Structures and Vibrational Frequencies of the Carbon Molecules C_2–C_{18} Calculated by Density Functional Theory

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Abstract: A density functional study of the molecular structure and vibrational frequencies of the linear and planar monocyclic isomers of the C_n ($2 \leq n \leq 18$) series was performed. A gradient corrected energy functional of the Becke–Perdew type and a triple-ζ valence basis with a polarization function was employed. The results show that for $n \leq 9$ the linear chains are generally more stable than the ring structures. A possible exception is C_6 where, in contrast to previous studies, the two forms were computed to be near isoenergetic. For $n \geq 10$ the cyclic structures dominate; however, only the C_{10}, C_{12}, and C_{14} monocyclic planar rings were found to represent minimas on the energy surface. Excellent agreement for the computed vibrational frequencies with experiment—whenever available—was found. Therefore the vibrational data presented here may help to interpret spectra of yet unidentified C_n species.

I. Introduction

Long before the discovery of C_{60} and the development of fullerene chemistry, the assembly of carbon atoms into all-carbon molecules has been the subject of both experimental and theoretical studies. In 1942, Hahn, Strassman, and co-workers[1] detected by mass spectrometry the formation of carbon ions from C_1^+ to C_{15}^+ in the vapor obtained by the electrical discharge between graphite electrodes. Later, larger carbon ions ranging up to C_{21}^+ were detected by mass spectrometric analysis.[2,3] With the advent of laser vaporization techniques in the early 1980s, all-carbon molecules and ions became the subject of intensive studies.[4-13] Molecules and ions of sizes ranging from C_2 to > C_{600} were detected in the supersonic beams produced by the laser vaporization of graphite and other carbon-rich materials.[14,15] Ion-cyclotron resonance experiments have been particularly valuable for generating mass-selected ion beams of significant lifetime, allowing the study of both physical and chemical properties of these ions. Alternatively, the spectral properties of some of the smaller carbon ions produced by the vaporization of graphite or the photolysis of acetylene have been studied in low-temperature matrices.[4]

The early studies on small carbon molecules were aimed at expanding the understanding of carbon based matter and were additionally fueled by the detection of an abundance of some of these molecules in interstellar space.[16-18] Today, the discovery of the macroscopic production method of fullerenes by resistive or arc-heating of graphite under inert atmosphere[19,20] and the ongoing exploration of the mechanism for carbon sphere formation in this unprecedented synthetic process add broad new interest into the study of small non-fullerenic all-carbon molecules. The originally proposed sequential graphitic shell closure mechanism for fullerene growth[18,21,22] is strongly contradicted by the isotopic scrambling[23-25] observed in fullerenes generated by arc-heating from mixtures of ^{12}C and ^{13}C-graphite. The reactant carbon source must undergo vaporization into atomic C and small carbon fragments such as C_2. A recent series of gas-phase studies[26] on carbon ions suggests that carbon growth continues sequentially by formation of linear chains and larger planar ring systems which subsequently coalesce to form, via carbocation rearrangements and loss of C_2,[8] stable fullerenes. This mechanism, in addition to alternative ones,[27-29] had previously been suggested to explain the formation of the new carbon spheres.[25,30] Following preliminary work by Rubin et al.,[31] McElvany et al.[32] showed by Fourier transform mass spectrometry that size selective growth of fullerences occurs through coalescence of cyclo[*n*]carbons,

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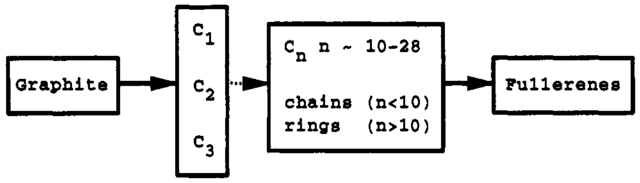

Figure 1. Possible mechanism for fullerene growth through assembly of carbon atoms and fragments.

molecular carbon allotropes consisting of monocyclic rings with *n* carbon atoms that can be prepared by mild laser desorption of structurally well-characterized precursor molecules. Whereas coalescence of cyclo[30]carbon (cyclo-C_{30}) produces predominantly buckminsterfullerene (C_{60}), the smaller rings cyclo-C_{18} and cyclo-C_{24} produce fullerene C_{70} through distinct intermediates. Additional strong support for the chain-to-ring-to-sphere mechanism for carbon growth was obtained by Bowers and co-workers in gas-phase ion chromatography experiments.[13,33–35] According to these studies, larger monocyclic, bicyclic, and tricyclic rings are involved in fullerene growth, and collisional heating of these rings induces isomerization to the corresponding fullerenes. Jarrold and co-workers showed by the same technique that C_{60}^+ ion formation generates, in addition to the fullerene, a mixture of planar polycyclic polyyne ring isomers that can be converted into fullerene C_{60} and, presumably, a large monocyclic C_{60} ring.[36]

