was not found as suggested in Ref. [16] but rather a strong contamination with the triplet excited state had to be eliminated. The electron affinity was calculated to be 0.25 eV, with the anion ground state being a ${}^3A_2''$ in the relaxed D_{3h} structure.

Interestingly, the five excited states of this carbene have high multiplicities and are either planar or linear isomers as shown in Fig. 1 (structures 1-3b through 1-3f). The first excited state is a quartet that has a C_{2v} triangular shape and lies 0.39 eV above the ground state. The two highest excited states are sextuplets, and the highest state is linear $C_{\infty v}$ with carbon at the end of the linear chain as shown in structure 1-3f of Fig. 1. The dipole moment of this cluster is quite high in all excited states (see Table 1), indicating a predominant ionic bond character when the cluster is excited. The frequencies of normal modes of vibration for all of these states are given in Table 2.

3.3. CLi_4

The ground state is a tetrahedral T_d structure in the 1A_1 state consisting of a metallic lithium cage around the carbon atom as shown in Fig. 1, 1-4a, which includes bond lengths and angles. The ground state binding energy is -8.1412 eV with a zero point energy of 0.223 eV and a charge on the carbon atom of $-0.68e$. These results are summarized in Table 1. In this very symmetric structure the dipole moment is zero and the C–Li bond lengths are 1.87 Å, in agreement with previous work [16] but shorter than the molecular orbital valence bond (MOVB) results

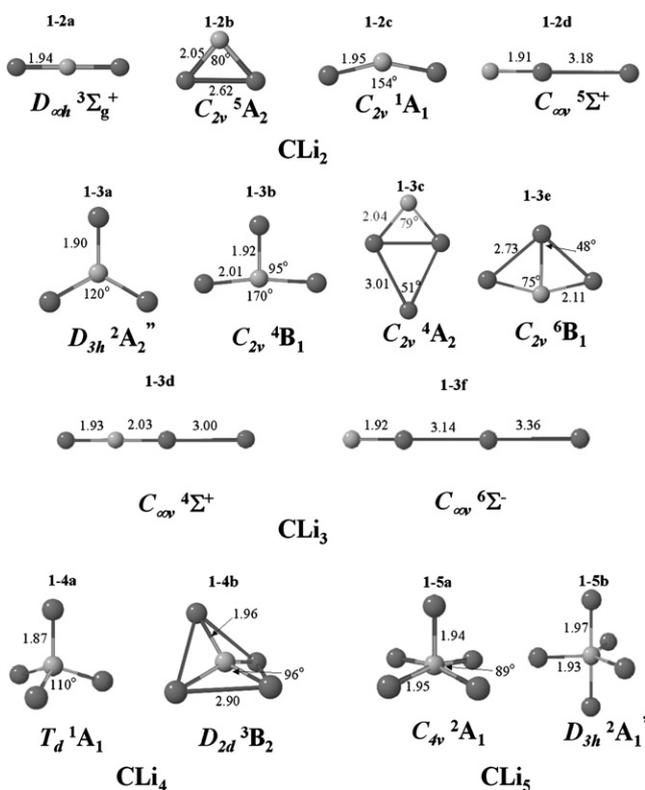


Fig. 1. The CLi_x ($x=1-5$) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

of 1.94 Å [17]. Additionally, the MOVb calculation yielded a binding energy 6.6 eV lower than in our study. The ground state of the relaxed CLi_4^+ is a 2B_2 in the D_{2d} structure. The IP, calculated to the cation $D_{2d} {}^2B_2$ ground state, is 4.23 eV and compares very well with one of the experimental results of 4.24 eV reported in Ref. [16]. The electronic affinity is 0.41 eV, being the ground state of the anion a $T_d {}^2A_1$.

We found that the first excited state 3B_2 is a very stable configuration in the D_{2d} structure with binding energy of -7.628 eV that lies only 0.51 eV above the ground state. This excited structure is depicted in Fig. 1, 1-4b. Our results differ from the MOVb work, where a D_{4h} structure was reported as the first excited isomer with a binding energy 5.7 eV lower than found in our study. The IP from this state is 3.71 eV, which is in agreement with the second experimental IP of 3.57 ± 0.20 eV reported in Ref. [16]. The electron affinity calculated from the relaxed anion in the $D_{2d} {}^2A_1$ state is 0.41 eV. Table 2 provides the frequencies of the normal modes of vibration of these two electronic states. In both of these states the dipole moment is zero due to the symmetry of the cluster.

3.4. CLi_5

This cluster is said to be the smallest hyperlithiated cluster [16]. The cluster was observed to have two different geometries almost degenerate in energy but having different structures C_{4v} and D_{3h} as shown in Fig. 1 (1-5a and 1-5b). The C_{4v} structure is a square pyramid with base containing the four lithium atoms in a plane, the carbon atom is slightly above that plane, and the fifth Li atom is at the apex. The state is a 2A_1 with binding energy of -10.0244 eV, dipole moment of 0.58 D, and Mulliken charge on the carbon of $-0.8e$. The D_{3h} isomer is a trigonal bipyramid with three lithiums surrounding the carbon in the central plane and the other two Li atoms located at the apexes. The state is a ${}^2A_1'$ with a binding energy of -10.0207 eV and zero dipole moment. Bond lengths and angles for these two structures are given in Fig. 1 and energies are reported in Table 1. The C–Li bond lengths are in agreement with those reported by Lievens et al. [16].

