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Structure of C_{20}: Bicyclic ring versus cage

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The relative stabilities of various geometries of 20-atom carbon clusters are investigated to determine the ground state, using a generalized tight-binding molecular dynamics technique. The 20-atom fullerene cage (relaxing to C_s symmetry due to Jahn-Teller distortion) is found to be the most stable structure even when compared to the recently proposed bicyclic ring structure.

I. INTRODUCTION

The discovery of caged forms of carbon clusters[1] has sparked renewed interest in pure carbon clusters.[2] Most of these have been devoted either to the study of small clusters ($N \leq 10$) or to C_{60}. Due to the computational complexities, accurate *ab initio* treatments have almost always been limited to small clusters.[3–6] Among the larger molecules, C_{60} is unique with regard to the high degree of symmetry it possesses. Clusters in the intermediate range, however, have been studied in lesser detail due to the relatively lower symmetries of these molecules and the many possible isomers. Theoretical studies of these clusters fall into two main categories: tight binding[7] or modified neglect of differential overlap,[8] both semiempirical. The comparatively lower stability of these clusters also limits investigation of them by means of mass spectroscopy measurements.[9] Experimental detection of structural isomers for carbon clusters were reported by McElvany *et al.*[10] Only recently, the method of ion chromatography has been applied to carbon cluster cations and anions.[11] Unfortunately, no experimental results are available for small neutral clusters.

It is now generally accepted that the ground state for carbon clusters for $N \leq 10$ consists of planar geometries with low coordination.[3,12] This can be attributed to the presence of substantial strain energy on account of the smaller covalent radius of the carbon atom which prevents the formation of close-packed structures ($n_b/N > 2$) found in clusters of atoms with larger covalent radii such as silicon for $N \leq 10$.

The structure of 20-atom carbon clusters is of special interest since the transition to three-dimensional ground state geometry is believed to occur here in the form of a dodecahedron. While fullerenes in general consist of carbon atoms arranged in the form of pentagons and hexagons, C_{20} is the only fullerene with no hexagons. This lack of six-membered rings would cause severe strain in this molecule, resulting in a geometry with considerably less symmetry than a regular dodecahedron. The studies of C_{20} isomerization have been the subject of some recent works.[13,14]

Theoretical investigations of C_{20} have been carried out using *ab initio*[15] and the local density approximation (LDA) schemes.[16] The *ab initio* method predicts that a fullerene cage with a reduced D_{5d} symmetry structure is favored when calculations are done at the correlated level.[15] It should be noted, however, that in this *ab initio* work only the I_h and the D_{5d} structures were optimized. Our damped molecular dynamics optimization scheme imposes no *a priori* symmetry restriction. The LDA calculation[16] predicts the ground state to be a distorted fullerene cage, but the specific symmetry of the equilibrium geometry was not reported. A recent *ab initio* work has suggested (from mass spectroscopy results on cations) that planar rings might be competetive in energy with smaller fullerenes and might in fact be the precursors to larger fullerenes.[11]

The interest in the the C_{20} cluster has been renewed by the recent experimental work where carbon ions were generated in a standard laser vaporization/supersonic expansion source.[11] The resulting spectra for the C_{20} cluster were dominated by planar monocyclic rings with minor amounts of bicyclic rings, all in the form of ions. This, coupled with the absence of fullerene or graphitic ions in the spectra, prompted the speculation that larger fullerenes may have monocyclic rings as their precursors.

In this paper we present a detailed study of the possible geometries of neutral 20-atom carbon clusters, including bicyclic rings, to determine the ground state, using the nonorthogonal tight-binding molecular dynamics scheme of Menon and Subbaswamy,[17,18] which generalized the conventional orthogonal tight-binding molecular dynamics scheme.[19,20] This approach has been used to obtain equilibrium geometries, bond lengths, and cohesive energies for carbon clusters of arbitrary size.[12] The results obtained for small clusters ($N \leq 10$) are in excellent agreement with available *ab initio* results.[3] For these clusters the method has yielded symmetry-lowering in-plane distortions for even numbered rings, in agreement with *ab initio* predictions. Simulations of bulklike diamond with a large cluster has produced the well known 2 × 1 reconstruction for the (001) face.[12] The bond lengths for bulklike diamond and graphitic structures are also in excellent agreement with experiments. This agreement for a wide range of well-studied carbon clusters has been obtained by using Harrison's universal parameter scheme[21] for the electronic structure determination and by fitting the repulsive parameter in the dimer regime. The present method has also been used successfully to predict the lowest energy configuration for an oxygen atom chemisorbed on C_{60}.[17,22] Our prediction that this happens for the "epoxide" structure has been confirmed experimentally.[23,24] The same approach has been applied to obtain equilibrium geometries for small silicon clusters,[18] in excellent agreement with *ab initio* results[25,26] for the lowest energy structures of silicon clusters of size up to $N = 10$ (for which *ab initio* results are available).

