Structure and Bonding in Carbon Clusters C_{14} to C_{24}: Chains, Rings, Bowls, Plates, and Cages

R. O. Jones
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

G. Seifert
Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany

(Received 7 April 1997)

Density functional calculations have been performed for many isomers of carbon clusters C_n ($14 \leq n \leq 24$, n even) using both local spin density and gradient-corrected approximations to the exchange-correlation energy. The stable isomers include chains, rings, graphitic ("plate" and "bowl"), and cagelike structures, and we observe a fourfold periodicity in several structural classes, not only the monocyclic rings. Stable cages exist for all clusters, and double rings are less stable than the monocyclic rings. Gradient corrections are significant, but quite regular within a given structural type. The bonding trends found should also apply to larger clusters. [S0031-9007(97)03601-6]

PACS numbers: 61.46.+w

The detection of carbon clusters C_n (as cations up to $n = 190$) [1] and the postulation of the "fullerene" structure for C_{60} [2] have led to intense interest in the structure and properties of stable, cagelike structures comprising hexagons and pentagons. Questions concerning the mechanisms for their formation have focused attention on smaller carbon clusters, long the subjects of interest to astrophysicists and molecular spectroscopists. These clusters are, however, highly reactive and difficult to prepare and analyze. The distinctly bimodal mass spectra [1] suggest a break in structural patterns near $n = 32$, and it is generally assumed that larger clusters, which are most prominent for even values of n, have structures that are formed by pentagons and hexagons [3].

Experimental work on smaller clusters has shown that several structural types occur, and the recent stabilization of linear isomers with 8 to 28 atoms by the addition of nonreactive terminal groups [4] provides the first evidence of an sp-hybridized allotrope. Early photoelectron (PE) spectroscopy on C_n^- anions [5] indicated linear structures up to $n = 9$, with monocyclic rings from $n = 10-29$. The change from chains to rings at $n = 9$ is supported by newer PE data on annealed clusters [6], although these data were interpreted to favor bicyclic rings for $n = 20-28$. Ion chromatograph studies have shown that there can be significant differences between the results for C_n^- and C_n^+ ions [7]. Linear anions are detected to C_{30}^-, for example, while the cations are not found beyond C_{10}^+. Annealing studies indicate that anion isomers for $n > 30$ include monocyclic, bicyclic, and tricyclic rings, graphitic, and fullerene structures. Ion drift measurements [8] indicate that bicyclic clusters are present in unannealed beams, but they anneal readily to monocyclic rings, which dominate for $n = 10-36$. The authors of Ref. [8] expect that graphitic structures will be more stable than monocyclic rings for $n \sim 30$, but find little evidence for their presence.

The difficulties in performing experiments on highly reactive clusters, the practical necessity of studying charged species, and the occasionally contradictory results present a challenge to theory. However, clusters of 10 to 30 atoms present immense difficulties for all parameter-free methods of calculation, and there have been studies of relatively few of the many C_n isomers in this range. Hartree-Fock (HF) calculations have been performed for four isomers of C_{20} (including two bicyclic rings) [9] and four isomers of C_{24} [10]. HF and second-order Møller-Plesset (MP2) calculations were performed for ring isomers from C_{18} to C_{36} and for cages with $n = 20, 24, 26, \ldots$ [11]. Moreover, the most reliable wave function-based calculations, which are computationally extremely demanding and possible only for fixed geometries, yield different orderings in the energies of C_{20} isomers. Quantum Monte Carlo calculations [12] predict that the relaxed graphitic (bowl) structure is more stable than ring or fullerene isomers, while coupled cluster (CC) calculations [13] indicate that the fullerene is slightly more stable than the bowl, with the ring considerably higher in energy.

The picture arising from density functional (DF) calculations is also ambiguous. While calculations with the local density (LD) approximation give rise to an isomer ordering that is similar to the CC results, the incorporation of gradient corrections lead to dramatic changes in the relative energies for C_{20} and C_{24} [14]. Other DF work includes LD calculations on a total of six isomers of C_{20} [13]. The main focus has been on cage structures with fivefold and sixfold rings alone, and we know of no published work on cage structures for $n = 14, 16, 18, 22$.