The ionization potential of CLi_5 is 3.87 eV, which is quite close to the calculated value of 3.902 eV in Ref. [16], but not as comparable to the experimental value of 3.24 eV reported in the same reference. The cation has also two almost degenerate bounded states 1A_1 and ${}^1A_1'$ with symmetries C_{2v} , both deformed from the neutral C_{4v} and D_{3h} , respectively. Ionization potentials to these two states are about the same 3.87 ± 0.02 eV. The electron affinity is 0.69 eV calculated using the ground state of the anion, which is the 1A_1 in the C_{4v} structure. Table 2 gives the calculated normal mode frequencies for this cluster. The strongest IR active mode of vibration for the C_{4v} is a degenerate mode at 265 cm^{-1} . The D_{3h} cluster has one frequency of vibration with strong IR active intensity at 261 cm^{-1} and a doubly degenerate mode at 245 cm^{-1} .

4. Carbon₂–lithium_x clusters, $x = 1, 2, 3, 4, 5$

The energetics and electronic properties for clusters C_2Li_x , with $x = 1-5$, are described in this section. Across this family of clusters, the C–C bond length remains about constant around 1.25 Å, which is characteristic of the triple bond in the singlet first excited state of C_2 . The CLi bond lengths tend to be shorter than in the family of clusters described in Section 3 and have values of about 1.92 Å. Except for C_2Li , these clusters are non-polar. A common characteristic is that these clusters are planar in the ground as well as in most of the excited state conformations. The binding energy as a function of the number of metal atoms in the cluster decreases almost linearly, with a gain of about 1.6 eV per extra Li. The Mulliken charge on the carbon atoms is symmetrically distributed in C_2Li ($-0.25e$ each) and in the clusters with even number of Li atoms ($-0.37e$ in C_2Li_2 and $-0.4e$ in C_2Li_4). However, the positive charge in C_2Li_4 on the Li atoms is not the same. The Mulliken charge on the C atoms in both C_2Li_3 and C_2Li_5 is not symmetric ($-0.42e$ and $-0.36e$), which is accompanied by an uneven distribution of charge on the Li atoms. The C–C stretching frequencies range from 1850 to 1905 cm^{-1} , slightly increasing as the number of Li atoms is larger. This is correlated with a slight decrease of the C–C bond length and an increase in negative charge on the carbons as the cluster grows larger.

The normal mode frequencies of vibration were calculated for all the isomers of each cluster size in this family. When these frequencies were used in the harmonic calculation of the Helmholtz free energy as a function of temperature, solid-like transitions were detected for C_2Li_2 and C_2Li_4 . These structural transitions are described in more detail in the paragraphs below enlisting the properties of these clusters. The ground state isomers of C_2Li , C_2Li_3 , and C_2Li_5 continue to be the most stable, with the lowest free energy, up to temperatures of about 1500 K.

4.1. C_2Li

The most stable geometry for this cluster is C_{2v} with ground state 2A_1 as indicated in Fig. 2 (2-1a) and Table 3. This isosceles triangular configuration has a binding energy of -10.777 eV and large dipole moment of 6.0525 D. The C–C bond is a triple bond with length 1.26 Å. The IP to the relaxed linear ${}^3\Pi$ state (Fig. 2, 2-1b) is 9.19 eV. States of the cation in the C_{2v} structure are saddles of various orders. The electron affinity is 1.63 eV with the anion lowest state being a 1A_1 in the C_{2v} structure.

We were able to locate five excited states, which are either C_{2v} or $C_{\infty v}$ structures as reported in Table 3 and shown in Fig. 2 (2-1a and 2-1b). The first excited state is a ${}^2\Pi$, which lies 0.69 eV above the ground state and corresponds to the linear cluster of Fig. 2 (2-1b). The other excited states have high multiplicities of 4 and 6 as shown in Table 3. Harmonic frequencies of the normal modes of

