Density functional study of carbon clusters C_{2n} $(2 \leqslant n \leqslant 16)$. I. Structure and bonding in the neutral clusters

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Density functional calculations have been performed for many isomers of neutral carbon clusters C_n $(4 \leqslant n \leqslant 32$, n even) using both local spin density (LSD) and gradient-corrected (Becke–Perdew) approximations to the exchange-correlation energy. The stable isomers include chains, rings, cages, and graphitic (''plate '' and ''bowl'') structures, and we observe a fourfold periodicity in several structural classes as n changes. Stable cages exist for all clusters with $n \geqslant 8$, and double rings are less stable than the monocyclic rings in all cases. Most planar structures have low-frequency out-of-plane vibrations. Gradient corrections often change the ordering of the energies of the isomers, but the effects are remarkably regular within a given structural type. © *1999 American Institute of Physics.* [S0021-9606(99)30210-5]

I. INTRODUCTION

While carbon clusters C_n have been the subjects of investigation by astrophysicists and molecular spectroscopists for decades, the identification of carbon cluster cations C_n^+ up to $n=190$ (Ref. 1) and the postulation of the ''fullerene'' structure for C_{60} (Ref. 2) caused an explosion of interest in the field. The prediction of new low-energy forms of carbon,[3] recent advances in carbon nanotubes,[4] and the preparation of a solid form of C_{36} (Ref. 5) have helped maintain interest in these clusters at a high level. Speculation concerning possible mechanisms for formation of the larger carbon clusters—often cagelike structures comprising hexagons and pentagons[4,6]—and the nature of the precursors involved has often focused on the isomers of smaller clusters and their relative stabilities. The mass spectra for carbon cluster cations are distinctly bimodal,[1] with clusters for $n \geqslant 32$ occurring mainly for even values of n, while smaller clusters occur for all n. It is often assumed that this break arises from a transition to structures that are formed by pentagons and hexagons.[7] It is interesting to note that early measurements[8] on carbon cations from C_3^+ to C_{28}^+ showed a variation in abundance that was odd–even to $n \sim 8$, but with a fourfold periodicity for larger clusters. This was interpreted as evidence for the presence of graphitic structures.

Small carbon clusters are highly reactive in the gas phase and difficult to prepare and analyze. Nevertheless, there is much evidence that a range of structural types occurs. Photoelectron (PE) spectroscopy on C_n^- anions[9] indicated linear structures up to $n=9$, with monocyclic rings from $n=10-29$. The transition from chains to rings at $n=9$ is supported by PE data on annealed clusters,[10] which were also interpreted to favor bicyclic rings for $n=20-28$. Significant differences between the results for C_n^- and C_n^+ ions are evident in gas chromatography studies;[11] linear anions are detected to C_{30}^-, while linear cations are not found beyond C_{10}^+. Recent high-resolution data assign the anions for $n=13,17,18,24$ to short carbon chains attached to a ring.[12] The C_{28}^+ ion can be found in abundance under certain experimental conditions.[13] Annealing studies indicate that anion isomers for $n>30$ include mono-, bi-, and tricyclic rings, graphitic, and fullerene structures. Bicyclic clusters observed in ion drift measurements of unannealed beams anneal readily to monocyclic rings,[14] which dominate for $n=10-36$. The authors of Ref. 14 found little evidence of graphitic structures, although they expected that they would be more stable than monocyclic rings for $n \sim 30$. The most detailed information on carbon clusters in the gas phase has been provided by infrared laser spectroscopy, but has been restricted so far to the linear triplet states of C_4 (Ref. 15) and C_6 (Ref. 16). The stabilization of linear isomers with 8–28 atoms by the addition of nonreactive terminal groups has been observed,[17] and photoelectron spectra of monocyclic C_n^- for $n=12,16,18,20,24$ have shown clear differences between the cases $n=4N$ and $n=4N+2$ (N integer).[18] Further measurements on C_n^- for $10 \leqslant n \leqslant 16$ provided evidence for the existence of ring and chain isomers under different conditions of laser fluence.[19] Recent Raman spectroscopic measurements on size-selected C_{16}, C_{18}, and C_{20} clusters in nitrogen matrices appear to rule out the bowl and ring isomers, favoring linear chains.[20]

The difficulties in performing experiments on highly reactive clusters, the practical necessity of studying charged species, and occasionally contradictory results present a challenge to theory. There have been numerous calculations on clusters with up to 10 atoms, with the main focus on the relative energies of the ring and chain isomers. However, larger clusters present immense difficulties for all parameter-free methods of calculation, and only a fraction of the many C_n isomers with between 10 and 30 atoms have been studied. Hartree–Fock (HF) calculation have been performed for isomers of C_{20} (including two bicyclic rings)[21] and C_{24}.[22] HF and second-order Møller-Plesset (MP2) calculations were performed for ring isomers from C_{18} to C_{36} and for cages with $n=20,24,26,\ldots$.[23] 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[24] predict that the bowl structure is more stable than ring or fullerene isomers, while coupled-cluster (CC) calculations[25] 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} (Ref. 26) and C_{24} (Ref. 27). Other DF work includes calculations on ring isomers of C_{18},[28] LD calculations on six isomers of C_{20} (Ref. 25) and calculations of the fully optimized structures and energies of the ring, bowl, and cage structures of C_{20}.[29,30] Calculations with a gradient-corrected functional and the Harris approximation[31] have been made for the structures and binding energies for some cage isomers for n between 8 and 120.[32,33] The Harris approximation has also been used in a study of fullerene molecules from C_{20} to C_{240} using a combination of molecular dynamics with DF calculations.[34] The main focus in these studies has been on cage structures with five and sixfold rings.

We describe here DF calculations of the energy surfaces of numerous isomers of carbon clusters with between 4 and 32 atoms, using both LSD and gradient-corrected (GC) approximations for the exchange-correlation energy. There are no constraints on symmetry. The large range of cluster sizes has been achieved by restricting the calculations to *even* numbers of atoms, although we have noted that these are often the most prevalent in mass spectra. References 35 and 36 contain references to theoretical work on clusters with odd numbers of atoms. The results on small clusters (with between four and ten atoms) allow comparison with earlier work, but there are some unexpected results even here, such as the cage forms of C_8 and C_{10}. The number of possible isomers increases very rapidly with increasing cluster size, and it is not possible to study all in clusters with up to 32 atoms. The present survey has nevertheless been very extensive and enables us to identify several bonding trends unambiguously.

In Sec. II we outline necessary details of the method of calculation, in Sec. III we present the results for the structures and relative energies for the isomers of different C_n clusters, and in Sec. IV we discuss the results with particular reference to the changes in bonding patterns with increasing cluster size. A forthcoming paper will discuss the anions C_n^- and cations C_n^+, ionization energies, vertical detachment energies, and the vibration frequencies of the stable clusters. Preliminary results of this work (C_{14} to C_{24}) have been published.[37]

II. DENSITY FUNCTIONAL CALCULATIONS

The structures and relative energies presented below were determined using all-electron DF calculations with an extended Gaussian basis set.[38] All structures were optimized separately using the LSD approximation and a nonlocal modification involving the gradient of the density. For the latter we used the ''BP'' form, with modifications to the exchange and correlation energies of Becke and Perdew, respectively.[39]

The structure of the most stable isomer is not known with certainty for any cluster size, and a range of starting geometries has been used in each. Many such structures were generated with (a) a DF-based tight-binding approach used previously to study the ionization energies of fullerenes,[40] and (b) a combination of DF calculations with simulated annealing (MD/DF) at temperatures between 20 and 550 K.[41] The latter technique allows us to study the stability of structures corresponding to shallow minima in the energy surface and to generate additional structures by modifying known forms. Examples are given by the cage structures in C_{22} (see Sec. III E), which were substantial distortions of structures derived from C_{24} cages by removing different pairs of atoms.