The details of the technique can be found elsewhere.[17,18] The method is based on van Schilfgaarde and Harrison's[27,28] generalization of total energy calculations in tight-binding theory by explicitly incorporating nonorthogonality of the atomic orbitals. The corresponding generalization of the force calculations using the Hellmann-Feynman theorem allows us to perform molecular dynamics for covalent systems with nontetrahedral and multicoordinated structures without invoking any cutoff in the interactions. The method is orders of magnitude faster than *ab initio* or LDA techniques and therefore permits a much larger sampling of the configuration space to determine minimum energy structures. The tight-binding method can also be used to obtain valuable electronic structure information. The electronic tight-binding parameters (e.g., $V_{ss\sigma}$, $V_{pp\pi}$, etc.) used here for carbon are generated using Harrison's[21] universal parameter scheme. The repulsive coefficient was fitted in the dimer regime.[12]

II. RESULTS

We have carried out calculations for carbon clusters of size $N = 20$ by considering various possible geometries. The planar structures we considered include carbon atoms in the form of a linear chain, a ring [Fig. (1a)], and a fivefold ring surrounded by five sixfold rings (a flat "corranulene") [Fig. (1b)]. We also considered several planar bicyclic rings with many different inter-ring connectivities as our starting configurations for molecular dynamics simulations. The result of one such simulation showing the initial and the final geometry is shown in Fig. 2. The three-dimensional geometries consisted of a corrannulene structure [which is made of a fivefold ring surrounded by five sixfold rings forming the cap of a C_{60} molecule; see Fig. (3a)], a C_{20} cage [Fig. (3b)], and a 20-atom cluster with carbon atoms placed at bulk diamond positions simulating a diamond fragment (Fig. 4).

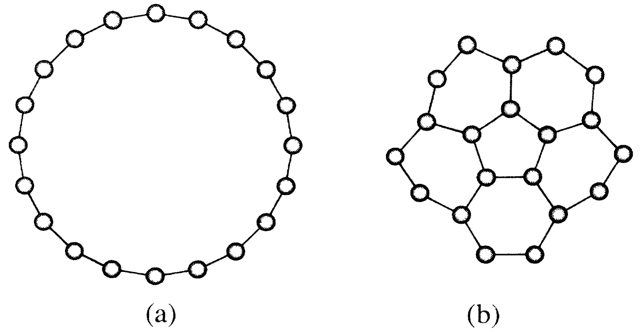
(a) (b)

FIG. 1. Equilibrium geometries of the planar low energy structures of 20-atom carbon clusters. (a) A ring and (b) a fivefold ring surrounded by five sixfold rings.

In our starting configuration all the nearest neighbor C-C bond lengths are taken to be identical (or to have a prespecified bond alternation). Damped molecular dynamics optimization is then performed to obtain the final equilibrium geometry. The atoms are allowed to relax by removing a small fraction ($\leq 1\%$) of each of the velocity components at every time step. The optimization is stopped when the largest velocity component of any atom falls below 54 m/s (corresponding to a temperature of about 10 K). The cohesive energies for various structures are calculated using the scheme given in Ref. 12.

A. Planar clusters

In Figs. 1 and 2 we show the stable final equilibrium geometries obtained by molecular dynamics simulations for 20-atom carbon clusters in a plane. The 20-atom linear chain was found to be highest in energy (see Table I where relative energies with respect to C_{60} are listed). This agrees with the LDA results which found the chain to be substantially higher in energy over other isomers considered.[16] The authors of Ref. 11 also found the linear chain to be highest in energy in their *ab initio* calculations where they optimized various C_{20} isomers using a 3-21G basis set. A direct comparison with experiment for this chain is not possible because experiments are performed with ions rather than neutral atoms.