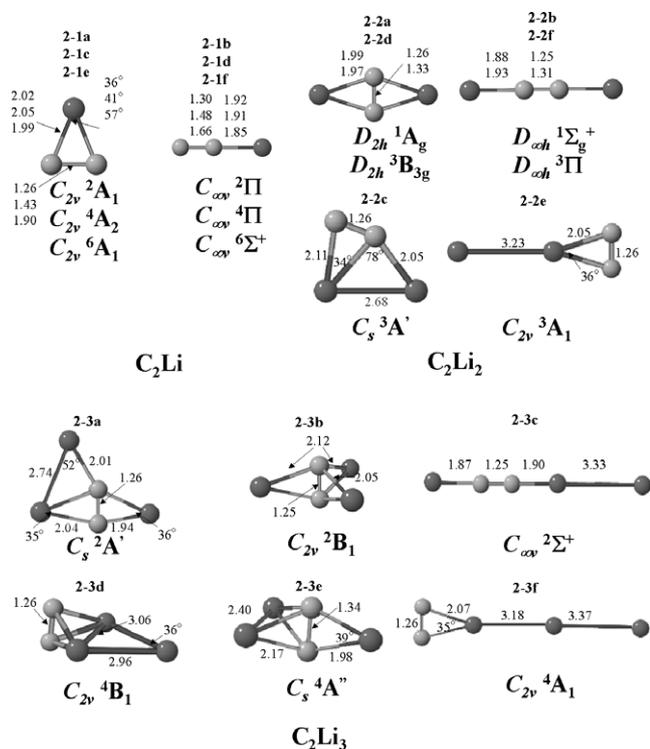


Fig. 2. The C_2Li_x ($x = 1-2$) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

vibration associated with the ground state and the six excited states are reported in Table 4. The strongest IR active mode of the ground state has a frequency of 617 cm^{-1} .

4.2. C_2Li_2

The most stable structure for this cluster is a rhombus belonging to the D_{2h} point group and the state is $^1A'$, as shown in Fig. 2 (2-2a). The binding energy for this structure is -14.3290 eV with zero dipole moment as reported in Table 3. The C–C bond length is 1.26 Å . The structure found is in agreement with the MOVb results of Ref. [17]. However, our calculated C–C bond distances are slightly larger than 1.24 Å , as reported in that reference. Once again, the binding energy from our study is higher by 5.48 eV than the MOVb calculation. The strong IR active vibrational modes appear at frequencies 53 , 192 , and 697 cm^{-1} . The ionization potential is 6.94 eV , being the cation a linear $D_{\infty h} ^2\Pi$. The electron affinity is low at 0.18 eV and the ground state of the anion is a $D_{2h} ^2B_{1u}$.

The first excited state of this cluster is the linear isomer $D_{\infty h}$ structure having in the $^1\Sigma_g^+$ state with binding energy of -14.0489 eV . This structure is in agreement with the MOVb results [17]. However, the MOVb binding energy of this excited state is 3.78 eV lower than our calculation and the C–C bond length of 1.22 Å is shorter than the 1.25 Å reported in Fig. 2. In Table 3 are reported relevant quantities for four additional excited states. For the ground

Table 3

Calculated binding energies and dipole moments of C_2Li_x ($x = 1-4$) for the ground state and various excited states

Species	Cluster	Group	State	E_b (eV)	D (Debye)
C_2Li	2-1a	C_{2v}	2A_1	-10.7771	6.05
	2-1b	$C_{\infty v}$	$^2\Pi$	-10.0830	9.13
	2-1c	C_{2v}	4A_2	-6.5858	4.36
	2-1d	$C_{\infty v}$	$^4\Pi$	-6.3682	7.67
	2-1e	C_{2v}	6A_1	-4.6547	5.11
	2-1f	$C_{\infty v}$	$^6\Sigma^+$	-4.2949	6.81
C_2Li_2	2-2a	D_{2h}	1A_g	-14.3290	0
	2-2b	$D_{\infty h}$	$^1\Sigma_g^+$	-14.0490	0
	2-2c	C_s	$^3A'$	-11.7022	0.7
	2-2d	D_{2h}	$^3B_3^+$	-11.1974	0
	2-2e	C_{2v}	3A_1	-10.9874	10.42
	2-2f	$D_{\infty h}$	$^3\Pi_u$	-10.2781	0
C_2Li_3	2-3a	C_s	$^2A'$	-15.6173	6.34
	2-3b	C_{2v}	2B_1	-15.0576	3.83
	2-3c	$C_{\infty v}$	$^2\Sigma^+$	-14.1759	3.67
	2-3d	C_{2v}	4B_1	-12.2254	1.09
	2-3e	C_s	$^4A''$	-12.0731	6.77
	2-3f	C_{2v}	4A_1	-11.2032	15.10
C_2Li_4	2-4a	C_{2h}	3B_u	-16.8584	0
	2-4b	C_s	$^1A'$	-16.8027	5.05
	2-4c	C_s	$^1A'$	-16.7317	6.96
	2-4d	C_s	$^1A'$	-16.7297	5.09
	2-4e	C_{2v}	3B_2	-16.6161	9.47
	2-4f	C_s	$^3A''$	-16.5333	1.86
	2-4g	C_{2h}	1A_g	-16.3054	0
C_2Li_5	2-5a	C_s	$^2A'$	-18.0675	1.87
	2-5b	C_1	4A	-17.6564	4.44
	2-5c	C_1	2A	-17.4514	6.55
	2-5d	C_s	$^4A'$	-17.3801	1.00
	2-5e	C_s	$^4A''$	-17.3772	2.57

The structure of the clusters is given in Figs. 2 and 3.

state the strong IR active modes of vibration were calculated to be 90 and 752 cm^{-1} with the former being degenerate and the latter having the highest intensity. All normal mode frequencies for the five excited states studied are reported in Table 4.