Currently ongoing research in our laboratory is aimed at a further experimental substantiation of the chain-to-ring-to-sphere mechanism for the assembly of carbon atoms from smallest species C_1–C_3 to the large fullerene spheres. Specifically, we intend to prepare small carbon molecules ranging from C_2 to $\approx C_{16}$ selectively from defined precursors with thermally or photochemically removable groups and monitor their coalescence in gas-phase ion processes. For this experimental work in analogy to the investigation with the cyclocarbons, it is useful to have on hand good information on the structures of the small carbon molecules prepared from the precursor molecules. The experimental recording of vibrational spectra, coupled with computed spectral predictions, has been shown a valid method for assigning geometries of small carbon molecules in the gas phase.[4] Both infrared absorption spectroscopy[37–42] and anion photoelectron spectroscopy[43,44] have been applied to obtain vibrationally resolved spectra of small carbon molecules and ions, and these spectra have subsequently served, by comparison to theoretical data, to assign linear or cyclic structures to the molecules.

A variety of theoretical investigations have been applied for predicting structures to small carbon molecules and to calculate their vibrational spectra.[45] Early molecular orbital calculations,[46,47] predicting that the small carbon molecules C_n ($n < 10$) have linear structures and that those larger than C_{10} prefer ring structures have been confirmed in various calculations at higher levels.[48–53] However, controversies exist in the predictions of the geometries and relative energies of constitutional isomers. Here we present the results of an extended structural analysis of the carbon molecules from C_2–C_{18} through application of density functional theory (DFT), which complements and sizably expands on the studies previously performed with other methods. Geometries and vibrational frequencies as well as relative stabilities of the structural isomers were calculated. DFT methods have made substantial progress and are now one of the most effective tools for the computation of structures and frequencies of molecules in their electronic ground state.[54] In a comprehensive study, Andzelm and Wimmer[55] have shown that DFT consistently reproduces molecular structures within 0.02 Å and 100 cm^{-1} for vibrational frequencies. Results of similar quality were reported for transition-metal complexes[56] which show electronic structures of a complexity similar to that encountered for some of the molecules of the present study. Since DFT performs well on the calculation of vibrational spectra, the data presented in this study should provide valuable guidance to experiments on small carbon molecules with the objective of elucidating the fullerene growth mechanisms in our as well as other laboratories.

II. Computational Details

All calculations were performed using the program DGauss,[55] which is part of the UniChem[57] system installed on the Cray Y-MP of ETH Zürich. DGauss uses a one-electron basis of contracted Gaussian type orbitals. In the present study we employed a triple-ζ valence type basis set augmented with a d type polarization function optimized for DFT calculations.[58] This basis consists of a set of 10s, 6p, and 1d functions for carbon which are contracted (segmented scheme) to 4s, 3p, and 1d functions, resulting in a total of 19 functions per carbon atom. DGauss uses auxiliary basis sets to represent the electron density and the exchange-correlation potential. The auxiliary basis denoted A2 (8s, 4p, and 4d; uncontracted)[59] was used. The local spin density exchange-correlation potential of Vosko, Wilk, and Nusair[60] was augmented by the gradient functional of the Becke–Perdew model.[61,62] All geometry optimizations were started from structures showing no symmetry. The convergence criterion was set to 5×10^{-4} Hartree/Bohr for the largest component of the nuclear gradient. Vibrational frequencies were calculated by means of finite differences of nuclear gradients. We assume that this numerical procedure combined with the remaining gradient at the optimized structure will lead to a numerical uncertainty of ±10 cm^{-1} in the calculated vibrational frequencies. The computations of the largest systems took up to 20 min of Cray Y-MP CPU time per nuclear gradient calculation.

III. Results

C_2 Molecule. C_2 appears in a variety of astrophysical objects and as an intermediate in many chemical reactions.[4] It also plays a key role in the fragmentation of larger carbon molecules.[8] A large number of experimental and theoretical investigations were devoted to the characterization of the electronic and vibrational

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Table 1. Calculated and Experimental Data for the Two Lowest Electronic States of C_2

	DFT	expt[64]
	$^1\Sigma_g^+$	
r_e (Å)	1.259	1.2429
υ_0 (cm^{-1})	1845	1855.7
intensity (km/mol)	0.02	
	$^3\Pi_u$	
r_e (Å)	1.316	1.3119
υ_0 (cm^{-1})	1643	1641
intensity (km/mol)	0.00	
	Relative Energy	
$^1\Sigma_g^+ - {^3\Pi_u}$ (cm^{-1})	5770	−176

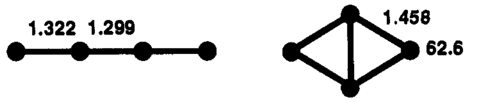
Table 2. Calculated and Experimental Data for the Ground State of C_3

	DFT	expt[a]
r_e (Å)	1.305	1.2897
bond angle	153.3	162.5
barrier to linearity (cm^{-1})	11	16.5
υ_0 (cm^{-1}) (intensity (km/mol))	84.5 (10.1)	63.4[b]
	1244 (3.4)	1224.5[c]
	2039 (612.0)	2040[b]