The equilibrium ground state obtained for the 20-atom

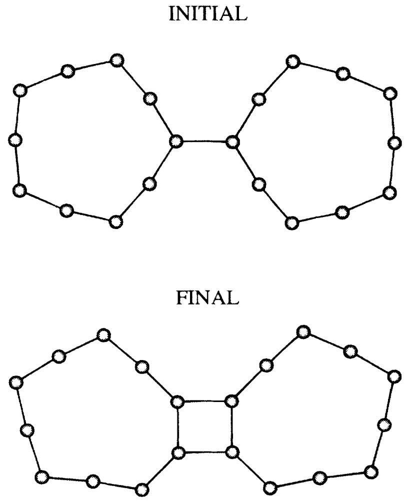

FIG. 2. Initial and final stages of relaxation for a bicyclic ring. The relaxed geometry (most stable structure for a bicyclic ring) shows a connectivity of two.

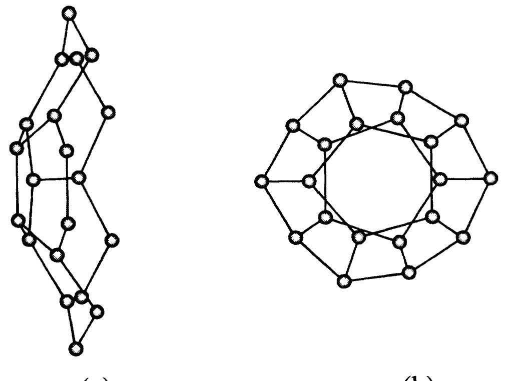

FIG. 3. The stable final equilibrium geometries for three-dimensional 20-atom carbon clusters obtained by molecular dynamics simulations. (a) Corranulene cap and (b) C_{20} cage.

ring [Fig. (1a)] shows a cumulenic D_{20h} (regular polygon) geometry, in agreement with *ab initio* results.[15] This should be contrasted with the results for ground state rings for $N \leq 10$, where the equilibrium configurations obtained deviate from the initial regular polygon structures, attaining lesser symmetry geometries, also in agreement with *ab initio* results.[3] The larger ring diameter results in sufficiently large angle between adjacent C-C bonds to minimize the overlap of the π electrons in the plane of the carbon atoms, which would otherwise have resulted in the symmetry lowering in-plane distortions. The equilibrium bond length is 1.34 Å [compared to the *ab initio* value of 1.27 Å (Ref. 15)]. When we started with an acetylenic ring (i.e., with bond alternation), the system relaxed back to a cumulenic ring indicating that the latter is lower in energy in our scheme. The LDA calculations,[16] however, reported a bond conjugation for this ring with bond lengths alternating between 1.25 Å and 1.33 Å. We find the highest occupied molecular orbital lowest unoccupied molecular orbital (HOMO-LUMO) gap for this structure to be 1.64 eV. In Table I we list the binding energy for this structure relative to that of C_{60} within our scheme. Also listed in the same table are the relative binding energies of other 20-atom cluster equilibrium geometries.

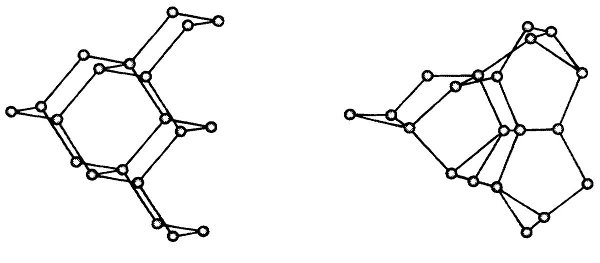

FIG. 4. The initial and final stages of relaxation for a 20-atom adamantane carbon cluster. Surface atoms have undergone strong relaxation and reconstruction at the end of the relaxation.

TABLE I. Relative energies per atom in eV for various C_{20} clusters with respect to C_{60}.

