

C_{60}^B BUCKMINSTERFULLERENE, OTHER FULLERENES AND THE ICOSPIRAL SHELL

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Abstract—It seems remarkable that though carbon has been studied exhaustively for decades a new highly symmetric form, in addition to diamond and graphite, has recently been discovered. The C_{60}^B molecule is a cage with *truncated* icosahedral symmetry analogous to that of a football, i.e. 12 pentagonal and 20 hexagonal faces. The molecule, buckminsterfullerene, is one of a family highly symmetric fullerene 5/6-face cage species. The spontaneous formation of C_{60}^B has led to the discovery of an icosahedral spiral (icospiral) network that explains the structure of carbonaceous particles such as soot. This new topological form solves the spheroidal wrapping problem using planar materials. Curiously giant fullerene structures can be generated as highly symmetric 3D cages by the introduction of only 12 pentagonal defects into a 2D hexagonal sheet network of any size.

INTRODUCTION

The discovery of the superstable C_{60} molecule in Sept. 1985 [1] has been rationalized on the basis of a new type of carbon compound: a graphitic closed cage in which the 60 atoms lie at the vertices of a truncated icosahedron, Fig. 1. The structure consists essentially of 12 five-membered rings separated by 20 benzenoid six-membered ones. Although historically this shape is listed as one of the semi-regular solids of Archimedes an interesting and highly appropriate historical reference structure is the hollow framework drawn by Leonardo da Vinci to illustrate the book, *De Divina Proportione*, by Pacioli [2].

Not only has the proposal that the species has this elegant symmetric structure given rise to much debate but so also has the name chosen [3-5]. The number of alternative names that have been proposed is large, however it is worth noting that in retrospect none has proven more appropriate than that chosen by us on the basis of the ideas of Buckminster Fuller [6] that led us to propose the structure in the first place [1]. Some favour the rather obvious (and somewhat dull) name footballene, but here there is a problem as in the U.S. this name applies to an ovoid structure and should be translated as soccerene. The appropriateness of the name, buckminsterfullerene (though perhaps a trifle long, does roll smoothly off the tongue—albeit an Anglo-Saxon one), will become apparent below and hopefully this will enable those allergic to the length to overcome their antipathy. Anyone afflicted by endemic pedantry might contemplate the IUPAC or *Chemical Abstract* names and if they can get them correct [7] so overcome the withdrawal symptoms. It is convenient to use the formula C_{60}^B to differentiate buckminsterfullerene from all other 60-carbon atom isomers, and perhaps prefix a symmetry symbol if necessary i.e. $(I_h)C_{60}^B$.

For the purpose of this article we are interested in that property which so often captivates the human imagination whether in childhood or as an adult (is there a difference?)—symmetry. There are few other molecules which fascinate, by their symmetry alone, more than does C_{60}^B . Organic chemists have long been driven to develop new synthetic techniques in order to produce new compounds with exotic structural symmetry. Perhaps the most famous recent example is the work of various groups that led to the elegant molecule dodecahedrane, a mammoth task, which was finally achieved by Paquette *et al.* [8]. As far as buckminsterfullerene is concerned its first appearance appears to have been in 1970 when Yoshida and Osawa [9, 10] in a highly perceptive piece of work on superaromaticity considered the possibility that such a molecule should be stable. They appear to have been influenced by the earlier very nice synthetic work of Barth and Lawton [11] who made corannulene, Fig. 2, and found that it was stable. C_{60}^B was also discussed subsequently by Bochvar and Gal'pern [12] and Davidson [13]. A rather remarkable idea which predates all these, however, was that of Jones (pseudonym—Daedalus of the *New Scientist*) who

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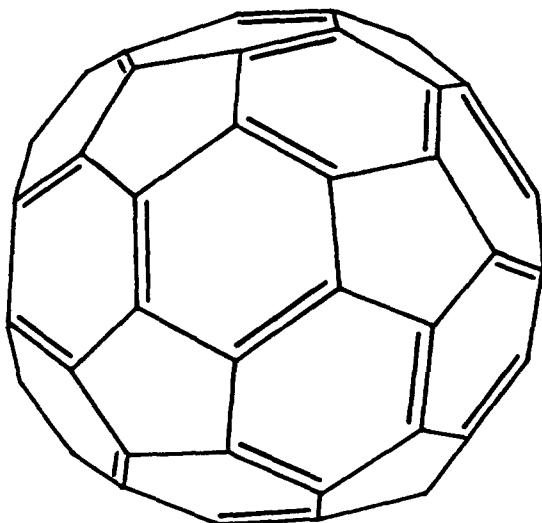