Many of the planar or near-planar structures have low-lying vibration frequencies (corresponding to shallow minima in the energy surface) or imaginary frequencies (corresponding to saddle points). Structure optimization can be time consuming in such cases, where simulated annealing (MD/DF) calculations have proved very useful to generate starting geometries. Initial coordinates for cage structures of C_{30} and C_{32} were taken from the results of DF-based calculations.[34] Numerous planar structures are closely related to well-known aromatic molecules. Examples are the C_{10} form related to naphthalene and the C_{14} forms related to anthracene and phenanthrene.

The MD/DF calculations use periodic boundary conditions with a (simple cubic) unit cell with lattice constant 20 a.u., and a plane wave basis set with a single point ($k=0$) in the Brillouin zone and an energy cutoff of 30 a.u. The electron–ion interaction is described by the nonlocal pseudopotential of Troullier and Martins,[42] using the *d*-component of the potential as the reference local part (''*sp*-nonlocality''). These calculations were all performed with the local spin density (LSD) approximation to the exchange-correlation energy, and we emphasize that they were used as a means of generating reasonable starting geometries for the subsequent calculations.

All structures and binding energies presented below were obtained using an all-electron density functional program DGAUSS,[38] which uses a one-electron basis of contracted Gaussian-type orbitals. The results described adopted a triple-zeta valence type basis with a *d*-type polarization function,[43] with the A2 auxiliary basis[38] to represent the density and exchange-correlation potential. This method was used previously by Hutter *et al.*[44] for linear and monocyclic isomers of C_2 to C_{18}. The first report on this study[37] gave results using a different triple-zeta basis.[45] We discuss the dependence of the results on the different basis sets in the Appendix.

The molecular states of the structures given below are singlet unless otherwise stated, but the incorporation of spin is often essential. The lowest energy states in the linear chains, for example, are triplets that are unstable to distortions to monocyclic rings. Higher spin states were also calculated if required by symmetry (e.g., the tetrahedral structure of C_{28}) or if the spin-free calculations led to a small gap

between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals.

III. RESULTS

Energies of different isomers are shown relative to that of the monocyclic ring structures, and the energies are for the *clusters*, not per atom. The lines joining the LSD and BP values represent the structural *type*: Full lines indicate cages, dotted lines with solid triangles represent double rings, and ''graphitic'' structures (squares) include both planar (''plate'') and bent (''bowl'') forms. The isomers of a given cluster are labeled according to the relative energies of the LSD calculations, e.g., 10(1) is the most stable form of C_{10}, and 10(4) the fourth most stable. Numerous isomers with energies far above the ring structure are not discussed. ''Bonds'' in the figures indicate that the atoms are separated by less than 1.70 Å.

The structural parameters determined using LSD and BP functionals are usually very similar, with LSD bond lengths usually being slightly shorter and the vibration frequencies correspondingly higher. Structural parameters given below are for the LSD approximation, and the coordinates of the most stable structures are available.[46] By contrast, the relative energies calculated using the two approximations show pronounced differences. The immense literature on carbon clusters in this size range has been reviewed by other authors, [4,7] and we focus here on recent work and that of immediate relevance to the present calculations.

A. C_4, C_6, C_8, C_{10}

The linear and ring isomers of C_4–C_{10} have been studied on many occasions. The present results for these and other isomers are shown in Fig. 1. The triplet chain 4(1) ($^3\Sigma_g^-$), with $r_{12}=1.312$ Å and $r_{23}=1.291$ Å [1.323 Å, 1.298 Å, BP] is the most stable form of C_4. The D_{2h} isomer [4(2), $r_{12}=1.445$ Å, $\alpha_{123}=62.0°$] lies 0.26 eV higher in the LSD calculation [BP: 0.60 eV, $r_{12}=1.460$ Å, $\alpha_{123}=62.4°$], with a high-spin (quintet) butterfly structure a further 3.54 eV [3.61 eV, BP] higher in energy.

Extensive coupled-cluster calculations[47] of the linear and rhombic forms of C_4 indicate that the energies are almost degenerate, and the calculated atomization energy is close to recent experimental estimates for the linear form.[48] The present calculations lead for C_4 to the familiar result that the cohesive energies calculated with the BP (gradient-corrected) functional (BP) agree better with experiment than do the LSD values. On the other hand, the LSD value of the energy separation between the two dimers is closer to the coupled-cluster value.

The cyclic form of C_6 [6(1), D_{3h}, $r_{12}=r_{23}=1.319$ Å, $\alpha_1=146.8°$, $\alpha_2=93.1°$] is more stable than the linear [6(2), $r_{12}=1.302$ Å, $r_{23}=1.288$ Å, $r_{34}=1.275$ Å] in both LSD and BP calculations, by 1.25 and 0.1 eV, respectively. The isomer observed by infrared laser spectroscopy[16] is a centrosymmetric linear triplet state with effective bond length 1.2868 Å. Coupled-cluster calculations of Hutter and Lüthi[49] and of Martin and Taylor[47] favor the ring structure by 0.46 and 0.47 eV, respectively. *Ab initio* calculations of Pless *et al.*[50] also show that the relative stability of the isomers depends on the way that electron correlations are treated, but multi-reference configuration interaction calculations suggest that the planar D_{3h} isomer is the most stable, ~0.3 eV below the linear form. The present calculations indicate that cage-like structures, including the D_{3h} prism, are unstable to annealing at low temperatures.

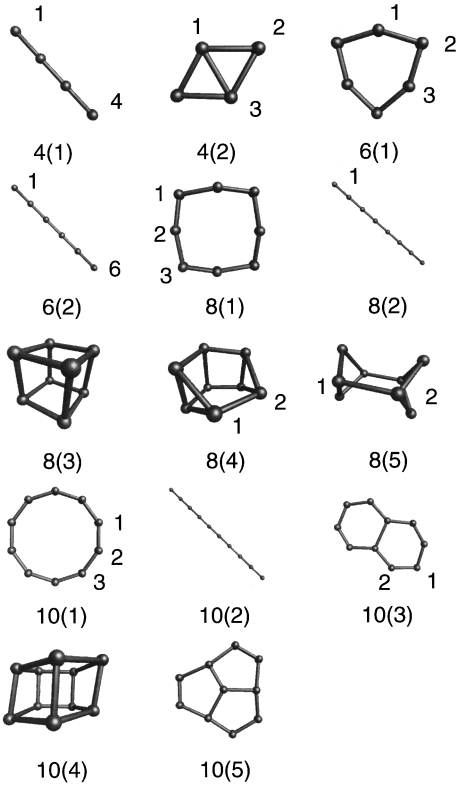

FIG. 1. Structures of isomers of C_4, C_6, C_8, and C_{10}.