[a] Fitted to experimental and ab initio data.[67] [b] Reference 70. [c] Reference 67, matrix value.

states of C_2.[4] Highly accurate ab initio calculations for the lowest lying electronic states characterized experimentally are available.[63] Since DGauss like most other DFT programs can only compute the lowest energy state of a given spin multiplicity, the two electronic states accessible are the X $^1\Sigma_g^+$ and the a$^3\Pi_u$ state. As in DFT the one-particle electron density is optimized, the calculated states are not eigenstates of S^2 but only of S_z. Table 1 shows the results obtained for the two states compared with the experimental data of Huber and Herzberg.[64] While the bond lengths and vibrational frequencies are in good agreement with experiment, the singlet–triplet splitting has the wrong sign and is in error by more than 18 kcal/mol. This overstabilization of the states of higher spin multiplicity is characteristic for the local spin density approximation[65] and is not resolved by the gradient correction to the density functional used in this study. This result is not unexpected since the accurate theoretical treatment of C_2 is a very demanding task[66] and has been resolved only rather recently.[63]

C_3 Molecule. C_3 is also found in the interstellar space and in flames. The ground state of C_3 shows very interesting rotational and vibrational properties due to its low-bending frequency of 63.4 cm^{-1}. Numerous theoretical and experimental investigations[4] were dedicated to this problem, and it is beyond the scope of the present work to contribute to this area of research. The energetically lowest state found by our DFT calculations is a bent singlet state. The calculated harmonic bending frequency of 84.5 cm^{-1} has to be compared with the barrier of 11 cm^{-1} to the linear molecule. This means that the DFT calculation predicts that the potential along the bending coordinate has a shallow double minima with a very small barrier. The analysis of the rotational and vibrational spectra of C_3 that assume this special form of the potential reproduced the experimental data best.[67] The calculated C–C bond length is 0.015 Å longer than the ab initio value of Kraemer et al.[68] which was used to obtain the fit to the experimental data shown in Table 2. Our DFT results of 1244 and 2039 cm^{-1} are in very good agreement with the experimental values of 1224.5[69] and 2040 cm^{-1} [70] for the symmetric and the asymmetric stretching vibrations.



(1) (2)

Figure 2. Optimized molecular structures of C_4. Bond lengths (Å) and bond angles (deg).

C_4 Molecule. For the carbon molecules C_n ($n > 3$), structural data are much more sparse than for C_2 and C_3. Most of these systems were detected and characterized via mass spectrometry and IR spectroscopy in molecular beams. For several of the larger carbon molecules vibrational data are also available from noble gas matrix spectroscopy.[4] The earliest theoretical investigations date back to the 60s,[46,47] and we will compare our structural and energetical results with the most recent ab initio calculations. The results of several groups indicate that the linear $^3\Sigma_g^-$ structure is slightly more stable than the rhombic ^1A_g isomers of C_4. Nygren and Pettersson[71] calculate at the MR-ACPF level (ANO-type basis 4s3p2d1f) an energy difference of 3.7 kcal/mol. Bernholdt et al.[50] give a best estimate based on coupled cluster calculations with a 5s2p1d basis of 0.49 kcal/mol. Our DFT calculations predict the linear structure to be 13.8 kcal/mol more stable. However, this energy difference appears to be too large. As in the case of C_2 we expect DFT to favor the high-spin (triplet) state relative to the closed shell state. The CASSCF (eight electrons in eight orbitals for the rhombic and 10 electron in 10 orbitals for the lienar structure) geometries reported by Parasuk and Almlöf[51] compared to the D-MBPT(4) geometries of Magers et al.[72] clearly show the bond lengthening effect of dynamical correlation. As DFT accounts for a considerable fraction of the dynamical correlation it appears to be well suited for the calculation of the equilibrium geometries of pure carbon molecules. Table 3 shows our DFT results for the harmonic vibrational frequencies in comparison with experimental data[42,43,73] and other theoretical predictions[74] at the MP2 level of theory. There are no conclusive experimental results that show the presence of the rhombic C_4 isomer. Recent Coulomb explosion[75] and beam hydrogenation experiments[76] indicate that production of rhombic C_4 may be possible. A characterization via its strong IR allowed vibration predicted at 1336 cm^{-1} seems promising (see Table 3).