We also found the transition state between the ground state and the first excited isomer. There is a barrier of 8.5 kcal/mol to overcome from the ground state structure to the first excited isomer and a release of 2 kcal/mol to reach the excited isomer. This barrier is higher than previous reports in Ref. [18] and the first excited isomer can certainly be reached if enough energy is available to induce the transition. As a matter of fact, within the harmonic approximation of the Helmholtz free energy as a function of temperature, using the calculated frequencies reported in Table 3, we can predict that there is a structural transition at or around 1400 K from the ground state isomer (rhombus) to the linear isomer of the first excited state. The bulk material exhibits a structural transition at about 800 K promoting a cubic modification from the low temperature isotopic Rb_2O_2 structure to an antiferroite structure with a disordered C_2 dumbbell at high temperatures [19].

Table 4
Calculated normal mode vibrational frequencies of C_2Li_x ($x = 1-4$) corresponding to the states reported in Table 3

Species	Cluster	Frequencies (cm^{-1})
C_2Li	2-1a	288,617,1853
	2-1b	129,272,629,1773
	2-1c	464,580,1151
	2-1d	237,366,608,1159
	2-1e	434,449,610
	2-1f	160(2),565,929
C_2Li_2	2-2a	53,192,299,575,697,1853
	2-2b	90(2),169(2),593,752,2002
	2-2c	91,245,293,424,497,1849
	2-2d	135,316,565,649,713,1457
	2-2e	22,42,138,271,587,1853
	2-2f	83,148,322,413,521,669,1622
C_2Li_3	2-3a	35,156,170,255,304,464,530,660,1878
	2-3b	82,127,154,193,351,444,510,566,1880
	2-3c	15(2),86(2),115,169(2),584,739,1995
	2-3d	80,158(2),168,207,277,394,432,1856
	2-3e	110,147,230,326,367,466,549,651,1452
	2-3f	15,22,68,77,96,206,263,573,1853
C_2Li_4	2-4a	32,99,147,237,256,286,362,415,490,494,589,1888
	2-4b	23,120,124,181,191,226,286,313,464,539,660,1891
	2-4c	62,83,144,171,211,212,270,313,479,548,686,1966
	2-4d	94,141,183,215,223,225,264,277,517,532,598,1901
	2-4e	67,116,190,197,241,294,389,426,441,560,640,1783
	2-4f	71,99,140,194,215,235,262,388,445,518,545,1850
C_2Li_5	2-5a	26,72,104,146,201,220,240,276,312,362,418,491,495,589,1902
	2-5b	66,108,133,177,205,222,254,277,350,373,408,473,553,580,1747
	2-5c	95,130,151,165,181,255,271,313,379,448,492,524,625,642,1602
	2-5d	2,61,107,137,144,228,241,267,278,358,419,461,505,578,1906
	2-5e	89,99,132,163,210,223,246,298,300,349,367,426,467,512,1809

4.3. C_2Li_3

The most stable structure of this cluster is a planar, non-symmetric C_s , with electronic state $^2A'$ and binding energy of -15.6173 eV as shown in Fig. 2 (2-3a) and reported in Table 3. This structure is built from the C_2Li_2 preferred structure with the extra Li decorating a side of the rhombus and producing a planar distortion that breaks the rhomboidal shape. The carbon-carbon double bond length remains at 1.26 Å, identifying a triple bond. The dipole moment for this geometry is calculated to be 6.335 Debye and the strongest IR active modes of vibration are 35 , 156 , 255 , 305 , 530 , 660 , and 1878 cm^{-1} . The ionization potential is 3.98 eV and the electron affinity is 0.74 eV. The ground states of cation and anion used in the calculation are $^3A'$ C_s (as the ground state) and 3B_1 C_{2v} (structure in Fig. 2 2-3b), respectively.

As shown in Table 3 and Fig. 2 (2-3b), the first excited state 2B_1 belongs to the C_{2v} point group with a binding energy of -15.0576 eV and dipole moment of 3.83 D. The second excited state is a linear $C_{\infty v}$ $^2\Sigma^+$, as shown in Fig. 2 (2-3c) and has a binding energy of -14.1759 eV. For the ground state the strongest IR active modes of vibration are 82 , 351 , and 444 cm^{-1} with 351 cm^{-1} being the dominant. All other normal mode frequencies are given

in Table 4, including those for the five excited states studied here.