For C_8, LSD calculations favor the ring structure [8(1), C_{4h}, $r_{12}=1.371$ Å, $r_{23}=1.261$ Å, $\alpha_1=162.1°$, $\alpha_2=107.9°$] by 0.60 eV over the chain [8(2)]. BP calculations show the opposite ordering, the magnitude of the energy difference being 0.48 eV. The coupled-cluster calculations lead to a ring structure that is more stable than the chain by 0.26 eV. The eight-atom cluster is the smallest in the present work for which cage structures [8(3,4,5)] are stable. Structure 8(3) [cubic (O_h), interatomic distances 1.468 Å] lies over 3 eV higher in energy than the other two, and its lowest vibration frequency is 720 cm^{-1}. It was discussed previously in Ref. 32. Two other structures that are the most stable forms of the phosphorus octamer[51] are also stable isomers of C_8. The C_{2v} structure 8(4) lies 1.18 eV above the cubic form and has a lowest vibration frequency of over 400 cm^{-1}. With the exception of r_{12} (1.69 Å), the bond lengths are in a narrow range between 1.42 and 1.46 Å. The D_{2h} form 8(5) lies more than 2.5 eV higher in energy than 8(4). In this case $r_{12}=1.68$ Å, with the bonds in the butterfly units being 1.44 Å long.

The ring isomer [10(1)] is by far the most stable in C_{10}, and it was the only one considered in the coupled-cluster calculations. Previous studies of C_{10} ring structures indicated that three monocyclic structures were essentially degenerate,[52] and it is apparent that the relative energies de-

pend sensitively on the basis set and method used.[53] Diffusion Monte Carlo calculations[24] indicate that the D_{5h} ring is 0.3 eV more stable than the cumulenic ring with D_{10h} symmetry, while DF calculations favor the latter. The present calculations also led to the latter structure, with $r_{12}=1.286$ Å. The chain structure [10(2)] is a saddle point in the energy surface, with imaginary frequencies corresponding to distortions into the ring structure. The ten-atom chain is the shortest associated with this instability, which occurs in all longer chains in the present study.

Ten-atom clusters also provide the first cases of other structural types. Small double rings usually distort into monocyclic structures, and this is true for the singlet state corresponding to the analog of naphthalene [10(3)]. The planar (C_s) structure shown is a triplet, and the highest occupied molecular orbital has its maximum amplitude on atoms 1 and 2. The lowest vibration frequency (160 cm^{-1}) corresponds to an out-of-plane bending mode. The C_{2v} structure 10(5)—analogous to tricyclodecapentene—is a saddle point in the energy surface that is unstable to an out-of-plane buckling. A pentagonal prism (D_{5h}) was considered in Ref. 33. The present calculations indicate that this is unstable against distortion to the singlet C_2 structure 10(4). The triplet state with this structure is a saddle point in the energy surface.

Carbon clusters with up to ten atoms are those that have been studied in most detail previously. The geometrical structures found in the present work agree well with other calculations, and we have found some additional structures. It is already apparent from these results, however, that the relative energies of the isomers can be quite different for the LSD and gradient-corrected (BP) approximations to the exchange-correlation energy. This will also be evident in larger clusters.

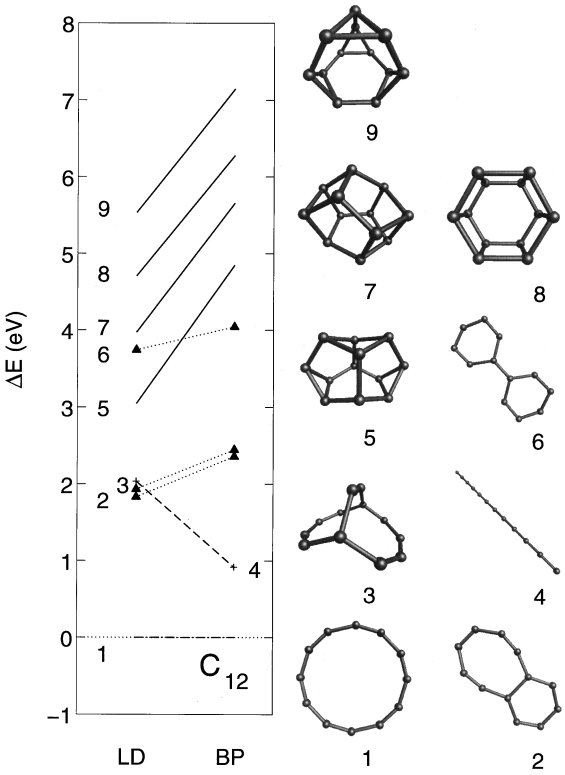

FIG. 2. Structures and energies (relative to the monocyclic ring) of isomers of C_{12} (eV). LSD and GC values are connected by lines representing the structural type full: Cages, dotted: Double rings, crosses: Chains, squares: Graphitic, dash–dot: Monocyclic rings. The structures are ordered in pairs from below according to the LSD energies.

B. C_{12}

The geometrical structures and relative energies of isomers of C_{12} are shown in Fig. 2. Previous DF calculations with the BP functional[44] showed that the ring structure 12(1) was more stable than the linear chain 12(4), and the present calculations show that this is true for the LSD functional as well. There are interesting features in the other isomers. The planar double-ring structure 12(2) is unstable to low-temperature annealing, on which it reverts to 12(1), and a second bicyclic structure 12(3) is buckled. The planar analog of the last is strained because the bond angles at the threefold coordinated atoms are quite different from their optimum values.

The cage structure 12(8) was considered in Ref. 32. The present calculations find two other cage structures [12(5), 12(7)] with lower energies, and a tetrahedral structure 12(9) with a higher energy. A particularly striking effect is repeated throughout this work: While gradient corrections have a pronounced effect on the energetic ordering of the isomers, the effect is very small *within* a given structural type. This is evident in the almost parallel curves corresponding to the four cage structures in Fig. 2. The three bicyclic structures show a similar effect of gradient corrections, although the changes are smaller in the cages. The linear chain is the only isomer where the number of bonds is *less* than in the monocyclic ring, and gradient corrections lead to a change of the *opposite* sign. However, the *number* of bonds is not the only criterion for the stability of a particular structure. The planar structure comprising two hexagons [12(6)] is more stable than the hexagonal prism 12(8) in both LSD and BP calculations.

C. C_{14}, C_{16}, C_{18}

The structures and relative energies of isomers of C_{14}, C_{16}, and C_{18} are shown in Figs. 3, 4, and 5, respectively. Previous wave function and DF calculations in C_{14} were apparently restricted to the monocyclic ring [14(1)] and linear chain [14(7)] structures. The former is the most stable isomer of C_{14} by more than 3 eV, but double ring and graphitic structures are also evident. The triple ring structures 14(5) and 14(8) are unstable to low-temperature annealing, opening into the ring 14(1). The cage structure 14(3) with D_{3h} symmetry comprises four- and five-membered rings and is a singlet. The planar structure 14(4), related to pyracylene, has been of interest in the context of fullerene isomerization, where it is the structural unit of the Stone–Wales rearrangement.[54] Isomerization can be viewed as the rotation of the central bond, with an interchange of the pairs of pentagons and hexagons.

