

Negative-Curvature Fullerene Analog of C_{60}

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An analog of the C_{60} buckyball structure is investigated, in which sevenfold rings play the same role as the fivefold rings of C_{60} . This periodic C_{168} structure is topologically ideal in the same sense as C_{60} : Every atom is in a topologically equivalent local environment, participating in one sevenfold and two sixfold rings. The excess energy per atom to create this structure from an ideal graphitic sheet is predicted to be *substantially less* than for C_{60} . If this material could be synthesized, we predict that it would have elastic constants comparable to those of Si, but with a density nearly half that of graphite.

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Much attention has been recently focused on the C_{60} form of carbon. This is a graphitic form in which substitution of sixfold rings by fivefold rings leads to a positive Gaussian curvature, and causes the graphitic sheet to curl up into a "fullerene" ball. We became intrigued by the question: What structures might develop if sixfold rings are replaced instead by sevenfold rings? In this case the graphitic sheet must acquire negative Gaussian curvature, and a structure with positive intensive genus (i.e., handles per unit cell) must result. Such structures are known as "plumber's-nightmare" structures. Idealized soap-film versions ("minimal surfaces") have long been studied by mathematicians [1-3], and physical realizations of amphiphilic lipid bilayer systems having this topology are known [4,5]. It would be most interesting if covalently bonded realizations of such structures could also be fabricated. Fullerene structures with eightfold [6] and sevenfold rings would seem to be the most promising systems to explore.

In this paper, we give a construction for one such structure which has a perfect local topology in the same sense as C_{60} : Each atom is shared by one sevenfold and two sixfold rings; every sevenfold ring is surrounded by only sixfold rings; and each sixfold ring is surrounded by alternating sixfold and sevenfold rings. Our structure has the global topology of a surface which would wrap around a diamond lattice and separate space into two percolating volumes: one containing the atoms and bonds, the other containing the interstitial regions. (The minimal surfaces of this type are known as " F surfaces" [1] or " D surfaces" [2].) Our structure might whimsically be referred to as a "buckygym," in analogy with "buckyball," as it more closely resembles a child's climbing gym than it does a soccer ball. Figure 1 shows one "double layer" of this structure as viewed from the (111) direction; the white tube which has been sliced through and which faces the viewer corresponds to a (111) bond of the diamond structure.

The structure is fcc with lattice constant $a=21.8 \text{ \AA}$. It

has 168 atoms per primitive cell, and belongs to the point group T_h and the space group $Fd\bar{3}$. The coordinates for the seven inequivalent sites in the unit cell are given in Table I. The remaining coordinates of the 84 atoms which make up one joint (the analog of the atom of the diamond superstructure) can be recovered by applying the twelve operations of the symmetry group T (proper rotations of a tetrahedron). The second joint in the unit cell is obtained by inverting the first and translating by $(a/4, a/4, a/4)$.

Many of the features of this structure are topologically determined. The D surface has unit genus per joint (two per primitive fcc cell). By the Gauss-Bonnet theorem, this requires twelve septagons per joint (just as twelve pentagons are required to form a ball). Since each atom belongs to exactly one sevenfold ring, we must have 84

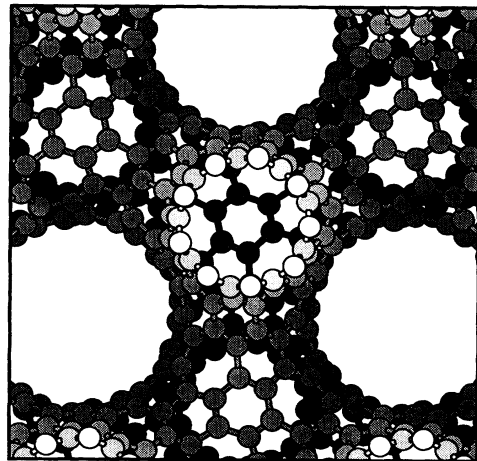


FIG. 1. One double-layer cut from the C_{168} structure, as seen from the (111) direction. Atoms are shaded according to distance from viewer. The view cuts through a plane of bonds of the diamond structure. Tubes protruding toward viewer would be connected to the next double layer in the full structure.