4.4. C_2Li_4

The ground state of this cluster was found to belong to the symmetric planar C_{2h} in the 3B_u state. The geometry is shown in Fig. 3 (2-4a). It is apparent from the figure that this cluster continues to build on the plane from the C_2Li_2 rhombus, which has now two Li atoms symmetrically decorating the rhombus sides. The C-C triple bond has length of 1.25 Å. The binding energy of this cluster was calculated to be -16.8583 eV and the dipole moment is zero as reported in Table 3. The ionization potential is 3.98 eV and the electron affinity is 0.68 eV, both calculated considering the ground states of the cation and anion clusters C_s $^2A'$ and C_s $^4A'$, respectively. The normal modes frequencies at 286 and 589 cm^{-1} are the strongest IR active. All other normal mode frequencies are given in Table 4.

The first excited state structure belongs to the planar non-symmetric C_s point group and the state is the singlet $^1A'$ as shown in Fig. 3 (2-4b). The binding energy was calculated to be -16.8027 eV and this planar structure is highly dipolar (5.05 D). The strongest IR active mode of vibration was calculated to be 313 cm^{-1} . The third excited

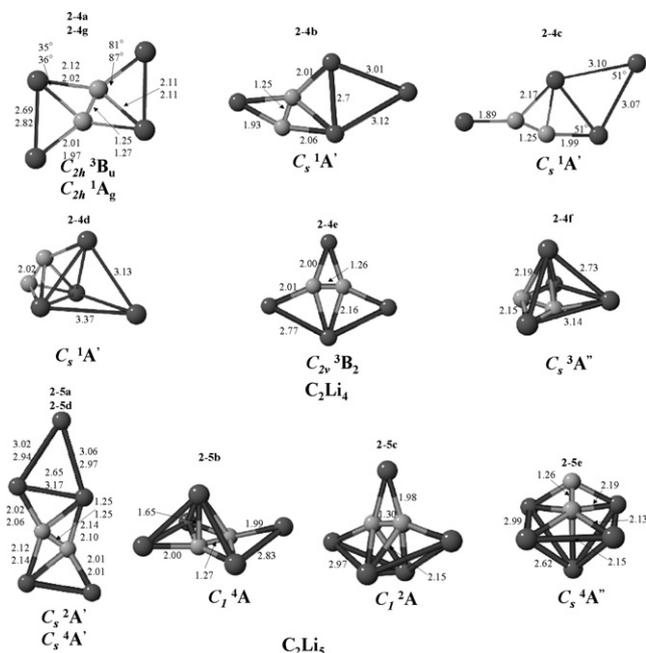


Fig. 3. The C_2Li_x ($x = 3-4$) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

state $^1A'$ is the only non-planar structure of this family of clusters. It is a C_s structure (Fig. 3 2-4d), which is barely 0.002 eV above the energy of the planar isomer depicted in Fig. 3 (2-4c). The C–C bond length remains unchanged in all of these excited states. Normal mode frequencies of vibration for the five excited states are reported in Table 4.

These results do not agree with previous theoretical studies of the C_2Li_4 [17,20]. In the older MOVB study, the ground state is a planar C_{2v} isomer identified as a doubly bridged structure with two Li in the *cis* position. This structure comes to be a highly excited isomer in the more recent calculation of Dorigo et al. where clusters were optimized at the MP2/6-31G* level. The first excited state in Jug et al. paper was identified as a D_{2h} ethylene like structure, which is not stable within the ab initio calculations of Dorigo et al. The ground state isomer of Ref. [20] agrees with our first excited state C_s isomer, whereas one of their highly excited states (isomer 6.7) agrees with the C_{2h} geometry of our ground state. Additionally, the first excited state C_{2v} reported in that reference (isomer 1.6) is unstable in our study.

By performing a harmonic analysis of the thermodynamic quantities at finite temperatures, we found that the ground state isomer C_{2h} undergoes a structural transformation into the first excited isomer C_s (Fig. 3, 2-4b) at 420 K. At that transition temperature the Helmholtz free energy of the C_s structure becomes more negative than the free energy of the C_{2h} and consequently the specific heat at constant volume presents a peak.

4.5. C_2Li_5

The ground state of this cluster is a $^2A'$ C_s planar structure in which a Li atom decorates one of the existing Li–Li

bonds in the C_2Li_4 ground state structure, as shown in Fig. 3 (2-5a). The C–C bond length is 1.252 Å, identifying a triple bond. The binding energy is -18.0675 eV, the ionization potential $IP = 4.05$ eV and the electron affinity is 0.23 eV, both energies calculated considering the ground states of the cation and anion to be C_1^1A and C_s^1A' , respectively.

Several excited isomers were also studied as shown in Fig. 3 (2-5b through 2-5f) and their energetics is provided in Table 3. Among these excited isomers, three-dimensional structures are apparent. In fact, the first excited state is a structure also grown from the rhomboidal-like C_2Li_4 (Fig. 3, 2-4a) with one extra lithium atom out of the plane. This excited isomer has a binding energy of -17.6564 eV with a C–C bond length of 1.268 Å.

The strongest IR vibrational frequency of the ground state is 589 cm^{-1} . All other normal mode frequencies are reported in Table 4.