The monocyclic ring 16(1) is also the most stable of the 16-atom isomers, and a bicyclic ring [16(3)] is related to the buckled isomer of C_{12} [12(3)]. It is closer to planarity than

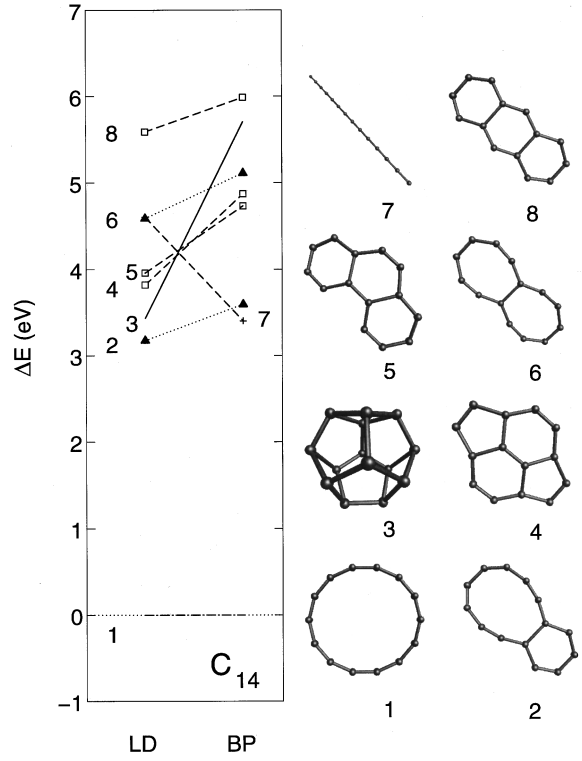

FIG. 3. Structures and energies (relative to the monocyclic ring) of isomers of C_{14} (eV). See caption to Fig. 2.

the latter, reflecting the reduction in strain with increasing ring size. A bowl structure [16(2)] is the second most stable in the LSD calculations. It has a central four-membered unit and is more stable than the planar graphitic structures 16(5)

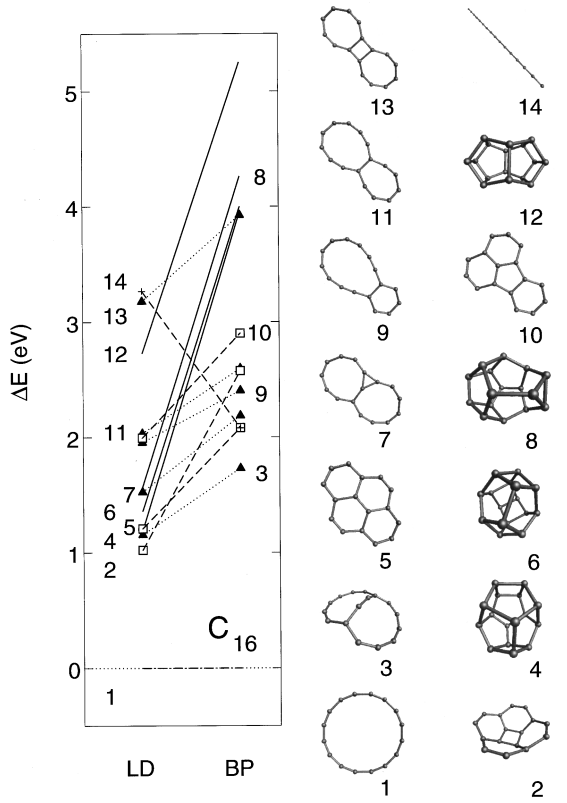

FIG. 4. Structures and energies (relative to the monocyclic ring) of isomers of C_{16} (eV). See caption to Fig. 2.

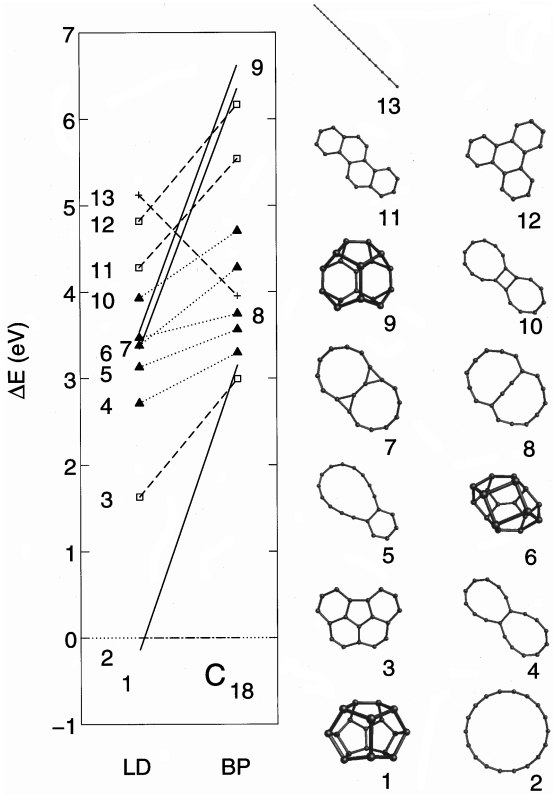

FIG. 5. Structures and energies (relative to the monocyclic ring) of isomers of C_{18} (eV). See caption to Fig. 2.

and 16(10). There are several cage structures, the most stable of which [16(4)] is closely related to 14(3). The cage structures all contain four- and five-membered rings, and 16(8) contains a three-membered ring. A structural type containing a triangle (related to cyclopropane) is evident for the first time in 16(7). This is also the first appearance of a double ring with a central four-atom unit, although this structure is unstable to out-of-plane (twist) deformations.

C_{18} is the first cluster in which a cage [18(1)] is the most stable form in the LSD calculations, although BP calculations predict the ring [18(2)] to be the most stable. The cage structures 18(1) $[C_{2v}]$ and 18(6) $[C_2]$ contain four-, five-, and six-membered rings. The cage 18(9) $[C_{2v}]$ is similar to 18(1) but lies significantly higher in energy, suggesting that combinations of four- and five-membered rings are favored over structures with three- and six-membered rings. The bowl structure [18(3)] is related to 16(2), but it is planar in C_{18}. The monocyclic ring [18(2)] has a cumulenic structure ($r_{12}=1.280$ Å, $\alpha_1=160°$) and is a local minimum in the energy surface. On the other hand, restricted Hartree–Fock calculations[28] lead to a polyyne (polyacetylenic) ring, and these authors attribute the difference to a tendency of DF calculations to favor allenic structures. The bicyclic rings 18(4), 18(5), and 18(8) correspond to local minima in the energy surfaces, but low-frequency out-of-plane (bending) vibrations occur in all. A bicyclic structure with *two* triangular units [18(7)] is stable in C_{18} and has low-frequency bending modes. As in the case of C_{16}, the highest-lying double-ring structure [18(10)] is unstable to out-of-plane (twist) deformations.

These three clusters demonstrate some interesting trends. First, the cage and graphitic structures become energetically favored with increasing cluster size. The bicyclic structures contain lobelike rings that are often far from circular. It is evident that the overall strain in a structure can be reduced by having ring sectors with small curvature. The relationship between the relative energies calculated with the LSD and BP functionals also applies to these systems. While there are significant differences between the ordering of the isomer energies, the changes within any structural type are small. It is not always possible to assign a structural type unambiguously, so that not all lines in the figures are parallel. An obvious example is the structure 16(2), which shows a behavior intermediate between the planar graphitic structures 16(5,10) and the cage 16(4). The overall trend is nevertheless clear.

