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We investigate the properties of a new class of compact carbon clusters with surface threefold coordination and bulk fourfold coordination. These clusters are the diamond analogs of fullerenes: they are characterized by icosahedral symmetry and almost perfectly tetrahedral bonding. A stable form of such structures could involve the saturation of surface dangling bonds by hydrogen. We use bond energies and electronic structure calculations to examine the relative stability of various sizes in both hydrogenated and pure form.

1. Introduction

Graphite, the most stable form of solid carbon, consists of *flat* layers of threefold coordinated atoms. The interactions between layers are due to rather weak van der Waals forces. Recently, a stable *curved* hollow structure, the C_{60} molecule, was discovered [1], which is also comprised entirely of threefold coordinated carbon atoms. Following this discovery, crystals of these units were produced [2], which are held together by van der Waals interactions in analogy to the interactions between the flat layers of graphite. Several other curved forms based on threefold coordinated carbon atoms were subsequently realized. They include larger hollow molecules (C_{70}, C_{84}, etc., dubbed "fullerenes"), concentric graphitic tubules [3], and concentric nestings of various size fullerene molecules [4]. In the latter two cases the bonding within a shell (a single tube or a single fullerene) is graphitic-like, while the interaction between shells is due to van der Waals forces. Thus the concentric tubules and spheres, like the fullerenes themselves, can be thought of as curved forms of graphite.

The question arises, is there a curved version of the second stable form of solid carbon, namely diamond, and under what conditions would such a structure be stable? We investigate these possibilities in this paper by studying in detail the properties of a novel set of carbon clusters which we proposed recently [5]. These new clusters, which are the diamond analogs of the fullerenes, are based on covalent bonding that is locally very close to tetrahedral, while the overall symmetry is that of the icosahedral group, as in C_{60}. There are two basic ideas which motivated the study of these models: first, under the proper experimental conditions the preferred bulk structure of carbon involves tetrahedral rather than graphitic bonding. For example, graphite can be transformed to the tetrahedrally bonded diamond structure under pressure [6]. Second, passivation of surface dangling bonds can give stable structures, a factor which is particularly important for small systems with high surface-to-volume ratios, such as the clusters discussed here.

2. Results

2.1. Bare clusters

We first describe the structure of these models in some detail. The clusters consist of concentric shells of carbon atoms. The atoms in a single shell are related to one another by the icosahedral group symmetries. However, unlike the cases of concentric tubules or nested fullerenes, the neighboring shells in our model are *covalently* bonded, resulting in dense structures with fourfold coordinated interior atoms.

Figure 1 illustrates the structure of the seven smallest such clusters, with all atoms of the same color belonging to one shell. The core of the new clusters is a dodecahedron of 20 threefold coordinated carbon atoms (white color), C_{20}, shown in fig. 1(a). This structure consists of pentagons with bond angles of 108°, which are very close to the tetrahedral bond angle (109.5°). Thus, the valence electrons of C_{20} form sp^3 bonding orbitals, leaving one sp^3 electron per atom unbonded. These dangling bonds would probably render C_{20} unstable as an isolated molecule. However, the hydrogenated version, $C_{20}H_{20}$, is known to exist experimentally [7]. Just as hydrogenation stabilizes $C_{20}H_{20}$, each dangling bond of an isolated C_{20} can lower its energy by bonding to a carbon atom placed radially outward from it in a second shell (pink color), shown in fig. 1(b). Unlike $C_{20}H_{20}$, however, this configuration would be highly unstable because of the large proportion of singly bonded carbon atoms on its surface. The 20 singly coordinated pink atoms can be stabilized by the addition of a third shell of 60 carbon atoms (purple color). This produces a structure (fig. 1(c)) in which the white and pink atoms are fourfold coordinated, while the purple atoms are threefold coordinated.

Continuing in a similar fashion, we can saturate the threefold coordinated surface atoms of fig. 1(c) by the addition of a fourth shell of 60 carbon atoms (green color) placed radially outward, shown in fig. 1(d). At this point we would