5. Carbon₃–lithium_x clusters, $x = 1, 2, 3, 4$

This family of clusters have planar structures in the ground state except for C_3Li_4 . Several clusters are built around the carbon trimer in triangular conformations with C–C bond lengths of 1.30 Å, characteristic of the triplet C_3 . However, the conformations of the larger clusters show decoration of a linear chain of three carbons with C–C bond lengths of about 1.25 Å, characteristic of the singlet C_3 . The C–Li bond lengths are slightly shorter than in the two families of clusters studied in previous sections, and have a value of 1.93 ± 0.05 Å. The ground state energy decreases linearly as a function of size, with a gain of approximately 1.9 eV per addition of one Li atom. Except for C_3Li_2 , the Mulliken charge distribution on the C atoms in these clusters shows the central carbon having a zero or slightly positive charge and the other two other C atoms carrying all the negative charge. The distribution of positive charge on the Li atoms is not symmetric either. Excited states have planar or linear conformations with only one exception for the fourth excited state of C_3Li_2 which is three-dimensional.

The normal mode frequencies of vibration were calculated for all the isomers of each cluster size. These frequencies were used in the harmonic calculation of the Helmholtz free energy as a function of temperature. In this family of clusters, the ground state isomer continues to be the most stable with the lowest free energy up to temperatures of about 1500 K. Solid-like structural transitions are not apparent for this family of clusters.

5.1. C_3Li

The ground state of this cluster (2A_1) has a C_{2v} structure in which the carbons form an equilateral triangle and the Li decorates one side of this triangle, as shown in Fig. 4 (3-1a). The binding energy for this cluster is -16.9756 eV, which is reported in Table 5. This cluster has a high dipole

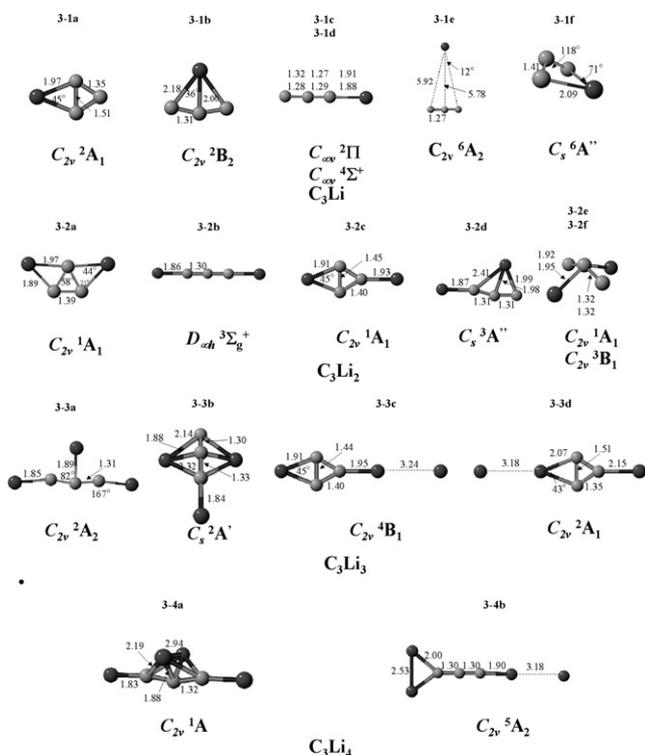


Fig. 4. The C_3Li_x ($x = 1-4$) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

Table 5
Calculated binding energies, and dipole moments of C_3Li_x ($x = 1-4$) for the ground state and various excited states

Species	Cluster	Group	State	E_b (eV)	D (Debye)
C_3Li	3-1a	C_{2v}	2A_1	-16.9756	5.71
	3-1b	C_{2v}	2B_2	-16.7375	5.14
	3-1c	$C_{\infty v}$	$^2\Pi$	-16.6833	10.44
	3-1d	$C_{\infty v}$	$^4\Sigma^+$	-15.3123	6.99
	3-1e	C_{2v}	6A_2	-10.8783	0.16
	3-1f	C_s	$^6A''$	-10.6330	5.16
C_3Li_2	3-2a	C_{2v}	1A_1	-19.7794	5.56
	3-2b	$D_{\infty h}$	$^3\Sigma_g^+$	-19.3380	0
	3-2c	C_{2v}	1A_1	-19.3284	3.55
	3-2d	C_s	$^3A''$	-19.1064	9.75
	3-2e	C_{2v}	1A_1	-18.9206	1.87
	3-2f	C_{2v}	3B_1	-18.9091	5.24
C_3Li_3	3-3a	C_{2v}	2A_2	-21.0959	3.02
	3-3b	C_s	$^2A'$	-20.9874	7.79
	3-3c	C_{2v}	4B_1	-20.6818	0.71
	3-3d	C_{2v}	2A_1	-19.5270	7.70
C_3Li_4	3-4a	C_{2v}	1A	-22.7609	4.18
	3-4b	C_{2v}	5A_2	-20.7463	13.31

The structure of the clusters is given in Fig. 4.

moment of 5.71 D. The stronger IR active modes of vibration are located at frequencies of 262, 377, and 626 cm^{-1} . These and other normal mode frequencies can be found in Table 6. The ionization potential and electronic affinities are 9.06 and 0.44 eV, respectively. The ground states of the cation and anion are both $C_{\infty v}$ with $^1\Sigma^+$ and $^3\Sigma^+$ states, respectively.