D. C_{20}

If ''fullerenes'' are defined to be polyhedral cages of n threefold coordinated carbon atoms with 12 pentagonal and $(n/2-10)$ hexagonal faces,[55] then C_{20} is the smallest. It is not surprising that it has been used as a test case in studies using a range of methods. As noted above, studies of several isomers were performed with Hartree–Fock and LDA methods.[21] While subsequent quantum Monte Carlo[24] and coupled-cluster[25] calculations gave contradictory results concerning the relative stability of the low-lying isomers, there is general agreement that the incorporation of gradient corrections in DF calculations results in large changes.[26] LDA calculations on bicyclic ring isomers[25] indicated that such structures were unlikely to be amongst the most stable.

The present LSD calculations shown in Fig. 6 agree very well with the fully optimized energies found previously.[29] The cage structure [20(1)] is ~4 eV more stable than the ring 20(6), with the bowl [20(2)] lying between them. The BP results differ in detail from earlier results, all of which were obtained with different gradient-corrected functionals and some of which used geometries optimized in Hartree–Fock calculations.[24] In addition to the C_{2h} structure 20(1), which is a (small) Jahn–Teller distortion of a dodecahedron (I_h), we find cage structures at higher energies containing four-, five- and six-membered rings. All bicyclic structures lie higher in energy and have low-frequency out-of-plane vibration modes. The buckled structure 20(8) shows a small departure from planarity.

The cage structures 20(3) and 20(5) are related by the Stone–Wales transformation, which changes the positions of pairs of pentagons and hexagons. The presence of four-membered rings means that these structures are not fullerenes as defined above, but they are smaller than the smallest fullerene [C_{28}, 28(2)] that supports such a transformation between enantiomers.[7] The energy difference between the two structures is 1.15 eV. The relative energies of the isomers are again remarkably similar within a particular structural type, although we note again the difficulty of assigning the bowl 20(2) and the planar structures 20(11,12) to the same class.

Raghavachari[56] has made an interesting study of the low-lying isomers of C_{20}, with the aim of clarifying the confusing picture that has arisen. The central idea is to take advantage of the fact—also evident in the results discussed here—that theoretical methods have similar bonding errors in similar bonding situations. If we consider isodesmic reactions, in which the number of bonds of each formal type is conserved, then errors in energy differences may be minimized. If reliable experimental data are available for some such differences, then useful assessments of the energy ordering of the isomers should result. Raghavachari was able to relate the formation energy of the ring isomer of C_{20} to the heats of formation of acetylene and diacetylene, and that of the bowl isomer to those of ethylene and benzyne. The final result was that the bowl and cage isomers are comparable in energy and significantly (~1.4 eV) more stable than the ring.

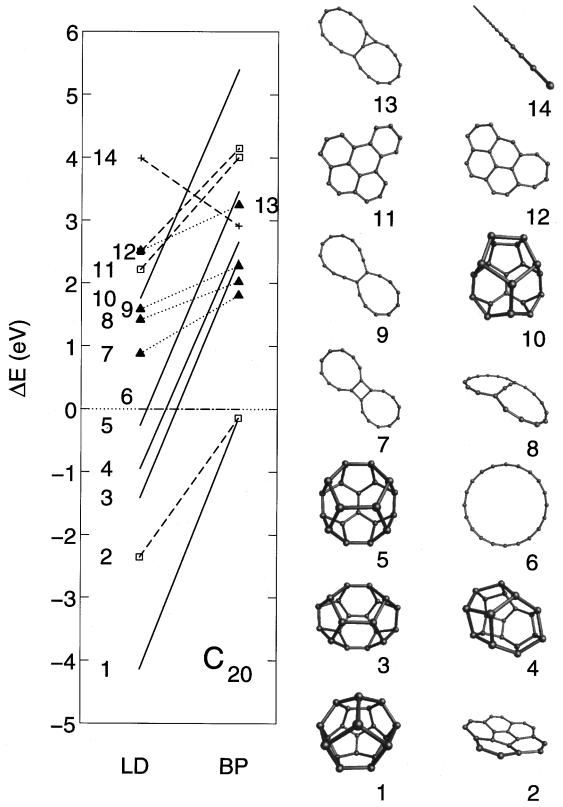

FIG. 6. Structures and energies (relative to the monocyclic ring) of isomers of C_{20} (eV). See caption to Fig. 2.

E. C_{22}

C_{22} is the only even-numbered cluster with 20 or more atoms that cannot exist as a closed structure containing pentagons and hexagons alone.[7] The statements that it does not exist as a closed cage[57,58] reflect perhaps the preoccupation with structures comprising five- and six-membered rings, and carbon cages with fourfold rings have been overlooked until recently.[37,59] Figure 7 shows that such structures are the most stable in the LSD calculations, although the monocyclic ring is favored by the BP functional. Structures 22(1) and 22(2) have C_2 symmetry, and 22(3) and 22(5) have C_{2v} symmetry. The cage structures have one, two, five, and six

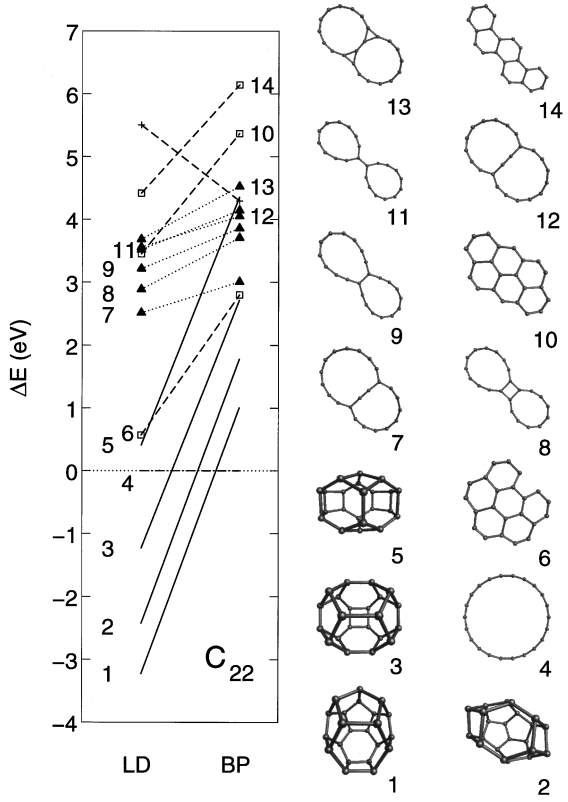

FIG. 7. Structures and energies (relative to the monocyclic ring) of isomers of C_{22} (eV). See caption to Fig. 2.

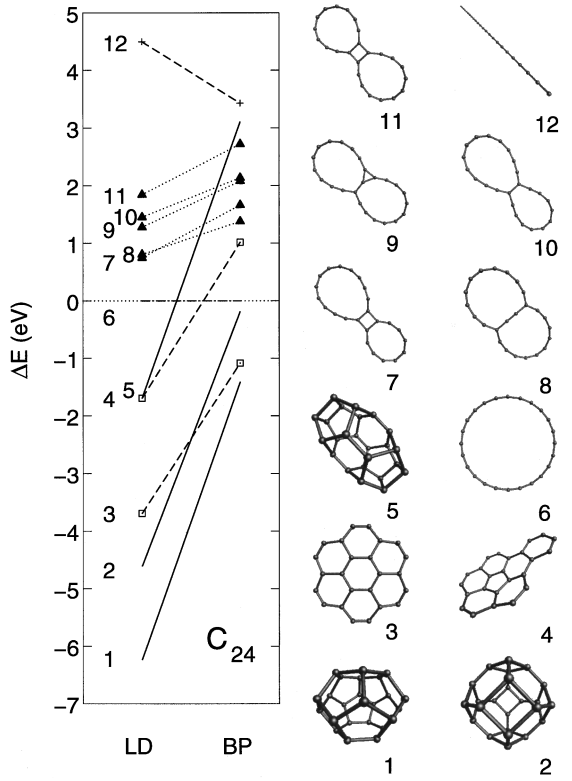

FIG. 8. Structures and energies (relative to the monocyclic ring) of isomers of C_{24} (eV). See caption to Fig. 2.

four-membered rings, respectively, and their stability decreases with increasing numbers of four-membered rings.