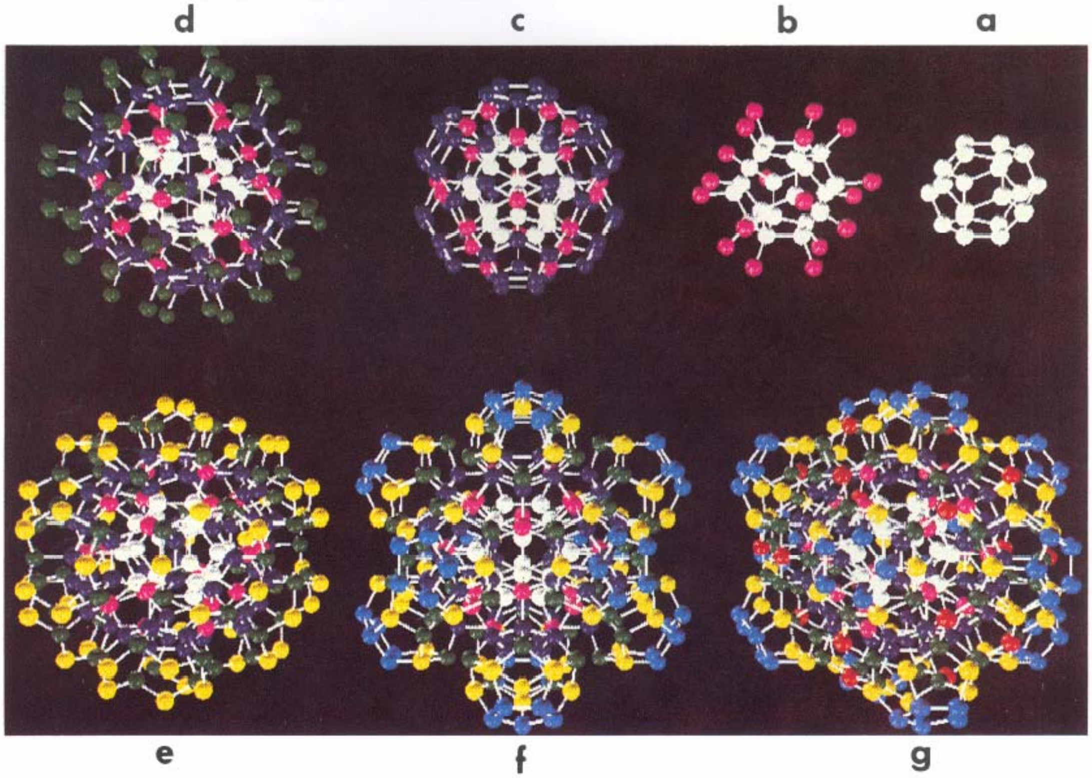

Fig. 1. Structure of the first seven icosahedral tetrahedrally bonded carbon clusters. Clusters containing one through seven shells (from C_{20} to C_{300}) are displayed counterclockwise. The various colors of atoms represent the successive shells. All atoms of the same shell are related by the icosahedral group symmetries.

again have an unstable configuration, similar to the situation shown in fig. 1(b), resulting from the single coordination of all the fourth shell atoms. Two of the three dangling bonds of each green atom can be saturated by the addition of a fifth shell of 60 atoms (yellow color), to produce the structure seen in fig. 1(e). Here the yellow atoms have two dangling bonds each, one of which can be saturated by the addition of a sixth shell of 60 atoms (blue color, fig. 1(f)), rendering both blue and yellow atoms threefold coordinated. The one remaining dangling bond of each green atom can be saturated by the addition of 20 (red color) atoms which comprise a seventh shell (fig. 1(g)). Each red atom bonds to three green atoms. This seven shell structure (fig. 1(g)) contains a total of 300 atoms, all of which are either fourfold coordinated (white, pink, purple, and green) and form the interior of the cluster, or threefold coordinated (yellow, blue, and red) and form the surface of the cluster.

Even larger structures of the same type can be constructed. The next size which has all interior atoms fourfold coordinated and all surface atoms threefold coordinated contains 650 atoms in 13 shells. We expect the clusters which consist of fourfold coordinated interior and threefold coordinated surface atoms to be the most stable structures in this class of icosahedral clusters. The 20-atom (fig. 1(a)), 100-atom (fig. 1(c)), and 300-atom (fig. 1(g)) structures are the smallest examples, followed by the 650-atom cluster. We examined the structural properties of these four clusters in detail. The icosahedral symmetry requirement does not uniquely determine the positions of atoms within each shell, but instead leaves between one and three degrees of freedom per shell. The atomic positions in each shell were optimized through a Monte Carlo minimization of the energy of each cluster, calculated with Tersoff's empirical potential [8]. This potential was fitted to give a reasonably accurate description of bonding in graphite and diamond, and it predicts the bond lengths of C_{60} to about 3% of the experimental values. The energy and diameter of the resulting optimized configurations are shown in table 1. The number of atoms per shell, average bond lengths of atoms in each shell and average bond length in each cluster are given in table 2. The increase in bond length with cluster size observed in table 2 is a consequence of the strain caused by deviations from tetrahedral bond angles. This elongation of bonds is reversed to some extent at the surfaces of the clusters where threefold coordination favors stronger bonds. In fact, in C_{300} and C_{650} the bonds *between* surface atoms are for the most part smaller than the *average* bond lengths of the outer shells shown in table 2. The ability of surface threefold coordina-