Fig. 1. The structure proposed for the superstable C_{60} carbon molecule discovered during laser vaporization of graphite [1]. The tetravalency of carbon is neatly accounted for as there are 12500 resonance structures.

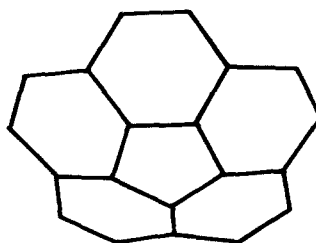


Fig. 2. The corannulene structure presented in perspective to highlight the fact that it is a saucer shaped molecule [11].

contemplated, in a most imaginative way, the possibility that large spheroidal carbon networks might be formed by some high temperature graphite production process [14, 15]. These ideas led some chemists to consider the possibility of synthesising C_{60}^B by traditional organic chemistry approaches. However, the most important aspect of the C_{60}^B discovery is undoubtedly the fact that such an elegant molecule actually forms spontaneously. A study of this and other aspects of C_{60}^B has, as discussed below, shed new light on the structure of materials and revealed new structures with symmetries and shapes which do not appear to have been discussed previously.

C_{60}^B buckminsterfullerene, the truncated icosahedral carbon cage

The experimental evidence for a stable C_{60} species is now unequivocal. It was observed that when carbon is laser vapourized into a helium atmosphere and the resulting plasma allowed to nucleate certain magic numbers are observed in the mass spectrum of the resulting products. The original observation showed that a C_{60} species exhibited spectacular resistance to further growth and to a lesser extent so also did C_{70} [1]. Almost immediately we came to the conclusion that the closed *t*-icosahedral cage structure could readily explain the observation for C_{60} [1]. From the point of view of the closure of a hexagonal network the inclusion of pentagons is very important. Jones in his original proposal [14, 15] was aware of an integral requirement for the closure elegantly presented in the beautiful book of Thompson [16] who writes:

“But here something strange comes to light, no system of hexagons can enclose space whether the hexagons be equal or unequal, regular or irregular, it is under all circumstances mathematically impossible. So we learn from Euler: the array of hexagons may be extended as far as you please, and over a surface either plane or curved, but it never closes in.”

Euler's law states that for any polyhedron,

$$C(\text{No. of corners}) + F(\text{No. of faces}) - E(\text{No. of edges}) = 2.$$

For a system consisting entirely of hexagons $C + F - E = 0$ and so such a system cannot close. In general the closure of a three-connected network is governed by the general relation [17]:

$$12 = 3 \cdot n_3 + 2 \cdot n_4 + 1 \cdot n_5 + 0 \cdot n_6 - 1 \cdot n_7 - 2 \cdot n_8 \dots$$

In the 5/6 cases this formula indicates that closure can occur for any system which includes 12 pentagonal configurations and an unlimited number of hexagonal ones. The C_{60}^B structure elegantly fulfills this topological requirement with a satisfying, chemically stable structure in which each pentagonal ring is completely surrounded by benzenoid hexagonal ones [18, 19]. A most interesting further property of these 5/6 fullerene cages is the fact that C_{60}^B is the smallest cage

that can contain completely isolated pentagons and this isolation cannot occur again until C₇₀ [18, 19]. The observation of 70 as the second most prominent magic number lends further weight to the closed fullerene structure proposal in general and the buckminsterfullerene structure of C₆₀ in particular.