The graphitic structure 22(6) has low-frequency out-of-plane vibrations is considerably more stable than the bicyclic structures, all of which are planar. *All* bicyclic and graphitic structures have low-frequency vibrations corresponding to out-of-plane bending modes.

F. C_{24}

Isomers of C_{24} have provided a valuable testing ground for methods of electronic structure calculation. Calculations on four isomers [24(1,2,3,6)] using second order Møller–Plesset theory[22] predicted that the graphitic structure 24(3) should be the most stable. The dramatic effect of gradient corrections on the relative energies of isomers was shown by single point calculations using Hartree–Fock geometries[27] for the isomers 24(1,2,3,5,6,8,12) shown in Fig. 8. We have calculated these and several bicyclic structures as well. A second bowl-like structure considered in Ref. 27 is much less stable.

Figure 8 shows that C_{24} is the first cluster for which cage structures are unambiguously the most stable in both LSD and gradient-corrected calculations. The fullerene structure 24(1) is more stable than the other cages 24(2) and 24(5), both of which contain four-membered rings. The graphitic structures 24(3) [D_{6h}] and 24(4) [C_s, the C_{20} bowl with four atoms added to form a ''ladle''] are amongst the most stable. The structural difference between 24(3) and 24(4) may be viewed as the transfer of a four-membered unit from the planar structure to form an external ring. The plate structure 24(4) now has a central pentagon and forms a bowl to lower the strain. The energy difference (LSD) between these structures is 2.0 eV (BP: 2.1 eV). An increase in the stability of the cage and graphitic structures relative to ring and chain structures is quite evident. The bicyclic rings show the same features that have become familiar in the smaller clusters: All structures are planar and have low-frequency vibration modes corresponding to out-of-plane bending. Several measurements have been interpreted as giving evidence for the presence of bicyclic rings in the gas phase, but the present study of the energy surfaces suggests that such rings deform readily into nonplanar structures. The effects of gradient corrections on the ordering of the isomer energies of a cluster increase as the number of bonds increases.

G. C_{26}, C_{28}, C_{30}, C_{32}

The most stable isomer in C_{26} by far is found to be a Jahn–Teller distortion [C_{2v}, 26(1)] of the most symmetric fullerene (D_{3d}) [Fig. 9]. The second cage structure considered [C_2, 26(2)] contains four-membered rings and lies more than 5 eV higher. The other isomers follow the trends already apparent. The graphitic structures [26(3,5,6)] are generally more stable than the bicyclic rings, and all planar structures have low-frequency out of plane bending modes. As is the case of other C_n clusters with $n=4N+2$, structure 24(10) has two triangular units.

C_{28} has been one of the most interesting clusters in the range considered here, as it is apparently the smallest carbon cluster that can trap another element inside. Earlier work[60,61]

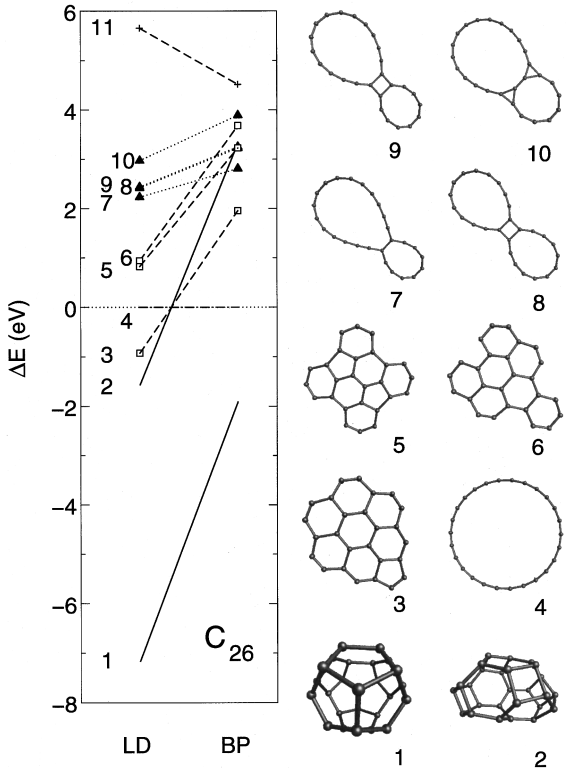

FIG. 9. Structures and energies (relative to the monocyclic ring) of isomers of C_{26} (eV). See caption to Fig. 2.

indicated that C_{28} was both tetrahedral and tetravalent, and the most stable isomer found here [28(1), T_d, quintet] found here agrees with this. Jahn–Teller distorted structures with lower spin multiplicity occur, and the corresponding singlet [28(1')] lies 0.2 eV above 28(1) in the LSD calculations. The second fullerene structure [28(2), singlet, a distortion of D_2 symmetry] is a further 0.3 eV higher. Other cage structures [28(3), 28(4), with seven- and four-membered rings, respectively] lie much higher in energy. The graphitic and bicyclic structures are higher in energy and susceptible to out-of-plane distortions. Structure 28(9) undergoes twists, for example, and 28(8) is unstable to both in-plane and out-of-plane bending. The graphitic structures with D_{2h} symmetry [28(6,10)] favor triplet structures.

There are many cagelike isomers of C_{30}, and the present calculations have been restricted to the structures comprising five- and six-membered rings alone [30(1,2,3)]. These are much more stable than the graphitic structure with the lowest energy [30(4), D_{2h}, triplet]. The two most stable structures [30(1,2), both with C_{2v} symmetry] are related by a single Stone–Wales transformation, and the energy difference between them (0.10 eV in both LSD and BP calculations) is much smaller than in the isomers of C_{20} that are related by the same transformation. Of course, the small energy difference does not imply that the energy barrier between them is small. The other fullerene structure 30(3) is a Jahn–Teller distortion of D_{5h} symmetry. LSD and BP calculations lead again to remarkably similar energy differences within a particular structural type.

The rapid increase in the number of isomers and increasing demands on computing resources with increasing n means that we have restricted the present study of C_{32} to fullerene structures and representative members of the other structural types. The cage structures are 32(1) [D_3], 32(2) [C_2], 32(3) [D_2], 32(4) [Jahn–Teller distortion of D_{3d}], and 32(5) [D_{3h}]. 32(4) is an example of a structure with stable single, triplet, and quintet states. The singlet is the most stable in both LSD and BP calculations, and the triplet and quintet states are 0.3 and 1.0 eV, respectively, higher (LSD). The simplified DF method of Adams *et al.*[34] leads to the same ordering of the energies of the cages in C_{30} and C_{32}, and all energies relative to the ring structures are within 0.3 eV of those found here. The planar and chain structures considered here lie much higher in energy. The differences between the relative energies calculated with the LSD and BP functionals remain extremely regular.