Table 1
Structural properties of icosahedral carbon clusters with tetrahedral bonding, containing fourfold coordinated inner (bulk) atoms and threefold coordinated outer (surface) atoms. Energies and structural relaxations were obtained by using Tersoff's classical potential

# atoms	# shells	# surface atoms	Energy (eV/atom)	Diameter (Å)
20	1	20	−5.78	4.29
100	3	60	−6.57	8.66
300	7	140	−6.54	15.54
650	13	180	−6.64	19.88

Table 2
Shell structure and bond lengths (in Å) of the four favorably coordinated icosahedral carbon clusters. Each row contains the number of atoms and average bond lengths of atoms in the specified shell. The shells marked with a star correspond to surface atoms, which are threefold coordinated. Unmarked shells correspond to interior (fourfold coordinated) atoms. The last row shows the bond length averaged over all shells of a cluster

shell #	# atoms	C_{20}	C_{100}	C_{300}	C_{650}
1	20	1.53⋆	1.57	1.59	1.59
2	20		1.54	1.59	1.59
3	60		1.51⋆	1.59	1.59
4	60			1.57	1.58
5	60			1.61⋆	1.61
6	60			1.55⋆	1.62
7	20			1.53⋆	1.62
8	30				1.62
9	60				1.67
10	20				1.67
11	60				1.62
12	60				1.58⋆
13	120				1.62⋆
Average		1.53	1.53	1.58	1.61

tion to prevent bond elongation is greatest in smaller clusters where, due to the larger surface-to-volume ratio, the favorable arrangement of the surface controls the overall structure of the cluster. In contrast, strain dominates over surface effects in larger clusters, producing the elonga-