In the present work, we use both local spin density (LSD) and gradient-corrected (GC) approximations in DF calculations of the energy surfaces of numerous isomers of carbon clusters with even numbers of atoms between 14 and 24. Most states are singlets, but higher spin states were considered if required by symmetry or by a small gap between the highest occupied and lowest unoccupied molecular orbitals (e.g., in the linear chains, where the lowest energy states are triplets that distort to monocyclic rings). These are the first parameter-free calculations for many of the isomers, and the results show interesting patterns in structure and energy. We give results from all-electron calculations using an extended Gaussian orbital basis [15], and vibration frequencies are calculated for all structures. Many starting structures were generated with (a) a DF-based tight-binding approach used previously, for example, to study the ionization energies of fullerenes [16], and (b) DF calculations with simulated annealing [17]. The latter have been invaluable in testing the stability of the final structures and in studying isomers derived by modifying known forms, e.g., by removing or adding atoms, as the structural changes were often large. Examples are the cage structures in C_{22}, which were derived from C_{24} cages by removing different pairs of atoms.

The most stable isomers found for C_{14}, C_{18}, and C_{22} are shown in Fig. 1, and those for C_{16}, C_{20}, and C_{24} are shown in Fig. 2. Also shown are the energies, relative to the monocyclic ring structures, calculated using the LSD and GC approximations. The energy values are connected by lines representing the structural *type*: The full lines, for example, indicate cages and the dotted lines indicate double rings. "Graphitic" structures (squares) include both planar ("plate") and bent ("bowl") forms.

LSD calculations predict that cages are the most stable isomers for $n \geq 20$, and there are stable cage structures for all n (including C_{14}). The latter result may be surprising. C_{22} cannot exist as a closed structure containing pentagons and hexagons alone [3], and it has been said that it does not exist as a closed cage [18]. Cages with fourfold rings, such as found here, are often overlooked in carbon clusters, for which they have been discussed only recently [19]. Graphitic structures and bicyclic rings are found for all clusters, and there are *nonplanar* forms of each for C_{16} and C_{20}. The monocyclic rings are more stable than the bicyclic forms in all clusters, which supports the findings of ion drift measurements.

The interest in carbon clusters has led over the years to discussions of the relative stabilities of their isomers. Kroto, for example, proposed that the existence of adjacent pentagons would be unfavorable for a cage structure [18], and Schmalz *et al.* [20] used semiempirical models to develop additional criteria involving the balance between π-electron bonding and σ strain. A fourfold ("$4n + 2$") periodicity related to the rules of Hückel for the stability of aromatic molecules was found long ago in semiempirical calculations of ring isomers of C_n [21]. A linear chain has two orthogonal ("ideal") π bonds per atom, with the exception of the unsaturated terminal atoms. There are no unsaturated atoms in the monocyclic rings, but only the π orbitals perpendicular to the plane of the ring are ideal. The strain that results depends on the curvature of the ring.