The first excited state is a different C_{2v} structure (Fig. 4, 3-1b) and the state is a 2B_2 with binding energy of -16.7375 eV. Four higher excited conformations are also studied with structures given in Fig. 4 (3-1c through 3-1f). The binding energies of these excited states are reported in Table 5 and the frequencies of the normal modes of vibrations are summarized in Table 6.

5.2. C_3Li_2

The ground state for this cluster has a symmetric planar structure C_{2v} built around the C_3 triangle with two decorated sides, as shown in Fig. 4 (3-2a). The state is a 1A_1 with binding energy -19.7794 eV and high dipole moment, as indicated in Table 5. The ionization potential and electron affinity are 6.51 and 0.18 eV, respectively. The ground states of the cation and anion clusters are both C_s $^2A'$, which are slightly deformed from the C_{2v} ground state structure. Additionally, the electron affinity of this cluster is very low and only comparable to that of C_2Li_2 .

Interesting to note is that the first excited state is a linear isomer $D_{\infty h}$ in the $^3\Sigma_g^+$ state with binding energy -19.3380 eV and zero dipole moment as shown in Fig. 4 (3-2b) and Table 5. The frequencies of the normal mode vibrations are given in Table 6 for the ground and the five excited states listed in Table 5 and depicted in Fig. 4 (3-2c through 3-2f).

5.3. C_3Li_3

The ground state for this cluster is a planar C_{2v} built from the first excited isomer of C_3Li_2 (Fig. 4, 3-2b) in which the newly added Li distorts the linearity of the chain of carbon atoms, as illustrated in Fig. 4 (3-3a). The state is (2A_2) with binding energy of -21.0959 eV and fairly large dipole moment, as shown in Table 5. The ionization potential and electron affinity are 4.13 and 0.44 eV, respectively. The cation and anion ground states are 3B_1 and 3A_2 , both slightly deformed neutral ground state C_{2v} geometries.

The first excited isomer is a non-symmetric C_s structure also built around the linear chain of C atoms. However, this is not a planar structure, as seen in Fig. 4 (3-3b). The binding energy for this excited state is -20.9874 eV and the dipole moment of 7.7947 D indicating that this is a highly polar cluster. The strong IR active modes of vibration for this three-dimensional isomer are 468, 628, 872, and 1639 cm^{-1} . The energetics and frequencies of the other five excited isomers depicted in Fig. 4 (3-3c through 3-3d) are given in Tables 5 and 6.

5.4. C_3Li_4

The ground state for this cluster has the C_{2v} structure with a 1A state and a binding energy of -22.7609 eV as shown in Fig. 4 (3-4a) and Table 5. This is the only non-planar ground state structure found in this family of clusters. The C-C bond length is consistent with the trimer

Table 6

Calculated normal mode vibrational frequencies of C_3Li_x ($x = 1-4$) corresponding to the states reported in Table 5

Species	Cluster	Frequencies (cm^{-1})
C_3Li	3-1a	262,377,626,887,1209,1631
	3-1b	152,251,418,622,1220,1724
	3-1c	112,118,315,407,599,1247,1866
	3-1d	127,127,442,442,620,1308,1650
	3-1e	17(2),434(2),1319,1712
	3-1f	134,382,450,582,968,1117
C_3Li_2	3-2a	206,284,296,467,643,704,1061,1101,1523
	3-2b	91(2),161(2),467(2),569,711,1336,1643
	3-2c	116,129,515,545,589,690,1054,1176,1573
	3-2d	112,133,186,443,510,617,677,1244,1576
	3-2e	172,201,289,370,484,596,810,1250,1608
	3-2f	209,243,287,525,532,807,868,1064,1129
C_3Li_3	3-3a	90,100,122,178,309,483,487,580,729,797,1320,1661
	3-3b	89,109,134,167,191,448,468,628,659,872,1243,1639
	3-3b	78,108,125,166,247,410,463,530,604,613,1304,1614
	3-3c	9,15,33,129,134,307,404,543,715,1038,1126,1531
	3-3d	5,30,49,97,149,270,277,341,512,842,859,1597
C_3Li_4	3-4a	86,103,110,132,201,210,228,463,483,583,745,753,830,1309,1748
	3-4b	16(2),37,89,132,136,164,272,442,471,485,523,621,1306,1643

of C_3 . This is in agreement with older results obtained with small basis sets [5,21]. The ionization potential is 3.46 eV and the electron affinity is 0.34 eV, when calculated from the cation ground state C_s^2A' and the anion C_s^4A'' state. The strong IR active vibrational frequencies are 745 and 1748 cm^{-1} , the latter corresponding to the C–C stretch. All other normal mode frequencies are reported in Table 6. The first excited state is also a C_{2v} structure but it is planar as shown in Fig. 4 (3-4b).