Structure	Figure	ΔE (eV/atom)
Chain		1.49
Ring (monocyclic)	1(a)	1.00
Ring (bicyclic)	2	0.97
Flat	1(b)	0.85
Cap	3(a)	0.79
Cage	3(b)	0.69
Adamantane	4	1.34

Another planar geometry considered is a fivefold ring surrounded by five sixfold rings [Fig. (1b)]. This structure is similar to graphite in that each interior atom is threefold coordinated. This cluster has lower energy than the monocyclic ring by 0.15 eV/atom, which results from the additional σ bonds formed. The equilibrium bond lengths for this structure lie between 1.35 Å for the interior atoms to 1.44 Å for the atoms on the exterior. The HOMO-LUMO gap for this cluster is 0.47 eV.

To complete the discussion on planar geometries we also considered bicyclic rings with many different inter-ring connectivities as our initial configurations. Starting configurations with unrelaxed as well as relaxed C_{10} dimers were considered; the latter yielded lower energy configurations than the former. The relaxed rings[12] have symmetry-lowering in-plane distortions (D_{5h}), the same, as obtained by the *ab initio* work in Ref. 3 rather than being of regular polygonal (D_{10h}) symmetry. A total of five different inter-ring connectivities representing several possible relative orientations for bonding were considered. The final equilibrium state consisted of two classes of inter-ring connectivities, (1) one inter-ring bond and (2) two inter-ring bonds forming sides of a four-sided rectangular ring, with the latter being lower in energy than the former. Figure 2 shows a simulation where an initially chosen class (1) geometry relaxed to a class (2) geometry (most stable bicyclic ring). The relaxed structure shows C_{2v} symmetry with the reflection plane bisecting the inter-ring bonds. The resulting rectangular ring has side lengths of 1.41 Å and 1.43 Å with the larger value belonging to the inter-ring bonds. The double bonds from adjacent rings have broken in the process and reformed as a four-sided ring consisting only of single bonds. The energy for this structure is slightly lower than that for the monocyclic ring (see Table I). This lowering of energy over the monocyclic ring is due to the formation of two additional bonds.

The authors of Ref. 11 have also compared monocyclic and bicyclic structures for C_{20}. They, however, find the bicyclic ring to be 4.3 eV higher in energy over the monocyclic ring while using a 3-21G basis set. This difference became 1.3 eV when they used a 6-31G* basis set and MP2 perturbation theory with the monocyclic ring still being lower in energy. On the other hand, we find the bicyclic ring to be lower in energy than the monocyclic ring. We believe the optimization employed for bicyclic rings by these authors may not have allowed the system to reach its true ground state since the individual components of the bicyclic rings had symmetry close to the regular polygon (D_{10h}), in contrast with an earlier *ab initio* work[3] where a detailed optimization was performed at the MP4/6-31G* level.

B. Three-dimensional clusters

In Figs. 3 and 4 we show all the stable final equilibrium geometries for three-dimensional 20-atom carbon clusters obtained by our damped molecular dynamics optimization scheme. The corranulene cap structure has equilibrium bond lengths in the range 1.35−1.42 Å. The corresponding LDA values are in the range 1.40−1.45 Å.[16] The HOMO-LUMO gap of this structure is 0.96 eV. The relaxed 20-atom fullerene cage shows a highly distorted geometry (C_s symmetry) with several distinct bond lengths. We started our simulations with the ideal dodecahedron (I_h symmetry). The bond lengths for the relaxed cage lie between 1.39 Å and 1.51 Å. In *ab initio*[15] and LDA (Ref. 16) calculations also the ground state obtained had lower symmetries than a regular dodecahedron. As already mentioned, the *ab initio* work only considered I_h and D_{5d} structures. The *ab initio* bond lengths are in the range 1.42−1.47 Å, while the LDA values lie between 1.42 and 1.49 Å. The cage is lower in energy than the corranulene by 0.10 eV/atom. This is in agreement with the LDA results,[16] but the corresponding energy difference was 0.04 eV/atom. The *ab initio* work did not consider the corranulene structure in their calculations. It found the fullerene cage to be the ground state when correlation effects were included at the MP2 level.

The reflection plane for the C_s cage structure obtained is defined by two bonds that are related by inversion symmetry in the undistorted I_h structure. A Mulliken population analysis shows that one of these two bonds is the weakest bond in the whole structure; one of its terminal carbons is the most reactive site, with almost a complete lone pair of electrons.