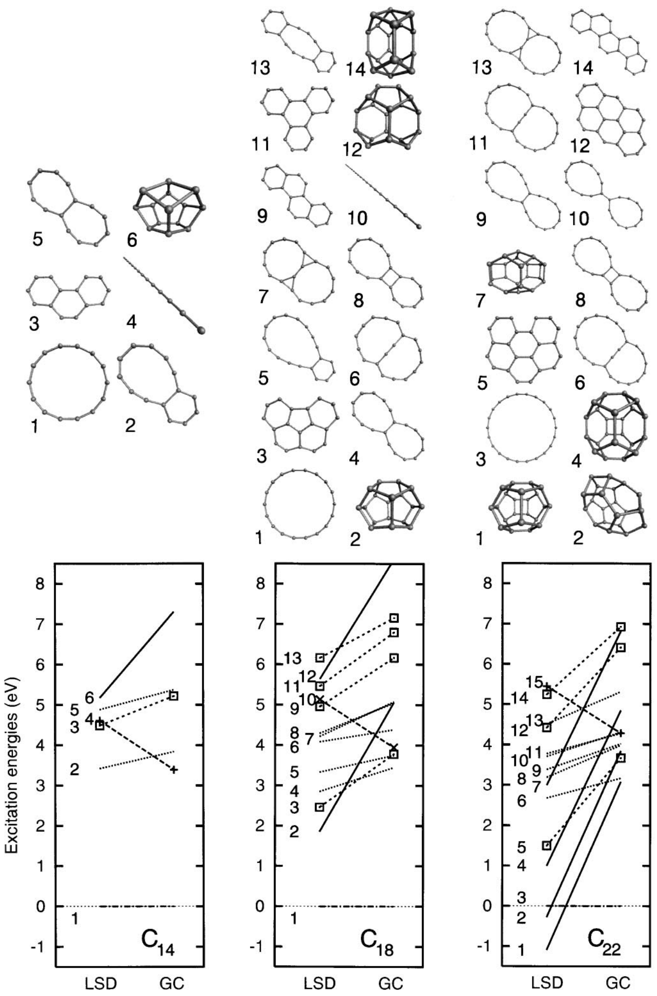

FIG. 1. Structures and energies (relative to the monocyclic ring isomer) of isomers of C_{14}, C_{18}, and C_{22} (eV). LSD and GC values are connected by lines representing the structural type—full, cages; dotted, double rings; crosses, chains; squares, graphitic; dash-dotted, monocyclic rings. The structures are ordered in pairs from below according to the LSD energies.

The balance between "strain" and "bonding" and the fourfold periodicity are also evident in the present results. The monocyclic rings are "cumulenic" (i.e., have identical bond lengths) in C_{14}, C_{18}, and C_{22}, but "polyacetylenic" (with alternating bond lengths) in the other four. Calculations for the structures of C_{16}, C_{20}, and C_{24} with all bonds of length 1.28 Å (the value found in the $4n + 2$ family) are marked with primes in Fig. 2. They are $\sim$1 eV higher in energy than the stable ring.

The results for the graphitic and bicyclic structures show interesting features. (a) The double ring structures generally comprise rings with even numbers of twofold coordinated atoms. The only exception shown here is 18(6), where the odd-numbered rings comprise almost linear C_3 segments [22]. Other odd-numbered rings with

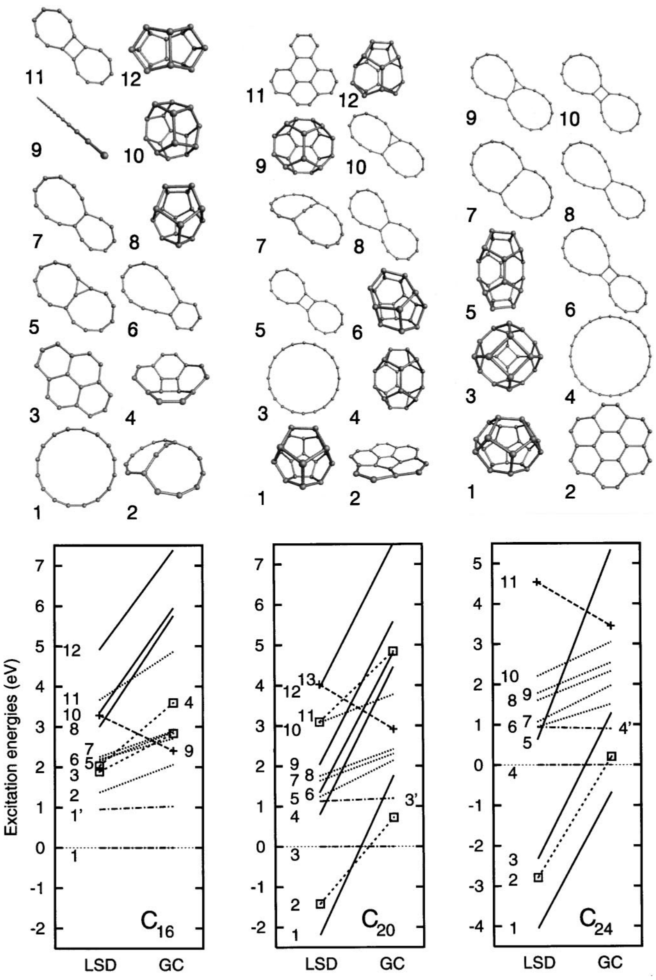

FIG. 2. Structures and energies (relative to the monocyclic ring isomer) of isomers of C_{16}, C_{20}, and C_{24} (eV). LSD and GC values are connected by lines representing the structural type. (See caption of Fig. 1.)