TABLE I. Relaxed positions of inequivalent atoms in the C_{168} structure, given in units of lattice constant $a=21.8 \text{ \AA}$. Coordinates of remaining atoms can be obtained using symmetries (see text).

| Atom | x | y | z |
|------|---------|--------|--------|
| 1 | 0.1134 | 0.0050 | 0.2415 |
| 2 | -0.0109 | 0.0303 | 0.2200 |
| 3 | 0.0272 | 0.0756 | 0.2435 |
| 4 | -0.0984 | 0.0826 | 0.1704 |
| 5 | -0.0662 | 0.1383 | 0.1542 |
| 6 | -0.0743 | 0.0402 | 0.2146 |
| 7 | -0.1915 | 0.0177 | 0.1649 |

atoms per joint. However, some features of our structure were unanticipated. For example, we found it to be impossible to build a structure which preserves the mirror symmetries of the diamond lattice, without introducing extra sixfold rings. (As a result, the sixfold ring at the very center of Fig. 1 is slightly twisted with respect to the "bonds" of the diamond superstructure.) Also, the interior and exterior of the fullerene sheet are not symmetrical with respect to one another, as they would be for the ideal D surface. We hypothesize that it is impossible to restore these symmetries without violating the ideal local packing of sixfold and sevenfold rings, but have no proof that this is so. Finally, we note that our analog of the C_{20} dodecahedron is a C_{56} structure which is obtained by an obvious deflation rule [7] from the C_{168} structure. (Actually, we constructed the C_{56} structure first, and then inflated it to obtain C_{168} .)

We now turn to a discussion of the physical properties of our hypothetical C_{168} structure. We relaxed this structure using an empirical interatomic potential of Tersoff [8] which has been optimized to reproduce structural properties for carbon in both diamond and graphite structures. The elastic constants for graphite are somewhat too stiff in this model (e.g., by 14% and 40% for C_{11} and C_{66} , respectively), and it has *not* been optimized for fullerene structures. Nevertheless, we believe that the qualitative predictions below can be trusted.

Table II summarizes our results on the structural properties of C_{168} as calculated within the model potential. The most remarkable feature is that the formation energy of C_{168} is only 0.11 eV/atom, compared to 0.67 eV/atom calculated for C_{60} with the same potential. (We use the term "formation energy" to mean total energy per atom relative to an ideal graphite sheet.) From Table II, it is evident that the primary reason for this difference is that the bond angles are much closer to 120° for the former. (The deviation of the average bond length of C_{60} from the graphite length is probably a consequence of the bond-angle variations, which lead to bond weakening within the model.) While it is impossible for a fivefold ring to have all 120° bond angles, a sevenfold ring can easily do so by buckling out of the plane. Such buckling is a natural

TABLE II. Calculated structural properties of relaxed C_{60} and C_{168} structures, compared to those of an ideal graphitic plane. d , θ , and E are the bond length, bond angle, and energy per atom, respectively; the subscript 0 indicates reference theoretical equilibrium property for an ideal graphite plane, and the overbar and rms indicate the mean and the rms deviation from the mean, respectively.

| | $\bar{d} - d_0$ (\AA) | d_{rms} (\AA) | $\bar{\theta}$ (deg) | θ_{rms} (deg) | $E - E_0$ (eV) |
|-----------|-------------------------------------|--------------------------------------|-------------------------|--------------------------------|-------------------|
| C_{168} | 0.004 | 0.029 | 119.6 | 2.1 | 0.11 |
| C_{60} | 0.026 | 0.017 | 116.0 | 5.7 | 0.67 |

feature of the C_{168} structure. It occurs to a similar extent even if the structure is relaxed using a model which is insensitive to bond angles, such as a model of central Hooke springs of zero equilibrium length. (It is an amusing fact that this Hooke model leads to a structure having each atom *exactly coplanar* with each of its three neighbors, so that the average bond angle is *exactly* 120° .) It might be that the model potential overestimates the importance of 120° bond angles and thereby underestimates the formation energy of C_{168} relative to C_{60} , but it seems highly unlikely that a more accurate calculation would change the fact that the energy is dramatically lower for C_{168} .

Alternatively, one may rationalize the lower formation energy of C_{168} from a continuum point of view, as follows. Recall that the Gaussian and mean curvatures are defined as $\kappa_1\kappa_2$ and $(\kappa_1 + \kappa_2)/2$, respectively, where κ_1 and κ_2 are the curvatures referring to the principal axes of the curvature tensor. κ_1 and κ_2 are of like sign for a sphere, but of opposite sign for a surface of negative curvature like the D surface. Consequently, while both the sphere and D surface have a Gaussian curvature of comparable magnitude, the mean curvature of the latter vanishes. Insofar as the elastic energy density can be expressed as a sum of Gaussian and mean curvature terms [4], it is clear that the latter term will be much smaller for the plumber's-nightmare structure than for the sphere [9].