IV. BONDING TRENDS

A. Structures

LSD calculations predict that cages are the most stable isomers for $n \geqslant 18$, and there are stable cage structures for all $n \geqslant 8$. 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, a finding that is consistent with ion drift measurements.

The interest in carbon clusters has led over the years to numerous 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,[57] and Schmalz *et al.*[62] used semiempirical models to develop additional criteria involving the balance between π-electron bonding and σ-strain. A fourfold ($n=4N+2$, N integer) periodicity related to the rules of Hückel for the stability of aromatic molecules was observed long ago in semi-empirical calculations of ring isomers of C_n.[63] 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 decreases with increasing ring size. A fourfold periodicity is also evident in the present results. The monocyclic rings are ''cumulenic'' (with identical bond lengths) in C_{14}, C_{18}, C_{22}, ..., but ''polyacetylenic'' (with alternating bond lengths) in the other four. The energy difference between the two families can be estimated by calculating the energies in C_{12}, C_{16}, C_{20}, ... with all bonds of length 1.28 Å (the value found uniformly in the $4N+2$ family). This difference is ~ 1 eV and decreases with increasing n. Density functional calculations for much larger rings[64] show that alternation is still observed for $n \sim 40$.

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. An exception is 18(7), where the odd-numbered rings comprise almost linear C_3 segments. Other odd-numbered rings with similar segments distorted during structure optimization to even-numbered rings with smooth variations in

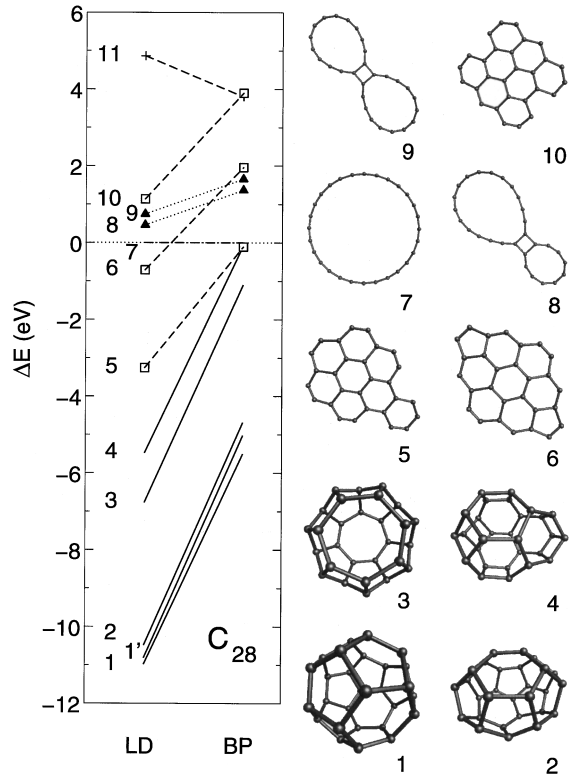

FIG. 10. Structures and energies (relative to the monocyclic ring) of isomers of C_{28} (eV). See caption to Fig. 2.

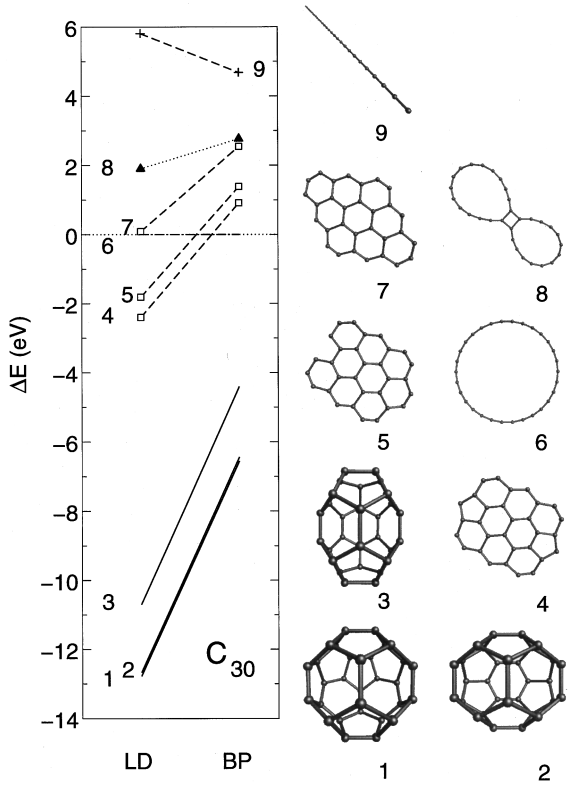

FIG. 11. Structures and energies (relative to the monocyclic ring) of isomers of C_{30} (eV). See caption to Fig. 2.

bond lengths and bond angles. Such cumulenic segments require an even number of twofold coordinated atoms, so that the triangular (cyclopropane) units occur singly for $n=4N$ in symmetric bicyclic rings, but in pairs for $n=4N+2$. (b) Strain effects manifest themselves in several ways. Buckling from the planar structure in the double rings 16(3) and 20(8) allows the bond angles at the threefold vertices to be closer to the optimum sp^2 value. 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(9,10).

There is a tendency among the graphitic isomers of a given cluster for the stability to decrease as the number of peripheral twofold coordinated atoms increases [see, for example, C22(6,10,14)]. In addition, six-membered rings appear to be more stable than five-membered rings. Both features are consistent with the model calculations of Ref. 62, which are based on the balance between π-bonding and σ-strain. It should be noted that graphitic covers both planar and nonplanar structures in the present work, and the distinction between π- and σ-bonding is not precise in the latter. The development of structures with central isolated pentagons can be seen for C_{16} to C_{20} in 16(10), 18(3), and 20(2). The last of these is clearly the most stable of the three, reflecting the relative compactness of the structure and the larger number of threefold coordinated atoms.

It is obvious that the structures shown here are not all possible isomers, particularly for the larger clusters. Even for planar structures, there is a dramatic increase in the number of multiple-ring and graphitic structures as n increases. We note that many topologically possible structures are energetically unstable, and that the energies of other structures lie well above the corresponding ring isomer. The calculations should nevertheless provide a reliable guide to the predictions of the LSD and BP functionals of the most stable isomer of each family. We now examine the variation with cluster size of the stability of the lowest-lying isomers of each type.

B. Cohesive energies

We have noted in Sec. I that several sets of experimental data have provided information about the trends in the structures of the energetically most favorable C_n isomers as n changes. The model calculations of Schmalz *et al.*[62] favored chains up to $n\sim10$, followed by graphitic fragments to $n\sim24$, when cages became the most stable. It is interesting that these qualitative results are consistent in part with the results of the present calculations.