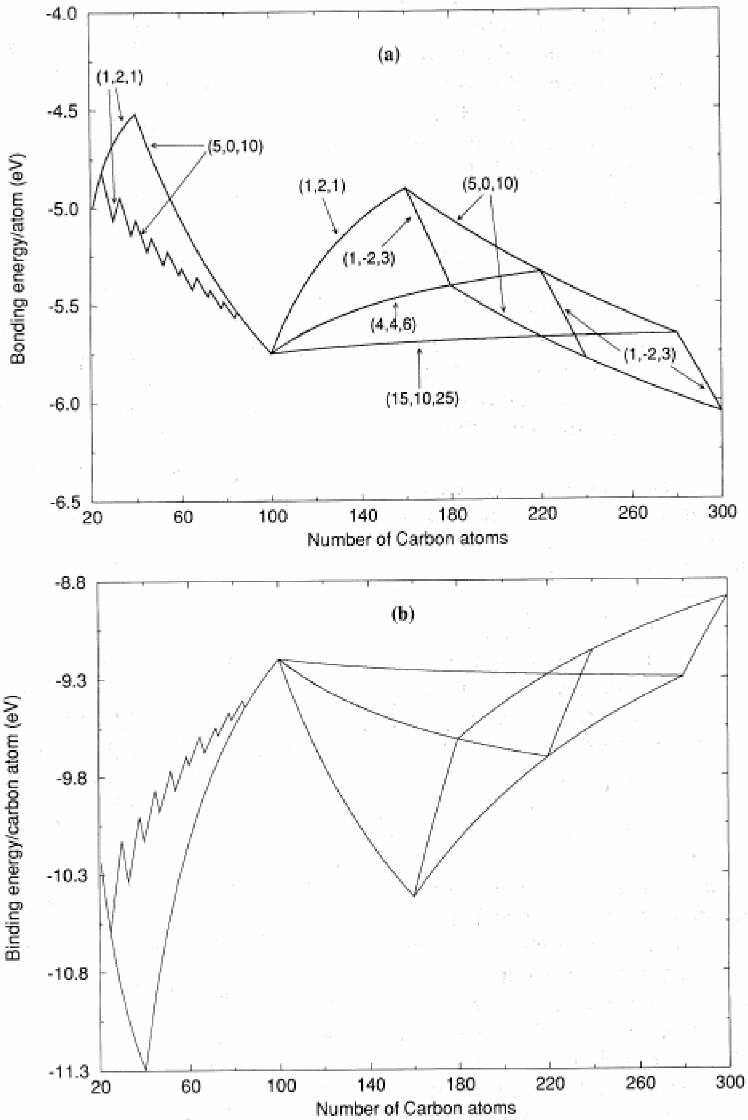

Fig. 2. Bonding energy of molecules built from icosahedral carbon structures with the dangling bonds of surface C atoms saturated by hydrogen. (a) Formation under conditions in which the chemical potential of H atoms is finite. The triplet of numbers labeling each curve represents the number of C atoms, H atoms, and C–C bonds added in each increment as the molecule is expanded along a given pathway. (b) Formation in an atmosphere containing an unlimited supply of H atoms (chemical potential of hydrogen vanishes).

tion of most bonds, as is seen, for example, in C_{650} (table 2).

2.2. Hydrogenated clusters

It is possible that even the clusters which have all inner atoms fourfold coordinated and all outer atoms threefold coordinated could be unstable as isolated molecules because the locally tetrahedral bonding arrangement leaves one unsaturated dangling bond per surface atom. However, if these dangling bonds were saturated by hydrogen atoms, the resulting molecules might be stable. Indeed, the smallest such hydrogenated icosahedral carbon cluster, $C_{20}H_{20}$, has already been produced experimentally [7]. Similarly, we expect that under auspicious experimental conditions, $C_{100}H_{60}$, $C_{300}H_{140}$, $C_{650}H_{180}$ could be rather stable. These molecules, as well as ones of intermediate sizes, could perhaps be formed under high pressure in the presence of hydrogen.

In order to investigate this surface passivation, we constructed a series of hydrogenated molecules by partially filling the second through seventh shells (from C_{20} to C_{300}) of the icosahedral structures shown in fig. 1. Each surface C atom of the incomplete shells is saturated with the proper number (between 1 and 3) of hydrogen atoms to render it fourfold coordinated. We calculated the approximate bonding energies of the resulting molecules by using tabulated values for the C–H and C–C single bonds (4.3 eV and 3.9 eV, respectively) [9]. The different bond lengths in the clusters (seen in table 2) examined here produce changes in the bonding energy which are small compared to energy differences between clusters. Hence, in this calculation we neglect variations in bond lengths. This effect could become more important in hydrogenated clusters larger than the ones considered here, where bond elongation is more pronounced as discussed above.

In order to make contact with realistic situations, we explored two different extremes of the experimental conditions: first, we considered an environment in which the hydrogen atoms required for saturation of the surface dangling bonds are obtained from H_2 molecules. In this case, the hydrogen atoms in the clusters must be freed from molecular hydrogen by breaking H–H bonds, so that clusters requiring more hydrogen are more difficult to form. The energy cost for obtaining atomic hydrogen can be described by a finite chemical potential for the hydrogen atoms. The energetics of this situation are shown in fig. 2(a) for clusters containing between 20 and 300 carbon atoms. Each curve represents a different pathway of expanding a cluster by partially filling the second through seventh shells. The triplet of numbers labeling a curve indicates the numbers of C atoms, H atoms, and C–C bonds added at each step as the cluster is expanded. The two curves in the 20 to 100 atom region of fig. 2(a) represent two different ways of creating molecules intermediate in size to the hydrogenated versions ($C_{20}H_{20}$ and $C_{100}H_{60}$) of the clusters shown in fig. 1(a) and fig. 1(c). The upper curve represents the path which fills the entire second shell (pink color) with C atoms before beginning to add atoms to the third shell (purple color). The 20 to 40 atom region of this curve corresponds to successive additions of 1 C atom to the second shell, producing 1 extra C–C bond for each such increment. Each C atom added to the second shell saturates the 1 dangling bond of a first shell atom (white color), but it also creates 3 new dangling bonds, requiring the net addition of 2 H atoms; hence this curve is labeled (1, 2, 1). The second part (40 to 100 atoms) of this upper curve corresponds to the addition of 5 C atoms (purple color) at each step, forming a pentagon of the third shell. Each such step adds a total of 10 new C–C bonds to the cluster: 5 of them are the bonds within the added pentagon, while the other 5 are bonds between the added atoms and atoms of the second shell. This increment requires no new H atoms because the 5 H atoms that were previously used to saturate second shell dangling bonds can now be used to saturate the 5 dangling bonds of the added (third shell) pentagon. Thus the upper curve in this region is labeled (5, 0, 10). The lower curve in the 20 to 100 atom region corresponds to partial but simultaneous filling of the second and third shells along the path which minimizes the number of H atoms. The molecules represented by this curve are constructed by adding second shell (pink color) atoms at nearest neighbor sites, so that entire pentagons of the third shell (purple color) can be added at intermediate steps. The accretion path of this lower curve produces more C–C bonds (and fewer C–H bonds) at each step and thus lies lower in energy than the pathway that fills one shell entirely before beginning to fill the next shell (upper curve). As cluster size increases, multiple paths for filling the shell structure become possible, some of which are illustrated in fig. 2(a).