C_5, C_7, and C_9 Molecules. In agreement with all other ab initio calculations, DFT predicts the ground state of C_5, C_7, and C_9 to be a linear $^1\Sigma_g^+$ state. The structural parameters of these three linear molecules are given in Figure 3. The harmonic vibrational frequencies are shown in Tables 4 and 5. The accuracy of the DFT vibrational frequencies for C_5 is comparable to the one achieved by the high level ab initio calculations of Botschwina and Sebald.[77]

Since linear C_7, like C_3 and C_{11}, has a HOMO of π_u type, the

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Table 3. Harmonic Vibrational Frequencies [cm^{-1}] of Linear and Rhombic C_4 as Calculated by DFT and MP2(6-31G*) Theory[d]

linear $^3\Sigma_g^-$ structure **1**				rhombic ^1A_g structure **2**		
symmetry	DFT	MP2[74]	expt	symmetry	DFT	MP2[74]
π_u	145(52.3)	187(33.3)	172.4[a]	b_{2u}	183(63.5)	374(316.1)
π_g	259(0.0)	419(0.0)	339 ± 55[b]	b_{1u}	529(38.9)	712(184.5)
σ_g^+	904(0.0)	951(0.0)		a_g	906(0.0)	934(0.0)
σ_u^+	1532(321.0)	1586(488.3)	1549[c]	b_{1g}	1007(0.0)	1103(0.0)
σ_g^+	2049(0.0)	2149(0.0)	2032 ± 50[b]	a_g	1246(0.0)	1298(0.0)
				b_{3u}	1336(236.8)	1428(1262.4)

[a] Reference 73. [b] Reference 43. [c] Reference 42. [d] Intensities (km/mol) are given in parentheses.

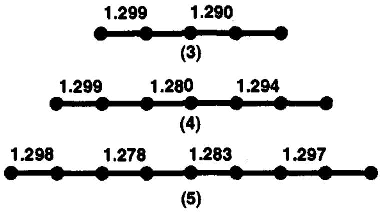

Figure 3. Optimized molecular structures of C_5, C_7, and C_9. Bond lengths (Å) and bond angles (deg).

Table 4. Harmonic Vibrational Frequencies of Linear C_5 Linear C_5 (Σ_{g-}) as Calculated by DFT and on the CEPA-1 Level of Theory[77]

symmetry	DFT[a]	CEPA-1[b]	expt
π_u	116(36.2)	119	101,[c] 118[d]
π_g	215(0.0)	209	222,[c] 218[d]
π_u	533(50.1)	570	512[c]
σ_g^+	776(0.0)	800(792)	798[c]
σ_u	1440(97.3)	1494(1478)	
σ_g^+	1969(0.0)	2033(2008)	
σ_u^-	2216(1648.8)	2198(2169)	2169[d,e]

[a] IR intensities (km/mol) in parentheses. [b] Adjusted force field values in parentheses. [c] Reference 43. [d] References 39 and 40. [e] Reference 38.

molecule is predicted to be highly nonrigid. Heath et al.[37,78] measured two IR bands at 1898 and 2138 cm^{-1}. These values compare very well with our calculations, which predict these frequencies at 1917 and 2216 cm^{-1}. Further they estimate the lowest bending frequency to be at 70 cm^{-1} which in the present work is calculated to occur at 66 cm^{-1}. The result may be somewhat fortuitous since this is the harmonic value for a most likely strongly anharmonic vibration. C_9 shows several very low-lying vibrational states. This results in a strong perturbation of the lines centered around 2000 cm^{-1}. Heath and Saykally[41] identified one single line at 2014 cm^{-1}. The nearest nonforbidden vibrational frequency calculated is 2073 cm^{-1} (Table 5). Another strong IR band is predicted at 2182 cm^{-1}.

C_6, C_8, and C_{10} Molecules. Several theoretical investigations have addressed the problem of the characterization of the ground-state structure of C_6. Raghavachari et al.[79] used perturbation theory and coupled cluster methods to calculate the energies of several low-energy structures at their Hartree–Fock optimized geometries. The authors predict a cyclic structure of D_{3h} symmetry (structure **7** in Figure 4) to be approximately 10 kcal/mol more stable than the linear structure **6**. However, the cyclic structures **7** and **8** were found to be near isoenergetic. They also concluded from their vibrational analysis at the Hartree–Fock level that the D_{6h} structure **8** is probably not a minimum on the potential hypersurface. In a more recent study, Parasuk and Almlöf[52] reinvestigated the molecular structure of C_6 based on MRCI calculations at the CASSCF optimized geometries. In their study the linear chain with cumulenic bonds was the most stable one. The two cyclic forms **7** and **8** were found to be isoenergetic and 37.2 kcal/mol less stable. In contrast to the results of Raghavachari and Almlöf et al. the present study indicates that the linear and a cyclic isomer are very close in energy and may be observed experimentally. We find the cyclic structure **7** 2.6 kcal/mol lower in energy than the linear structure **6**. However, given the fact that DFT tends to overestimate the stability of the high-spin electronic states the splitting between the linear and the cyclic form should be corrected to a larger value. Applying this empirical correction to our results supports the assessment of Raghavachari et al. Raghavachari and Almlöf et al. point out the possible importance of the correlation of the entire valence charge (see section "note added in proof" of ref 52), but neither of the two studies perform the corresponding investigation at the required level of theory. Therefore a more elaborate investigation to establish the ordering of the lowest energy structures of C_6 seems in place. In agreement with the work of Raghavachari et al. the cyclic structure with D_{6h} symmetry **8** is a saddle point on the energy surface and 11 kcal/mol less stable than structure **7**. However we only find one imaginary frequency. A distortion along the eigenvector of this imaginary mode transforms structure **8** into structure **7**. For several of the vibrational frequencies of C_6 given in Table 6 the assignment is not assured. The two asymmetric streching modes were unambigously characterized by Kranze and Graham[80] using Fourier transform infrared spectroscopy of C_6 in an Ar matrix. The other modes have been measured by Neumark and co-workers[44] using photoelectron spectroscopy with a typical accuracy of ±50 cm^{-1}. The two low-frequency modes were measured through their overtone. The excellent agreement of our computed frequencies with the other experimental data supports the assignment of Neumark and co-workers of the line at 1315 cm^{-1} observed in the photoelectron spectra[43] to an electronic transition. The $^1\Delta_g$ state was predicted by MRCI calculations[52] to be $\approx$1200 cm^{-1} higher in energy than the $^3\Sigma_g{}^-$ ground state.