From a symmetry point of view the C₆₀^B structure is extremely interesting in that it is *the* one which allows the maximum number of atoms to be distributed so that all are equivalent in terms that all positions are related by proper symmetry operations. From the point of view of chemical stability it is important to note that for extended carbon aggregates, hexagonal, followed by pentagonal, ring configurations are by far the most preferred structures. These factors endow C₆₀^B with unique geodesic *and* chemical structural stability. Such a structure is now accepted as also further stabilized by aromaticity and the fact that it will have a closed electronic shell configuration [20, 21]. For example this molecule has 12,500 resonance structures and on the basis of this criterion some degree of resonance stabilization is to be expected [22]. Perhaps more important than anything else is the fact that the molecule has no weakness, so from the point of view of chemical attack it should be as impregnable as the surface of graphite. It may be that this molecule is the most stable molecule that exists. Although it may be unstable relative to graphite in the bulk form there is now no doubt that it is stable relative to a flat sheet of hexagonal graphite with 60 atoms because such a sheet must have *ca* 22 dangling bonds on the edge which in the case of C₆₀^B are completely eliminated by intramolecular bond formation with the consequential gain in bond energy. A macroscopic piece of graphite (whatever that is!), may gain by having additional interlayer stabilization energy and this probably overcomes the destabilization due to unsatisfied valences at the edge when their numbers become insignificant in the bulk. The edges almost certainly will be cauterized by other atoms such as hydrogen in practice.

Other small fullerenes

In the original experiments it was already clear that 60 was not the only magic number, 70 was also relatively prominent. In addition, these two magic numbers were soon to be joined by some others [23]. If the closed cage C₆₀^B structural proposal were correct it seemed likely that these further observations should also be susceptible to explanation in terms of the closure principle. Such has turned out to be the case. It can be shown that varying degrees of relative geodesic/chemical stability are to be expected for certain numbered cages. The stability depends mainly on the how many pentagonal faces abut and the symmetry of disposition of these pentagonal faces [18, 19] and a careful study of the possible cage structures that are feasible leads rather satisfyingly to an extensive set of magic numbers: 24, 28, 32, 36, 50, 60 and 70 [18, 19] in excellent agreement with observation [23, 1]. We will call these structures, in general, fullerenes (neatly allowing us to retain buckminster—as a prefix for the C₆₀^B founder member of the family [4]). This is where the appropriateness of the name becomes evident as Buckminster Fuller's patents apply to a range of 5/6 ring structures and not just the 60 vertex one, in addition there is the possibility of giant fullerenes (see below), of the kind envisaged by Jones [14, 15], with many more than 60 atoms and there is actually some evidence that species with as many as 240 atoms form.

In the case of the small fullerenes it is worth noting that C₂₀^F with no benzenoid hexagonal rings at all is the smallest and is expected to be by far the least stable. By analogy with dodecahedrane it should presumably be called dodecahedrene. It is also worth noting that no C₂₂^F species can exist [24, 19] as the second fullerene must have at least one benzenoid ring and this can not occur until there are at least 24 atoms as in C₂₄^F. It is most gratifying that in at least one experimental observation the fullerene family appears to start fairly clearly at C₂₄ [25]. During the two-and-a-half or so years that have elapsed since C₆₀^B was detected, occasionally the C₂₈ cluster would also, under certain nucleation conditions, appear very prominent. It is thus most exciting that the simple cage theory predicts that the first high symmetry, relatively well-stabilized species that can be constructed is C₂₈^F with a rather neat tetrahedral structure, Fig. 3 [18]. This species has a most intriguing family relationship with Gomberg's triphenyl methyl, which was the fore-runner of free radical organic chemistry [26]. This result, if correct, suggests that the tetrahedral hydrocarbon C₂₈H₄, in which the carbon atoms at the centres of the four sets of trigonally abutting pentagons are hydrogenated, might be a relatively stable tetrahydrofullerene. Steps in stability are also to be expected for larger cages such as C₃₂^F and C₃₆^F [18]. There are other structures which are predicted to show some extra

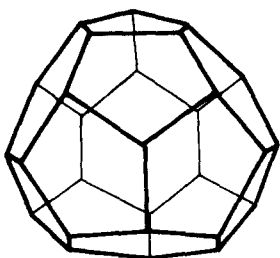


Fig. 3. After the first possible fullerene, C_{20}^F (dodecahedrene) which must be the most unstable, the first highly symmetric fullerene is the tetrahedral C_{28}^F cage shown here.