The electronic level structure near the Fermi level for the undistorted and distorted cages is shown in Fig. 5. The degeneracies, where they exist, are also noted. The arrow denotes the Fermi level. The regular dodecahedron (our starting configuration) has metallic character, with a partially filled fourfold degenerate g_{1u} level (HOMO) with no HOMO-LUMO gap. The degeneracies can be removed by a Jahn-Teller distortion, lowering the energy. Indeed, in our relaxed configuration these degeneracies have been found to be completely removed, opening up a HOMO-LUMO gap of 0.96 eV.

To complete the discussion we have also considered a 20-atom carbon adamantane cluster. In Fig. 4 we show the initial and final configurations for this cluster. As seen in the figure, the equilibrium configuration shows considerable relaxation and reconstruction, particularly for the surface atoms. Notice that even though the final structure is more compact than the initial starting configuration, no carbon atom is more than fourfold coordinated. This attests to the peculiar chemistry of the C-C bond which prevents the formation of close-packed structures (coordination in excess of 4) for any size cluster. This can be attributed to the smaller covalent radius of carbon which can generate considerable strain energy preventing the formation of close-packed structures. The final equilibrium structure shown in Fig. 4 is found to be the least stable of all 20-atom clusters in three-dimensions considered here, with an energy 0.65 eV/atom higher than that of the cage. The bond lengths for this cluster are in the range 1.35−1.55 Å.

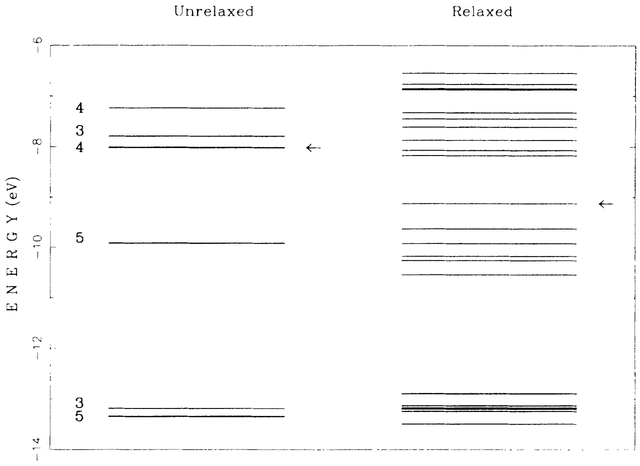

FIG. 5. The electronic level structure near the Fermi level for the unrelaxed (left) and relaxed (right) cages.

The present method can also be easily used to obtain vibrational frequencies for clusters by explicitly constructing the dynamical matrix. For a C_{60} molecule we obtained a radial "breathing mode" (A_g symmetry) frequency of 503 cm^{-1}. The frequency for the "pentagonal-pinch" mode (also of A_g symmetry) was determined to be 1597 cm^{-1}. The experimental values for these modes are 496 cm^{-1} and 1470 cm^{-1}, respectively.[29] This agreement is excellent when we consider that the parameters used in our calculations were fitted in the dimer regime and this gives us reason to believe in the reliability of the method when used to estimate vibrational frequencies for other clusters.

The computed vibrational frequencies for the C_s symmetry C_{20} cage are listed in Table II. There are 29 modes of A symmetry and 25 modes of A′ symmetry. The symmetric breathing mode has a frequency of 543 cm^{-1}. All modes should be ir and Raman active for different experimental geometries.

III. CONCLUSION

We have applied an efficient generalized tight-binding molecular dynamics scheme to study equilibrium geometries of 20-atom neutral carbon clusters and find the fullerene cage to be the ground state in agreement with *ab initio* and LDA results. The cage structures benefit from having threefold coordination for all component atoms on account of the cage closure.

For the C_{20} cage we predict a lower symmetry (C_s) than those considered by *ab initio* investigations so far

TABLE II. The computed vibrational frequencies for the C_s-symmetry relaxed cage (cm^{-1}).

A	A	A′	A′
543	1306	559	1499
557	1380	565	1536
560	1414	739	1634
731	1449	755	1653
756	1573	762	1661
763	1645	820	1691
823	1656	827	1707
891	1658	883	1717
922	1666	895	1725
1094	1691	1138	1745
1119	1707	1164	
1148	1711	1190	
1179	1747	1199	
1196	1771	1343	
1213		1419	

(D_{5d}).[15] We also find that for the sizes of the clusters considered in this work the relaxed adamantane fragments are not competitive with three-dimensional carbon clusters containing threefold coordinated atoms in the form of cage and corranulene. Even the planar structures, with the exception of the linear chain, are found to be more stable than the adamantane fragment for this size.