Parasuk and Almlöf[81] recently investigated the relative stability of cyclic versus linear C_8. Based on calculations with different basis sets and different levels of theory to account for electron correlation, they conclude that the two forms are essentially isoenergetic. They found the cyclic structure of C_8 to have alternating bond lengths and angles, resulting in a structure of C_{4h} symmetry. This confirms the earlier results of Raghavachari and Binkley.[48] Our DFT calculations converged to a structure (**10**, Figure 5) that only exhibits C_{2h} symmetry. We were not able to optimize a ring structure with C_{4h} symmetry which indicates that the geometry found by Parasuk and Almlöf might be a saddle point on the potential surface. The linear structure **9** was calculated to be 12 kcal/mol more stable than the cyclic structure **10**. The two lines observed in the photoelectron spectra[43] of C_8 at 565 and 1130 cm^{-1} were tentatively assigned by the authors to a symmetric stretching vibration (predicted at 500 cm^{-1} by DFT) or to a electron transition to a low-lying $^1\Delta_g$ state.

C_{10} is the second molecule in the Huckel (4*n* + 2)-electron series after C_6. In agreement with all previous studies we find that the cyclic structures are much more stable than the linear form. A cumulenic ring structure with D_{5h} symmetry was found

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Table 5. Harmonic Vibrational Frequencies [cm^{-1}] as Calculated by DFT[a]

Linear C_7: Symmetry $D_{\infty h}$, Electronic State $^1\Sigma_g^+$

66 (π_u, 59.9), 157 (π_g, 0.0), 240 (π_u, 200.1), 480 (π_g, 0.0), 513 (π_u, 160.0), 586 (σ_g^+, 0.0), (σ_u^-, 4.5), 1545 (σ_g^+, 0.0), 1917 σ_u^-, 677.4), 2150 (σ_g^+, 0.0), 2216 (σ_u^-, 2695)

Linear C_8: Symmetry $D_{\infty h}$, Electronic State $^3\Sigma_g^-$

55 (π_u, 132.0), 128 (π_g, 0.0), 209 (π_u, 85.2), 337 (π_g, 0.0), 457 (π_u, 122.5), 478 (π_g, 0.0), 497 (σ_g^+, 0.0), 935 (σ_u^-, 90.2), 1355 (σ_g^+, 0.0), 1703 (σ_u^-, 984.8), 1969 (σ_g^+, 0.0), 2093 (σ_u^-, 24.7), 2109 (σ_u^-, 1366.3)

Cyclic C_8: Symmetry C_{2h}, Electronic State $^1A_1$

97 (a_g, 0.0), 132 (a_g, 0.0), 343 (a_u, 0.0), 374 (b_g, 0.0), 394 (a_u, 10.2), 402 (b_g, 0.0), 471 (a_g, 0.0), 487 (b_u, 76.4), 550 (b_u, 62.6), 574 (a_g, 0.0), 950 (a_g, 0.0), 1018 (b_u, 69.3), 1083 (b_u,55.9), 1229 (a_g, 0.0), 1845 (a_g, 0.0), 1864 (b_u, 496.2), 1885 (a_g, 0.0), 1921 (b_u, 669.1)

Linear C_9: Symmetry $D_{\infty h}$, Electronic State $^1\Sigma_g^+$

49 (π_u, 161.2), 116 (π_g, 0.0), 184 (π_u, 435.0), 255 (π_g, 0.0), 442 (π_u, 13.0), 458 (σ_g^+, 0.0), 496 (π_u, 110.8), 500 (π_g, 0.0), 905 (σ_u^-, 12.1), 1247 (σ_g^+, 0.0), 1624 (σ_u^-, 376.5), 1903 (σ_g^+, 0.0), 2073 (σ_u^-, 3030), 2182 (σ_u^-, 2324), 2209 (σ_g^+, 0.0)

[a] The symmetry and the intensity (km/mol) of the modes are given in parentheses.