similar segments distorted during structure optimization to even-numbered rings with smooth variations in bond angles. A direct consequence is the fourfold periodicity apparent in the bicyclic structures involving triangular C_3 units, which occur in pairs in $4n + 2$ double rings, but singly in the other family. (b) Strain effects manifest themselves in several ways. The buckling in the double rings 16(2) and 20(7) allows the bond angles at the threefold vertices to be closer to the optimum sp^2 value than in the planar structure. Ring segments with small curvature occur in numerous lobelike structures, in bicyclic structures with four atoms common to each ring, and in structures with rings of different size, e.g., 14(2), 16(6). The energy ordering of the *graphitic* structures can be related to the numbers of 6π rings and unsaturated atoms. These considerations and all results will be discussed in detail elsewhere.

The calculated cohesive energies (binding energies per atom) of the most stable isomer of each type (Fig. 3) show that gradient corrections lower the LSD values by ~1 eV, a change similar to that found in clusters of other main group elements [23]. However, the effects of gradient corrections differ significantly for different structural types. They are largest in cagelike structures (Figs. 1–3), followed by the graphitic (plate) and double ring structures, i.e., the effects diminish as the average coordination number decreases. There are fewer bonds in the (metastable) linear chains than in the monocyclic rings, and the gradient corrections *reduce* the energy difference between them. The changes are remarkably similar *within* a given structural family, with the lines connecting LSD and GC results being close to parallel in all cases, but are large enough to change the predictions for the most stable isomers of C_{20}, C_{22}, and C_{24}. Unambiguous experimental evidence of the nature of the most stable isomer in these clusters would provide a direct and valuable test of the relative merits of LSD and different GC approximations. Recent improvements in the latter [24] have resulted in simple approximations free of empirical input, and we are studying their applicability in the present and other contexts.

Experimental measurements, the final tests of any theoretical prediction, are complicated by the high temperatures often used to generate the clusters and the use of ions for mass separation. We have focused on the energy surfaces of neutral clusters, and the relationship to charged

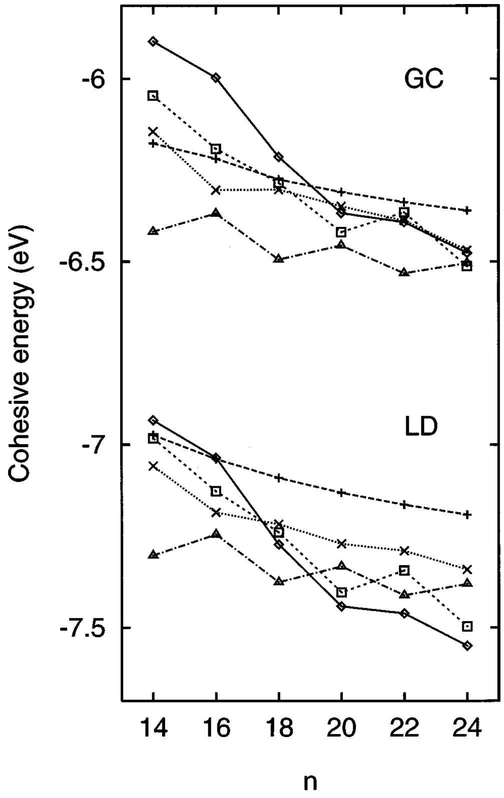

FIG. 3. Cohesive energies (binding energies per atom, eV) of the most stable of the different isomer classes in $C_{14}-C_{24}$. (See caption of Fig. 1.)

clusters not in equilibrium is not immediate. Nevertheless, the observed stability of ring structures relative to multiple rings is found here for clusters of this size, and we expect that the bonding trends will also be evident in larger clusters. We conclude with observations that could aid the comparison between theory and experiment.