6. Conclusion

In conclusion, this study gives a detailed description of the energetics, structure and vibrational frequencies for three families of compounds containing C, C_2 , and C_3 decorated with lithium. Several highlights are as follows. The most stable structures are planar in the ground state with the exception of CLi_4 , CLi_5 , and C_3Li_4 . For the larger clusters within a family, there are a number of excited state isomers that acquire three-dimensional structures. Within the size range studied, the addition of one extra metal atom to the cluster takes about 1.2–1.9 eV. It is possible to identify that the geometry of C_2Li in the ground state structure is a repetitive building block of the larger structures. There is a tendency of the carbon atoms to be grouped together, either as linear chains or in more compact structures. These carbon atoms are never intercalated with lithium. For each family compounds, the ionization potential decreases as the number of lithium atoms are added. However, there is no specific trend for the electron affinities. For each cluster, as a general rule the cation and anion display the same structural characteristics in their ground states. The compound C_2Li , which is identified as a building block, has the highest ionization potential and electron affinity of all

of the clusters studied. While the neutral C_2Li cluster is planar the cation is linear and the anion remains planar.

Structural transitions are predicted for C_2Li_2 and C_2Li_4 at 1400 and 420 K, respectively. These clusters are thermodynamically stable.

Acknowledgments

We acknowledge the Computational Materials Science Center of George Mason University for providing us with the high performance computing facilities.

References

- [1] P.H.M. Budzelaar, P.v.R. Schleyer, K. Krogh-Jespersen, *Angew. Chem. Int. Ed. Engl.* 23 (1984) 825.
- [2] W. Koch, G. Frenking, J. Gauss, D. Cremer, A. Sawaryn, P.v.R. Schleyer, *J. Am. Chem. Soc.* 108 (1986) 5732.
- [3] J.B. Collins, J.D. Dill, E.D. Jemmis, Y. Apeloig, P.v.R. Schleyer, R. Seeger, J.A. Pople, *J. Am. Chem. Soc.* 98 (1976) 5419.
- [4] W.D. Laidig, H.F. Schaefer, *J. Am. Chem. Soc.* 100 (1978) 5972.
- [5] E.D. Jemmis, D. Poppinger, P.v.R. Schleyer, J.A. Pople, *J. Am. Chem. Soc.* 99 (1977) 5796.
- [6] Y. Apeloig, P.v.R. Schleyer, J.S. Binkley, J.A. Pople, W.A. Jorgensen, *Tetrahedron Lett.* 17 (1976) 3923; G. Rauscher, T. Clark, D. Poppinger, P.v. R Schleyer, *Angew. Chem.* 90 (1978) 306; E.D. Jemmis, J. Chandrasekhar, P.v.R. Schleyer, *J. Am. Chem. Soc.* 101 (1979) 2848; A. Kos, D. Poppinger, P.v.R. Schleyer, W. Thiel, *Tetrahedron Lett.* (1980) 2151.
- [7] D.J. Hankinson, J. Almlöf, *J. Mol. Struct. (Theochem.)* 338 (1996) 245.
- [8] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [9] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [10] M.J. Frisch et al., Gaussian Inc., Pittsburg, PA, 1998.
- [11] J.P. Perdue, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, *Phys. Rev. B* 46 (1992) 6671.

- [12] J.P. Perdue, K. Burke, Y. Wang, *Phys. Rev. B* 54 (1996) 16533.
- [13] F. van Duijneveldt, J. van Duijneveldt-van de Rijdt, J. van Lenthe, *Chem. Rev.* 94 (1994) 1873.
- [14] A. Ricca, C.W. Bauschlicher, *Chem. Phys. Lett.* 244 (1995) 32.
- [15] F.B.C. Machado, R. Bravo, O. Roberto-Neto, *J. Mol. Struct. (Theochem.)* 464 (1999) 7.
- [16] P. Lievens, P. Thoen, S. Bouchaert, W. Bouwen, F. Vanhoutte, H. Weidele, R.E. Silverans, A. Navarro-Vázquez, P.v.R. Schleyer, *Eur. Phys. Lett. J. D* 9 (1999) 289.
- [17] K. Jug, N. Epiotis, S. Buss, *J. Am. Chem. Soc.* 108 (1986) 3640.
- [18] P.v.R. Schleyer, *J. Phys. Chem.* 94 (1990) 5560.
- [19] U. Ruschewitz, R. Pottgen, *Z. Anorg. Allg. Chem.* 625 (1999) 1599.
- [20] A. Dorigo, N.J.R. v. Eikema Hommes, K. Krogh-Jespersen, P.v.R. Schleyer, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1602.
- [21] P.v.R. Schleyer, *Pure Appl. Chem.* 56 (1984) 151.