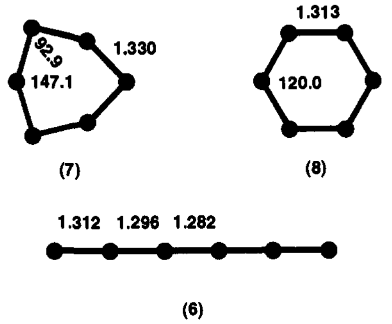

Figure 4. Optimized molecular structures of C_6. Bond lengths (Å) and bond angles (deg).

(coupled cluster,[81,82] CISD,[83] LDF[84]) to be lowest in energy, but electron correlation reduces the energy difference to other possible ring isomers. In fact at the CCSD(T) level of theory Parasuk and Almlöf[81] calculated the cumulenic structure with D_{5h} symmetry and an acetylenic-type ring structure within 1.5 kcal/mol. In a detailed investigation of part of the potential energy surface for C_{10} ring structures Watts and Bartlett[82] showed that the relative stability of the different structures is highly basis set and method dependent. Our DFT calculations were started from a nonsymmetric structure and converged to the cumulenic structure with D_{5h} symmetry. The calculations did not converge to a structure with the full D_{10h} symmetry. We also optimized C_{10} in a linear structure. The subsequent analysis of the second derivative matrix revealed a negative eigenvalue whose eigenvector corresponds to a bending of the linear chain. This confirms the theoretical argument given by Liang and Schäfer[85] that the linear structure is not necessarily an energy minimum.

C_{11}, C_{13}, C_{15}, and C_{17} Molecules. Martin et al.[86] investigated the relative stability of several isomers of C_{11} at the MP2 level of theory. The structures taken into account were a linear one, two monocyclic planar rings, and a three-dimensional structure proposed by van Vechten and Keszler.[87] This three-dimensional structure turned out to be the least stable structure (200 kcal/mol less stable than the lowest energy structure). The linear structure was only 4.9 kcal/mol less stable than their most stable monocyclic ring structure. This structure had C_{2v} symmetry and the vibrational analysis showed a very small imaginary frequency. The authors concluded that this may be an artifact of the method and that this structure in fact corresponds to the most stable isomer.

We optimized the structures of C_{11}, C_{13}, C_{15}, and C_{17}, again constrained to linear and monocyclic planar isomers. All of the optimized ring structures exhibit C_{2v} symmetry. For all these systems our calculations confirm the results of Hoffmann[47] that cyclic structures are more stable than the linear chains (see Figure 8). However, the molecules in this series showed imaginary frequencies. In all cases the modes associated with these frequencies are of a ring puckering type. Our results therefore strongly indicate that the ground states of C_{11}, C_{13}, C_{15}, and C_{17} have three-dimensional structures and are possibly polycyclic systems.

C_{12}, C_{14}, and C_{16} Molecules. In analogy to C_{10} we can expect that the ground states of C_{12}, C_{14}, C_{16}, and C_{18} also are highly symmetric monocyclic rings. The $(4n + 2)$-electron series is predicted by DFT to have cumulenic type bonds, whereas the $4n$-electron series is of polyacetylenic type (Table 8). The bond angles in the larger rings become equal. The vibrational analysis shows that C_{12} and C_{14} are minima on the energy hypersurface, whereas C_{16} has one, and C_{18} shows three imaginary frequencies. In contrast to the molecules with an odd number of carbon atoms these modes are not of a ring puckering but of a ring folding type.

C_{18} Molecule. The relative stabilities of the different C_{18} isomers has been a subject of some controversy. At the Hartree–Fock level of theory, Diederich, Houk, and co-workers[88] found the acetylenic form of C_{18} to be the lowest energy structure with a rather large margin. The two cumulenic forms with reduced D_{9h} and full D_{18h} symmetry were 37.6 and 58.3 kcal/mol less stable. In a later study Almlöf and co-workers[89] confirmed these SCF results, but pointed out that electron correlation plays a major role in the determination of the minimum energy structure of C_{18}. Their MP2 results indicate that electron correlation stabilizes the fully symmetric cumulenic form relative to the acetylenic form by more than 2 eV, thus making it the lowest energy form. In a more recent study, Bartlett and co-workers[82] question the applicability of MP2 theory for these systems and advocate higher level of correlation treatments. In their study Almlöf and co-workers are confronted with considerable symmetry-breaking effects at the SCF level which make it impossible to consistently treat these structures at the MP2 level of theory. Based on the results of the present study, there is strong indication that the difficulties encountered by these authors are related to the fact that their symmetry constrained optimization yielded a saddle point rather than a local minimum energy structure. For an extensive discussion of symmetry breaking in C_{10} and similar systems see ref 85.