We also calculated the elastic constants of the C_{168} structure. These are given in Table III, and compared with those of C and Si in the diamond structure. As mentioned above, the elastic constants are not expected to be highly precise, but should be accurate enough to give a

TABLE III. Calculated elastic constants and bulk modulus of C_{168} , compared with experimental values for C and Si in the diamond structure (all values in mbar).

| Material | C_{11} | C_{12} | C_{44} | B |
|--------------|----------|----------|----------|-----|
| C_{168} | 2.9 | 0.3 | 0.8 | 1.1 |
| C (diamond) | 10.8 | 1.3 | 5.8 | 4.4 |
| Si (diamond) | 1.7 | 0.6 | 0.8 | 1.0 |

good qualitative picture of the properties of the material. The elastic constants of C_{168} are similar in overall magnitude to those of Si, although somewhat different in character. [For example, the Poisson ratio in the (100) direction is only 0.08, compared to 0.26 for Si; and the sign of the cubic anisotropy $C_{11} - C_{12} - 2C_{44}$ is opposite to that of both diamond and Si.] With a density about a third that of diamond or half that of graphite, C_{168} would be a relatively lightweight and strong material.

Electronic and optical properties of the C_{168} material remain completely unexplored. We have not even determined whether it is likely to be an insulator or a metal. It would presumably be easy to dope by placing impurity atoms at the centers of the joints (or at the tetrahedral interstitial positions, which are the corresponding joints of the interstitial volume). Some atoms, such as alkalis or rare gases, might be highly mobile within one volume but incapable of crossing through the fullerene layer into the other volume.

Of course, all of these unusual physical properties will be irrelevant if there is no possibility of synthesizing the structure. To be sure, this is likely to be a formidable problem. However, the synthesis of C_{60} also appeared to be intractable until recently, and it is now available in large quantities. Conceivably, the admixture of some tetrahedral molecules in the right concentration to intercalate in the tetrahedral joint positions could seed the formation of the structure. Or perhaps one of the known amphiphilic plumber's-nightmare structures [4,5] could be polymerized and used as a substrate for growth. In any case, we should not preclude the possibility that an ingenious or fortuitous solution will be found. And even if synthesis of the C_{168} structure *per se* proves to be impossible, some existing forms of carbon (e.g., low-density amorphous carbon) may be found to bear some resemblance to a disordered plumber's-nightmare fullerene. Finally, the C_{168} structure may be a worthy object of study for intrinsically theoretical reasons. For example, it might be illuminating to study the electronic properties of a structure that shares some of the properties of C_{60} (local ring topology, density of odd-fold rings) but not others (fivefold versus sevenfold rings, finite versus infinite extent, positive versus negative Gaussian curvature). This might help one to trace certain properties (e.g., features in electron density of states) to certain structural features.

In summary, we have constructed a geometric model of a periodic plumber's-nightmare fullerene having the same ideal local ring topology as C_{60} , but with fivefold rings replaced by sevenfold rings. This C_{168} structure is predicted to have a formation energy per atom which is substantially *less* than that of C_{60} , because the bond angles can stay closer to 120° . We suggest that this structure is a natural candidate for further theoretical investigation and for attempts at synthesis.

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Note added.—During the preparation of this work for publication, we became aware of a closely related work by Lenosky *et al.* [10]. These authors study a C_{216} *D* surface with full cubic symmetry and extra sixfold rings (i.e., imperfect local ring topology).

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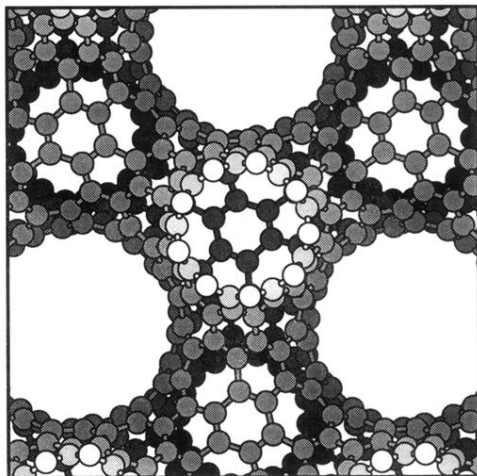


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