Different structures have markedly different distributions of vibration frequencies. In C_{24}, for example, the three-dimensional structures (1,3,5) have upper frequencies of 1500–1600 cm^{-1}, with lowest frequencies of 200, 370, and 68 cm^{-1}, respectively. All remaining isomers have much broader vibration spectra (with maxima at 2000–2200 cm^{-1}) and low-frequency bending and twisting modes (20–60 cm^{-1}). There are many vibrational modes in clusters of this size [66 in C_{24}], but even the identification of single modes could eliminate possible structures. The observation of a vibration frequency of 2200 cm^{-1} in C_{20} [6], for example, indicates that the cage structures 20(1) (calculated frequencies from 200–1430 cm^{-1}), 20(4) (445–1600 cm^{-1}), and 20(6) (185–1530 cm^{-1}) are not favored under the conditions of the experiment. Photoelectron spectroscopy, which investigates vertical transitions from low-lying states of cluster anions to states of the neutral cluster, provides additional information. The calculations are being extended to larger n and to the C_n^- anions with the aim of analyzing these and other data.

We thank K. Vietze for assistance with generating initial geometries, and G. S. thanks P. W. Fowler for helpful discussions. The Forschungszentrum Jülich and the German Supercomputer Center (HLRZ) have provided generous access to the Cray T916/12512, T3E/512, and YMP/M94 computers in the Forschungszentrum Jülich.

---

[1] E. A. Rohlfing, D. M. Cox, and A. Kaldor, J. Chem. Phys. **81**, 3322 (1984).
[2] H. W. Kroto *et al.*, Nature (London) **318**, 162 (1985).
[3] See P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes* (Clarendon Press, Oxford, 1995) for a systematic discussion of fullerene structures from $n = 20-100$.
[4] R. J. Lagow *et al.*, Science **267**, 362 (1995).
[5] S. Yang *et al.*, Chem. Phys. Lett. **144**, 431 (1988).
[6] H. Handschuh *et al.*, Phys. Rev. Lett. **74**, 1095 (1995).
[7] A survey of the results using this technique is given by N. G. Gotts, G. von Helden, and M. T. Bowers, Int. J. Mass. Spectrom. Ion Process. **149/150**, 217 (1995).
[8] K. B. Shelimov, J. M. Hunter, and M. F. Jarrold, Int. J. Mass Spectrom. Ion Process. **138**, 17 (1994).
[9] G. von Helden *et al.*, Chem. Phys. Lett. **204**, 15 (1993).
[10] F. Jensen and H. Toftlund, Chem. Phys. Lett. **201**, 89 (1993).
[11] M. Feyereisen *et al.*, J. Chem. Phys. **96**, 2926 (1992).
[12] J. C. Grossman, L. Mitas, and K. Raghavachari, Phys. Rev. Lett. **75**, 3870 (1995).
[13] E. J. Bylaska *et al.*, J. Phys. Chem. **100**, 6966 (1996).
[14] C_{20}: K. Raghavachari *et al.*, Chem. Phys. Lett. **214**, 357 (1993). C_{24}: K. Raghavachari *et al.*, Chem. Phys. Lett. **220**, 385 (1994).
[15] DGAUSS program, UNICHEM package of Cray Research, Inc. (triple zeta basis with polarization functions TZ94P, auxiliary basis TZ94AUX). LSD approximation: S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **53**, 1385 (1980). Gradient corrections: A. D. Becke, Phys. Rev. A **38**, 3098 (1988) (exchange energy); J. P. Perdew, Phys. Rev. B **33**, 8822 (1986) (correlation energy).
[16] G. Seifert, K. Vietze, and R. Schmidt, J. Phys. B **29**, 5183 (1996).
[17] CPMD Version 3.0, J. Hutter *et al.*, MPI für Festkörperforschung and IBM Research, 1990–1997.
[18] H. W. Kroto, Nature (London) **329**, 529 (1987).
[19] See, for example, Y.-D. Gao and W. C. Herndon, J. Am. Chem. Soc. **115**, 8459 (1993); P. W. Fowler *et al.*, J. Phys. Chem. **100**, 6984 (1996).
[20] T. G. Schmalz *et al.*, J. Am. Chem. Soc. **110**, 1113 (1988).
[21] See, for example, K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1959); R. Hoffmann, Tetrahedron **22**, 521 (1966).
[22] Isomers are denoted here by the number of C atoms and the corresponding label in Fig. 1 or Fig. 2. For example, 18(6) denotes isomer 6 of C_{18} in Fig. 1.
[23] See, for example, P. Ballone and R. O. Jones, J. Chem. Phys. **100**, 4941 (1994) (P, As).
[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).