The second extreme case of an experimental environment consists of an unlimited supply of atomic hydrogen. In such a system, there is no energy cost to obtain the H atoms needed to saturate the dangling bonds of a given cluster. This situation corresponds to a zero chemical potential for the H atoms. One way of incorporating this feature into the study of relative stability is to calculate the energy per carbon atom, shown in fig. 2(b). We note that the curves in this figure resemble a mirror image of the curves in fig. 2(a). Since formation of a C–H bond is energetically favored over formation of a C–C bond [9], when there are plenty of H atoms available for bonding (as in the situation represented by fig. 2(b)), pathways which increase the relative number of H to C atoms are energetically favored as the cluster is expanded. The opposite effect is seen in fig. 2(a): pathways which increase the relative number of hydrogen to carbon atoms become less energetically favorable as the cluster is expanded, due to the energy cost of obtaining H atoms from the H_2 reservoir. Thus the experimental conditions under which hydrogenated clusters are produced are important in determining which structures are most likely to form. As is seen in fig. 2, under both extremes discussed above, there exist a number of larger hydrogenated molecules which have lower bonding energies than $C_{20}H_{20}$, a molecule known to exist experimentally. We therefore suggest that such molecules are likely to be stable and should be interesting candidates for experimental investigation.

2.3. Electronic structure

In order to gain a better understanding of the properties of the hydrogenated and pure icosahedral carbon clusters, we studied their electronic

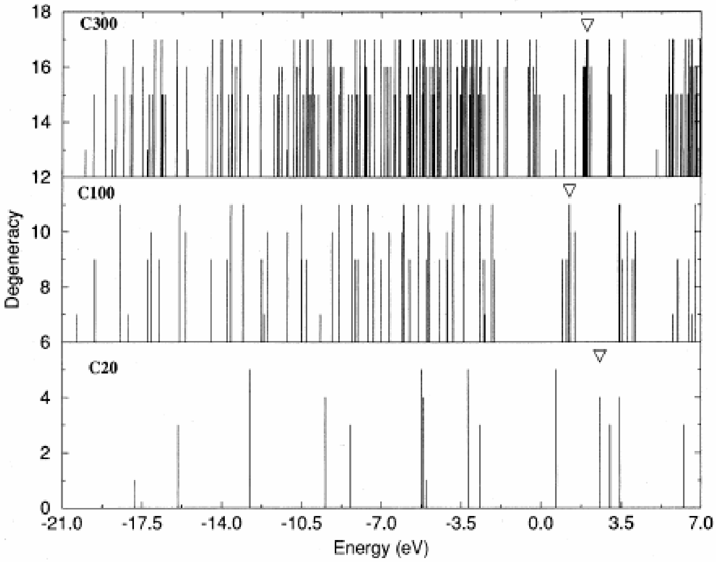

Fig. 3. Density of states vs. energy for the C_{20}, C_{100} and C_{300} clusters. The *y*-axis represents degeneracy. (The C_{100} and C_{300} states are shifted upward by 6 and 12 units, respectively, for clarity.) Triangles mark the position of the Fermi level for each structure. The zero of the energy scale corresponds to the top of the valence band in bulk diamond (see ref. [10]).

states by using the tight binding approximation with parameters from ref. [10]. We have incorporated a d^{-2} dependence in the tight binding parameters to account for varying bond lengths. This approach gives an excellent representation of the band structure of bulk diamond. Since the bonding in our models, like that of diamond, is locally tetrahedral, we expect the tight binding calculations of the electronic states of these clusters to be reasonably accurate. The density of states as a function of energy for the C_{20}, C_{100}, C_{300} clusters is shown in fig. 3. All structures have only the degeneracies allowed by the dimensions of the irreducible representations of the icosahedral symmetry group (1, 3, 4, and 5). We note that C_{20} has the highest Fermi level, as a result of the inability of its surface dangling bonds to lower their energy by forming bonding combinations. This lack of bonding among surface dangling orbitals can be understood by studying the eigenfunctions of electronic states near the Fermi level. We find that there are two types of surface states, both of which reduce bonding: the first type is comprised primarily of dangling bonds on 8 *nonadjacent* atoms of the dodecahedron, so that there are no nearest neighbor orbitals with which these dangling bonds can interact. The second type consists of orbitals which form a bonding combination with one neighbor, but an antibonding combination with another neighbor.