The calculated cohesive energies (binding energies per atom) of the most stable isomer of each type are shown in Fig. 13. The most striking effect is that gradient corrections lower the LSD values by ~1 eV, a change similar to that found in clusters of other main group elements.[65] However, the effects of gradient corrections on the total energy are quite different for different structural types. Figures 1–12 show that they are smallest in cages, followed by the graphitic (plate) and double ring structures, i.e., the effects decrease as the average coordination number increases. There are fewer bonds in the (generally metastable) linear chains than in the monocyclic rings, and the gradient corrections

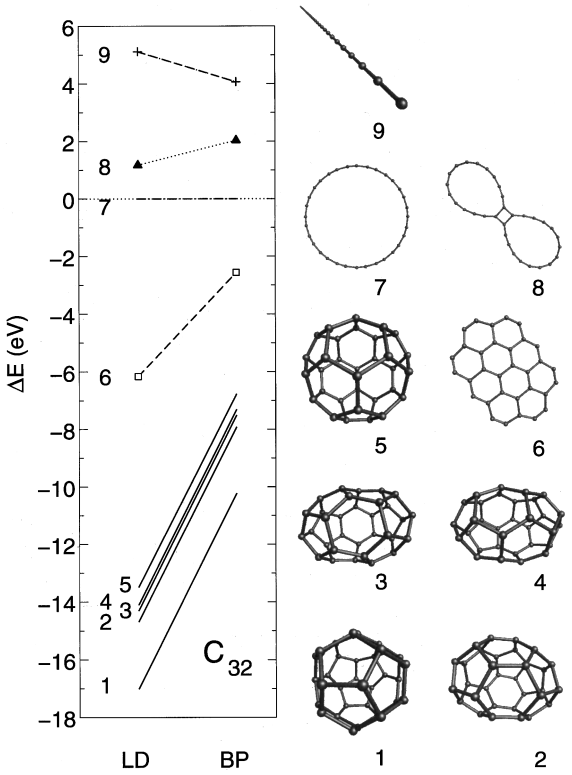

FIG. 12. Structures and energies (relative to the monocyclic ring) of isomers of C_{32} (eV). See caption to Fig. 2.

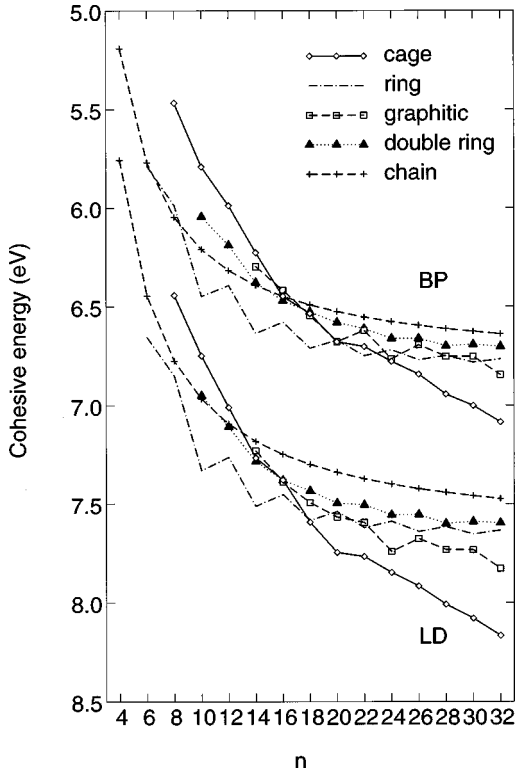

FIG. 13. Cohesive energies (binding energies per atom, eV) of the most stable of different isomer classes in C_4–C_{32}. See caption of Fig. 2.

reduce the energy difference between them. Although the relative energies of the isomers are remarkably similar *within* a given structural family (the lines connecting LSD and BP results in the figures are nearly parallel in all cases), they change the predictions for the most stable isomers in several cases.

One of the interesting trends apparent in Fig. 13 is the increased stability of cage structures as n increases. Apart from C_{20}, where increased stability is associated with the first fullerene structure, the variation in both the LSD and BP results with increasing n is remarkably regular. In particular, the cohesive energies of the nonfullerene structures C_{18} and C_{22} can be obtained by extrapolating the values for the fullerene structures of the larger cages. The cohesive energies of the monocyclic rings shows the expected fourfold periodicity, and the LSD and BP curves are almost exactly parallel. This reflects the fact that the number of bonds per atom is constant (unity) for all such rings. There is a weak fourfold periodicity in the bicyclic ring structures, and the graphitic structures show pronounced stability for C_{24} and C_{32}. The chains show a very smooth variation as the length changes. The number of bonds per atom decreases uniformly with increasing n, and the difference between LSD and BP cohesive energies increases smoothly.

V. CONCLUDING REMARKS

The present work describes the results of an extensive density functional study of the structural and cohesive properties of carbon clusters with up to 32 atoms. The results show clear trends in the relative stabilities of different structural types with changing cluster size, and they show distinct differences between the predictions of calculations using the LSD and Becke–Perdew (gradient-corrected) approximations to the exchange-correlation energy. In the case of structures of the *same* structural type, e.g., cages, the two approximations give remarkably similar predictions of the relative energies. It would be interesting to see further studies using correlated wave functions on some of the clusters discussed here.

The experience with calculations using the LSD and BP approximations leads to an observation that should be relevant for similar studies. For clusters of 20 or more atoms it has been common practice to adopt geometries optimized with one method (e.g., Hartree–Fock) for single-point energy calculations with a different approximation. As noted in Ref. 29, this can lead to significant errors. The use of HF geometries in C_{20} leads to LSD energies for the ring that are $\sim$1 eV too high, with smaller errors for the bowl and cage.[24] In the present work the use of LSD geometries for BP calculations leads to errors in the relative energies of the latter of up to 0.5–1 eV. If higher accuracy is required, geometries and energies should be optimized separately for each method under consideration.

Experimental measurements are the final judges of any theoretical prediction, and the experimental identification of the most stable isomers in these clusters would test—amongst other things—the relative merits of different DF approximations. However, experiments on such clusters are complicated by the high temperatures often used to generate them and the use of ions for mass separation. We have focused on the energy surfaces of neutral clusters, and the re-

lationship to charged clusters far from equilibrium is not immediate. Calculations of the vibrational entropy in isomers of C_{20}, for example, indicate that the ring structure is favored above a certain temperature.[30] It is striking that several measurements have identified the presence of C_n isomers that are not the most stable found in these and other calculations. Reference 6 emphasizes, in fact, that there is no experimental verification for any structures besides linear chains and planar rings for clusters with less than 30 atoms. The generation of clusters that are not the most stable energetically was also found in our earlier work on sulfur anions,[66] where the experimental conditions could be adjusted to produce anions of S_6 and S_7 with both the ring and the less stable chain forms.

A subsequent article will be devoted to measurable quantities, such as vibration frequencies, multiplet structures, and ionization energies of the neutral clusters, and to the ionization energies (also known as the vertical detachment energies) of the C_n^- anions. The results will be compared with available experimental data.

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APPENDIX: BASIS SET EFFECTS

The preliminary results of this study (for C_{14}–C_{24})[37] used a triple-zeta Gaussian basis with polarization functions,[45] optimized for the purposes of DF calculations. When applied to smaller clusters (C_4, C_6), however, the relative energies of different isomers showed significant differences from the results of earlier DF studies. An extended series of calculations with different basis sets and DF methods [other Gaussian basis sets of double-zeta (DZVP)[38] and triple-zeta (TZVP)[38] quality, MD/DF calculations with an extended plane-wave basis] was then performed to investigate the source of these differences.

A comparison of these results and those of earlier calculations with different basis sets (C_4, C_6, …, C_{20}, …) showed unambiguously that the relative energies of C_n isomers calculated with the TZ94P basis are less reliable than the others. The main effect was that the relative stabilities of the more compact structures (such as cages) were too low in the TZ94P calculations. This was not expected, since the TZ94P and TZVP bases differ mainly in the exponent of the (d-) polarization function. The calculations for *all* structures were then repeated with the TZVP basis,[38] and are the basis of the results presented here. The geometrical *structures* calculated with plane wave, DZVP, TZVP, and TZ94P bases were very similar in all cases tested.

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