In the present study we do not find a local minimum structure as the optimization converged toward a saddle point geometry. It seems, however, that given the optimization constraints applied here, the fully symmetric cumulenic structure is the most stable planar monocyclic ring structure. The question of the minimum

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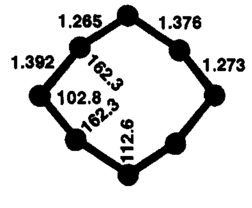
Table 6. Harmonic Vibrational Frequencies of Linear and Cyclic C_6 as Calculated by DFT and ab Initio Methods Compared to Experimental Values

linear $^3\Sigma_g^-$ structure 6				ring ^1A_g structure 7		
symmetry	DFT	MP2[1]	expt	symmetry	DFT	HF[2]
π_u	94(121.1)	108(22)	97[a]	a_2''	404(3.3)	458
π_g	185(0.0)	223(0)	240[a]	e''	507(0.0)	575
π_u	328(46.2)	432(0.6)		a'_1	548(0.0)	888
π_g	480(0.0)	551(0)	489[b]	e'	599(34.7)	738
σ_g^+	645(0.0)	673(0)		a'_1	1197(0.0)	1269
σ_u^-	1176(60.3)	1244(332)	1197[c]	e'	1210(1.8)	1285
σ_g^+	1676(0.0)	1759(0)		a'_2	1433(0.0)	1349
σ_u^-	1972(800.8)	2009(1457)	1952[c]	e'	1746(749.9)	1764
σ_g^+	2123(0.0)	2167(0)	2061[b]			

[a] Reference 43. [b] Reference 44. [c] Reference 80, matrix values.

(9)



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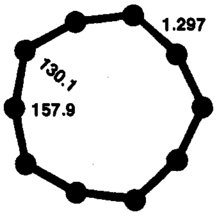

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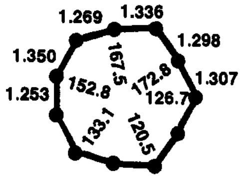
Figure 5. Optimized molecular structures of C_8 and C_{10}. Bond lengths (Å) and bond angles [deg].



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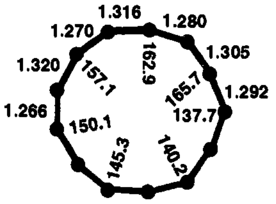

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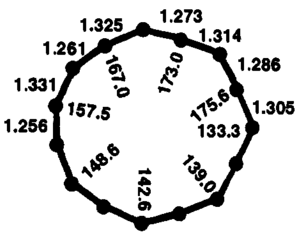

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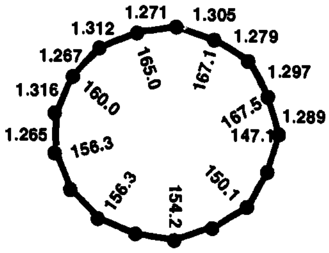


(15)

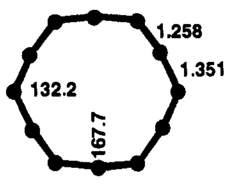
Figure 6. Optimized molecular structures of C_{11}, C_{13}, C_{15}, and C_{17}. Bond lengths (Å) and bond angles (deg).

energy structure of C_{18} therefore remains to be addressed in a more comprehensive study.

IV. Summary and Conclusions

Our DFT calculations confirm the well-established view that the lowest energy form of C_n species with $n < 10$ is the linear chain. The only exception is C_6, the first member of the $(4n + 2)$-electron Huckel series, where the lowest energy structure is still subject to some controversy. Within the Huckel series, ring structures were computed to be particularly stable (see Figure 8). Indeed our results show that for C_6 the ring form 7 is marginaly more stable than the linear chain 6. This result takes an intermediate position between two independent ab initio studies, which either favor the linear form[52] or the distorted ring structure.[79] The issue of the ordering of the lowest energy structure of C_6 will have to be addressed in a more rigorous study.

For C_n, $n \geq 10$, planar monocyclic structures are more stable than the linear chains. However, only C_n with $n = 10, 12, 14$ were found to represent true (local) minima. All the other systems



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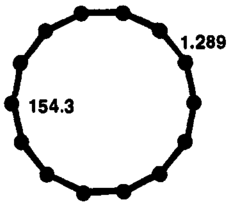

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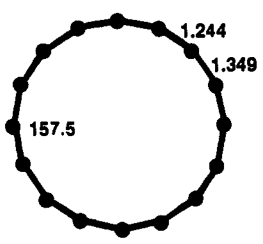

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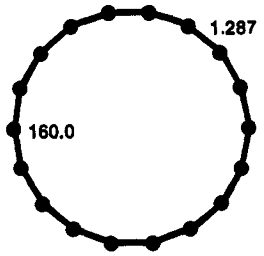

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Figure 7. Optimized molecular structures of C_{12}, C_{14}, C_{16}, and C_{18}. Bond lengths (Å) and bond angles (deg).