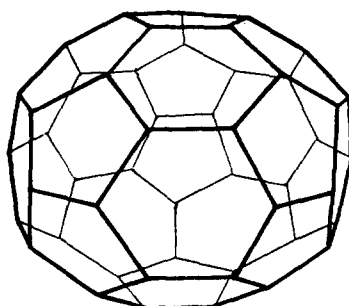


Fig. 4. One possible highly symmetric structure is depicted for a C_{50}^F cage which can avoid the involvement of fused triplets of pentagons.

stability, such as the rather elegant C_{50}^F structure depicted in Fig. 4 [18, 19]. The C_{50} signal is often seen to be prominent and it is most satisfying that the cage proposal is consistent with this observation also.

Probably as important as any other observation is result that C_{70}^F which is shown in Fig. 5, is the first cage, after C_{60}^F , which can be constructed without abutting pentagons [18, 19]. This cage is effectively two-halves of C_{60}^B separated by a ring of 10 carbon atoms and has a more-or-less ovoid shape. The observation that the C_{70} peak is second only to C_{60} in strength [1] can thus be readily explained and represents the most compelling further observation lending support to the fullerene closed cage structure proposal that is available at present.

THE ICOSPIRAL PARTICLE AND THE GIANT FULLERENES

The most intriguing aspect of the whole C_{60}^B story is the contention that such a symmetric molecule forms spontaneously. In order to explain this a straightforward scheme has been developed for nucleation leading to extended networks of sp^2 hybridized carbon atoms. It is proposed that the process is governed by two major factors:

- (1) Energy driven nucleation, will lead to curved carbon network [27, 28]. (Note that this is in complete contradiction to the traditional assumption that flat graphitic microcrystals form spontaneously.)
- (2) All further network growth takes place under epitaxial control [28].

The reason for factor (1) is straightforward as a flat hexagonal benzenoid C_{60} network will possess some 22 or so dangling bonds whereas a curved one will be able to eliminate these by bond formation, resulting in the most energetically favourable structure in the case of complete closure.

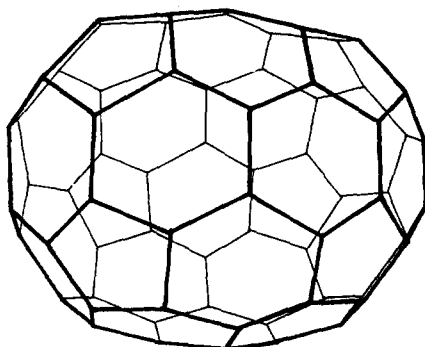


Fig. 5. It is curious that for fullerenes C_n^B with $n \leq 70$ the only ones that can be constructed without abutting pentagons are C_{60}^B itself and the C_{70}^F structure depicted here. The former has the shape of a football (or U.S. soccerball) whereas the latter has the shape of a rugby ball (or U.S. football). The above structure is readily produced by splitting C_{60}^B into two halves rotating by 36° and inserting a ring of 10 extra carbon atoms.