The bicyclic ring has been found to be more stable than the monocyclic ring. The connectivity of the bicyclic rings shows the reformation of double bonds from adjacent rings into a four-sided rectangular ring consisting of single bonds. The relaxed structure exhibits only a (C_s) symmetry. The neutral C_{20} cage was found to be lower in energy even when compared to the bicyclic ring structure. The mass spectroscopy results of Ref. 11 thus suggest that the ground state structure of clusters in this size range might depend drastically on the charge state.

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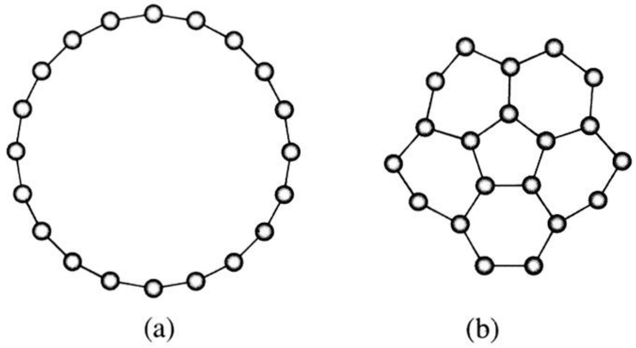


FIG. 1. Equilibrium geometries of the planar low energy structures of 20-atom carbon clusters. (a) A ring and (b) a fivefold ring surrounded by five sixfold rings.

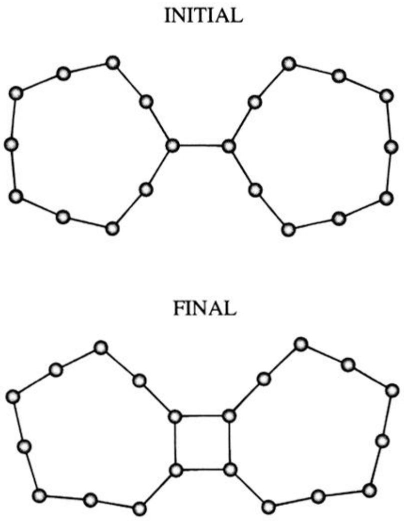
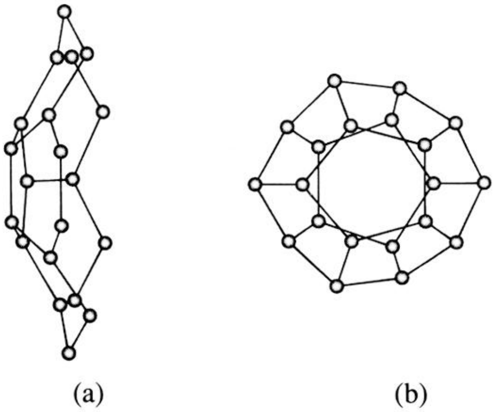
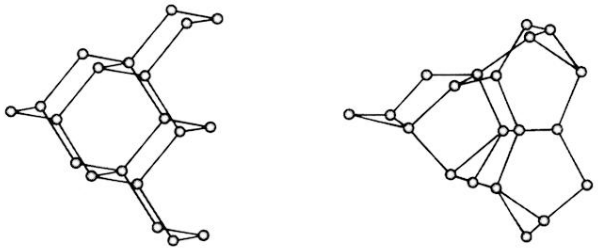


FIG. 2. Initial and final stages of relaxation for a bicyclic ring. The relaxed geometry (most stable structure for a bicyclic ring) shows a connectivity of two.



(a) (b)

FIG. 3. The stable final equilibrium geometries for three-dimensional 20-atom carbon clusters obtained by molecular dynamics simulations. (a) Corranulene cap and (b) C_{20} cage.



INITIAL FINAL

FIG. 4. The initial and final stages of relaxation for a 20-atom adamantane carbon cluster. Surface atoms have undergone strong relaxation and reconstruction at the end of the relaxation.