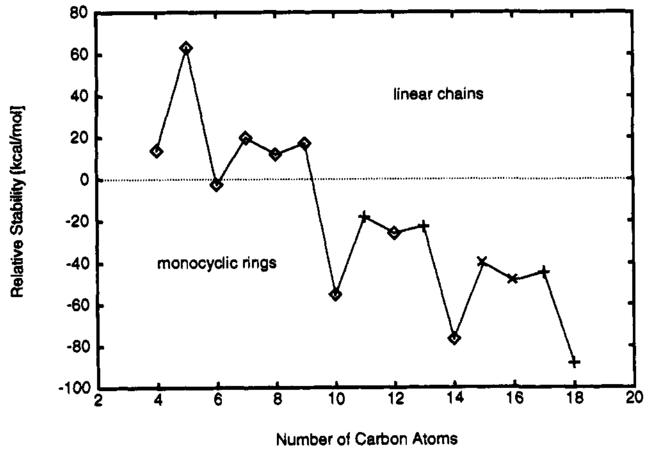

Figure 8. Relative stability of linear versus planar monocyclic isomers for C_n, $n = 2$–18 as calculated by DFT: (◇) minimum structures, (+) saddle point structures, and (×) possible saddle point structures.

Table 7. Harmonic Vibrational Frequencies [cm^{-1}] as Calculated by DFT[a]

Cyclic C_{10}: Symmetry D_{5h}, Electronic State $^1A'_1$
184 (e'_2, 0.4), 226 (e_2'', 0.0), 305 (a'_2, 2.0), 359 (a_2'', 7.1), 413 (e_2'', 0.0), 446 (e'_2, 1.8), 450 (e_1'', 1.2), 490 (e'_1, 43.4), 802 (a'_1, 0.0), 1045 (e'_1, 105.4), 1482 (e'_2, 2.2), 1558 (a'_1, 0.0), 1901 (e'_2, 1.0), 2024 (e'_1, 332.1)

Cyclic C_{12}: Symmetry C_{6h}, Electronic State ^1A_g
105 (e_{2g}, 0.0), 149 (e_{2u}, 0.0), 192 (b_u, 0.0), 263 (b_g, 0.0), 333 (a_u, 10.1), 342 (b_g, 0.0), 406 (e_{2u}, 0.0), 414 (b_u, 0.0), 426 (e_{1g}, 0.0), 438 (a_g, 0.0), 460 (e_{2g}, 0.0), 492 (e_{1u}, 266.8), 724 (a_g, 0.0), 866 (e_{1u}, 100.9), 1233 (e_{2g}, 0.0), 1453 (b_u, 0.0), 1860 (a_g, 0.0), 1910 (b_u, 0.0), 1998 (e_{1u}, 1395.7), 2010 (e_{2g}, 0.0)

Cyclic C_{14}: Symmetry D_{14h}, Electronic State ^1A_g
90, 143, 255, 270, 305, 357, 386, 393, 434, 441, 450, 455, 545, 827, 1190, 1442, 1589, 1911, 2055, 2096

[a] The symmetry and the intensity (km/mol) of the modes are given in parentheses.

Table 8. Comparison of Symmetry and Structural Parameters for Planar Moncyclic Ring Structures with an Even Number of Carbon Atoms

	symmetry	bond length	bond angles
C_4	D_{2h}	1.458	117.4, 62.6
C_6	D_{3h}	1.330	92.9, 147.1
C_8	C_{2h}	1.265, 1.392	112.6, 162.3
		1.273, 1.376	102.8, 162.3
C_{10}	D_{5h}	1.297	157.9, 130.1
C_{12}	C_{6h}	1.258, 1.351	167.7, 132.3
C_{14}	D_{14h}	1.289	154.3
C_{16}	C_{8h}	1.244, 1.349	157.5
C_{18}	D_{18h}	1.287	160.0

were found to represent saddle points on the energy surface with at least one imaginary frequency. The only possible exceptions are C_n (n = 15, 16) where the imaginary frequency computed is very small, and may be, due to methodological reasons, subject to some numerical error.

Systems with an odd number of carbon atoms tend to form ring structures with alternating (polyacetylenic type) bond lengths. The ring systems of the (4n + 2)-electron series show perfect cumulenic bonds. The smaller rings with six and ten carbon atoms have alternating bond angles, whereas the C_{14} and C_{18} molecules were computed to have also equal bond angles.

Already for C_{11}, the lowest energy isomer may exhibit a three-dimensional structure. C_{11} is the first system in the series where the out-of-plane distortion modes have a negative force constant.

For the bond lengths computed we generally find excellent agreement with high level ab initio calculations where all valence electrons are correlated, whereas Hartree–Fock and MCSCF results show consistently 0.01–0.02 Å shorter bonds. Good agreement for the computed vibrational spectra with the experimental data whenever available has been obtained. This applies for high as well as for low-frequency modes. Thus the computed spectra for the systems where no experimental information is available will be rather reliable.

As far as the methodical aspect is concerned, the present study shows that for the computation of structural and vibrational (electronic ground state) information on pure carbon molecules, methods based on DFT are useful tools. This is shown by the rather good agreement of our results with high-level ab initio calculations for the well-documented systems. The quantitative correctness, i.e., the predictive power of the method applied here, will have to be confirmed by either better functionals or computations of the CCSD(T) quality. However, in the case of large systems which are no longer accessible for post-Hartree–Fock methods DFT is currently the only method which allows the making of studies with a high level of accuracy.

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