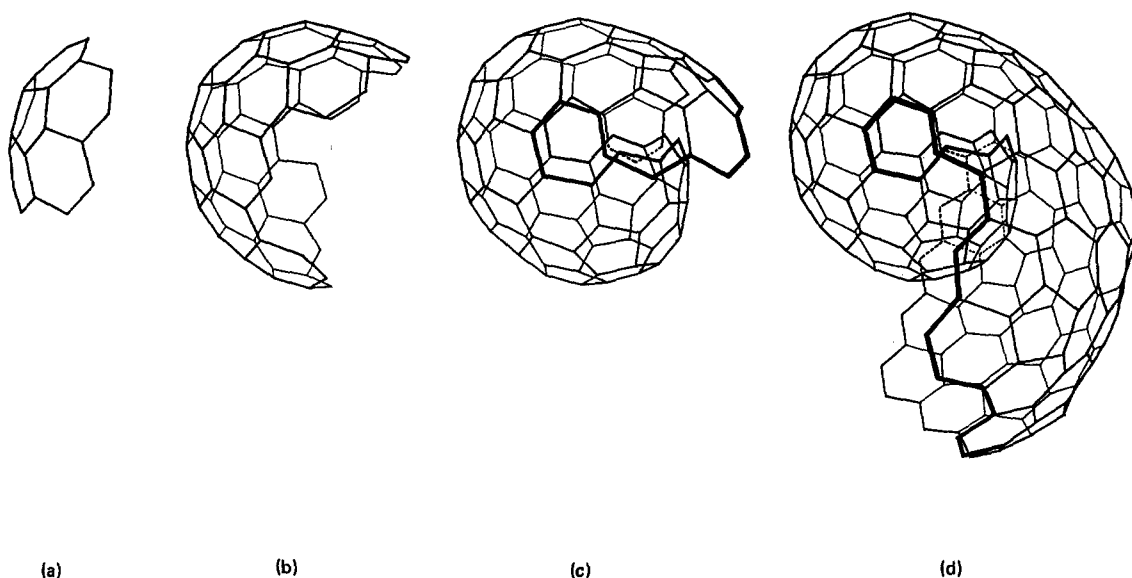


Fig. 6. Hypothetical initial growth sequence evolving from a corannulene carbon framework (a) through a broken egg-shell structure (b) to (c) a species in which edge by-pass occurs to an embryo in which the second shell is forming (d). The sequence leads in a natural way to both carbon particles and closed cages, fullerenes.

The network can curve towards closure by including five-membered rings. A typical nucleation scenario is depicted in Fig. 6 [28] in which we see that, in general, the mechanism results in an incompletely closed shell in which edge overlap occurs. To understand the structural implications of such a growth scenario the second premise (2) is required. As the spiral shell grows it is important to recognize that 12, and only 12, pentagonal configurations will occur in any 360° spheroidal section of the shell. One must also be aware that essentially all the curvature resides in these corannulene type cusps. It is at this point that a most interesting shape controlling effect becomes evident as the growing spiral evolves to form an object of ever increasing size. As fresh network forms it is likely to do so in such a way that the cusps in successive shells lie above each other, in other words the pentagons will be localized along radii emanating from the centre of the growing spiral. This is basically the epitaxial growth requirement.

As the object grows somewhat like a snowball accreting new surface, the resulting cluster should take on a shape consistent with that of a giant fullerene of commensurate size. Our study of the shape revealed a surprising result that as fullerenes grew in size the more-or-less round shape of C₆₀^B was effectively replaced by a polyhedral one [28]. This is depicted clearly in Fig. 7 where the change in shape on passing from the small to the symmetric giant fullerenes is shown. Here we see the remarkable result that as the cages get larger the object takes on an effectively icosahedral shape. The truncation still exists at the atomic dimensions but is lost on the macroscopic scale. In the closed object the 12 cusps in the surface are linked by a more-or-less smooth hexagonal net in the giant fullerenes. In fact the best way to think of this object is as a more-or-less flat flexible hexagonal net with 12 pentagonal defects which cause the net to fold and enclose space. As mentioned previously, such objects may actually form at least up to 240 atoms.

In general however the nucleation results in a spiral which grows to form a giant molecule/quasi-crystal consisting of concentric shells of quasi-icosahedral polyhedra. There is strong evidence in the elegant transmission electron microscope work of Iijima [29], that carbon particles do indeed possess such internal onion-like structure, which can further be explained in terms of the quasi-icosahedral spiral shell described here [28]. Of course in practice only approximate symmetry is to be expected though the basic polyhedral shape should be evident. This observation lends strong support not only to the nucleation mechanism in general but also to the C₆₀^B structure proposal in particular.

As far as the production of C₆₀^B itself is concerned, it is predicted that very occasionally, as the edges of the initial single shell embryos approach during growth, closure occurs and C₆₀^B or some