These unfavorable effects are not as pronounced in the C_{100} structure, where all neighboring surface atoms are coplanar, forming pentagonal rings (fig. 1(c)). This surface configuration allows more effective bonding between dangling bonds than is found in C_{20}. In contrast to the case of C_{100}, the surface structure of C_{300} is unfavorable to bonding between dangling orbitals. Similar to the dangling bonds of 8 nonadjacent atoms of C_{20}, the 20 red atoms of C_{300} (fig. 1(g)) have *no* neighboring surface atoms; thus the dangling bonds of these atoms have no neighboring orbitals with which they can interact. Furthermore, as in C_{20}, the non-planar arrangement of surface atoms in C_{300} suppresses bonding among dangling orbitals belonging to the yellow and blue atoms. Consequently, C_{300} has a Fermi level higher than that of C_{100}. The effectiveness of surface bonding is as important as the ratio of surface-to-bulk atoms: even though C_{100} has a higher surface-to-bulk ratio than C_{300}, it has a lower cohesive energy per atom (table 1), probably as a result of its more favorable surface arrangement.

We next focus on the electronic states of C_{100}, which appears to be the most likely candidate for a stable cluster of the new class of structures discussed here. While the states of the other clusters differ from that of the C_{100} near the Fermi level, as discussed above, the low lying states of all three clusters are qualitatively similar. Most of the weight of these low energy wavefunctions is on s orbitals, and a large part of it is on orbitals of inner atoms, which are fourfold coordinated. For example, the lowest energy state of C_{100} has 96% of the weight of its wavefunction on s orbitals, with 72% of the weight in orbitals of the inner 40 atoms. Higher energy states exhibit a gradual shift of weight from s to p orbitals and from bulk to surface atoms: for example, the 12th state from the bottom of the energy scale has 84% of its weight in s orbitals and 85% of its valence charge density on surface atoms. States near the Fermi level, on the other hand, have most of the weight of their wavefunctions on the 60 surface atoms, and mostly in p orbitals: The states in the -2.1 eV to 1.5 eV range have between 85% and 99% of their valence charge density on surface atoms and between 78% and 93% of their total charge density on the p orbitals of these atoms. When the outer carbon atoms are saturated with hydrogen, the electronic spectrum of $C_{100}H_{60}$ (not shown) contains no states in the gap range (-2 to 5 eV). This result illustrates how hydrogenation can saturate dangling bonds to produce molecules that are likely to be stable, which have large separations between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gaps).

Finally, we comment on some aspects of our models which we believe make them potentially suitable for interesting applications. First, the icosahedral symmetry of the clusters eliminates the presence of any easy cleavage planes. Hence, these structures would be strongly resistant to fracture, which usually occurs by propagation of cracks along easy cleavage planes. A material composed of the new icosahedral units may therefore be an extremely hard substance. Second, the hydrogenated versions of our molecules have large HOMO–LUMO gaps which are enhanced by quantum confinement (absence of dispersion in the electronic spectrum due to finite cluster size). Assemblies of these clusters deposited on carefully chosen surfaces may possibly form negative affinity systems in analogy to the hydrogenated diamond (111) surface [11]. Both possibilities deserve further theoretical study which is beyond the scope of the present work.

3. Summary

In summary, we have discussed the properties of a new class of compact carbon clusters. These clusters, which are the diamond analogs of the fullerenes, incorporate tetrahedral rather than graphitic-like bonding, into spherical units with icosahedral symmetry. The clusters of size 20, 100, 300, and 650 which satisfy the requirement of fourfold coordination of interior atoms and threefold coordination of surface atoms were examined in detail. The electronic spectrum of the clusters near the Fermi level shows that the dangling bonds resulting from threefold coordination of surface atoms are more favorably accommodated through bonding combinations in C_{100} than in either C_{20} or C_{300}. Hydrogenation of the surface atoms, which removes the gap states, is likely to produce clusters which would be more stable than the bare carbon clusters. The experimental conditions controlling the chemical potential of hydrogen are of central importance in determining the relative stability of various hydrogenated structures.

Acknowledgements

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