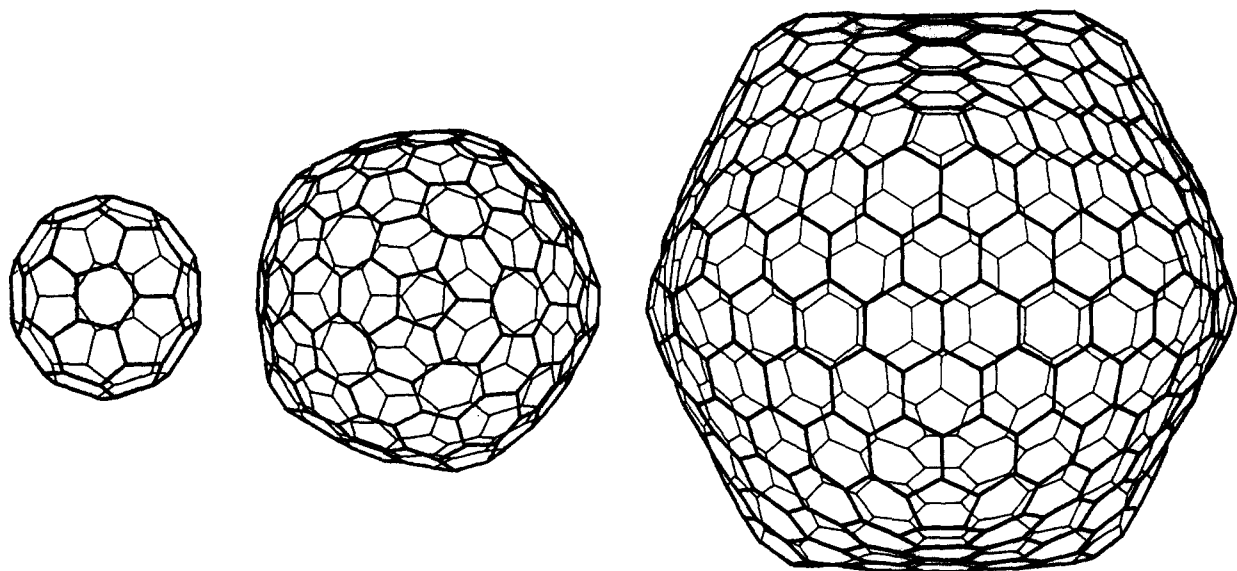


Fig. 7. A set of models for the closed symmetric fullerenes C_{60} , C_{240} and C_{540} . The diameters of the latter cages are two and three times that of C_{60} . The rapid shift towards quasi-icosahedral symmetry is striking.

other member of the fullerene family forms. There may be some evidence that there is an extra tendency to form the most favoured C_{60}^B cage in the fact that C_{62} peak is always weak relative to all other neighbouring ones. On closure no further growth can occur as the reactive edge has been eliminated. The nucleation scenario thus indicates that C_{60}^B is the *lone survivor* of the process and should *not* lie at the centre of a soot particle in general. The discovery that out of a chaotic system a single molecular species can remain when essentially all other carbon atoms have been absorbed into bulk material is a truly unique discovery. In this way it is most exciting to conjecture that C_{60}^B has been around since time immemorial and in particular is produced wherever carbon particles form both in the fireplace and in the outflows of carbon-rich red giant stars. In the latter case it may be detectable by some optical characteristic and as far as the ion C_{60}^{B+} is concerned it may even be responsible for the diffuse interstellar bands [30]. The point that it is the only molecule to survive out of chaos delineates C_{60}^B (and its positive ion) from all other contenders that have previously been proposed as carriers of the diffuse bands.

SUMMARY OF SYMMETRY ASPECTS

Some new and fundamental results on carbon particles have been described from the basis of their symmetry. It seems curious that although carbon has been the subject of so much study over so many years that the underlying symmetries addressed in this article have remained hidden for so long. Only now can such elegant structures be contemplated on the basis of the remarkable observation of the superstability of the C_{60} molecule which must be ubiquitously distributed both on earth and in space [30–32]. Nowhere is this more clear than in the work of Gerhardt *et al.* [33] who have shown that C_{60}^+ is a dominant ion in a sooting flame. This observation lends some of the strongest support for the nucleation mechanism we have proposed [27, 28] a key aspect of which is the prediction that C_{60}^B will be a by-product of carbon nucleation in general and soot formation in particular. It seems almost unbelievable that such a species could have remained unsuspected for so long. It is however the lone molecular survivor of the soot formation process and so probably lies hidden and difficult to separate and identify. Even so the intriguing aspect from the point of view of this article is that the work has led to molecules with most beautiful symmetries:

- (1) C_{60}^B with a closed almost round *t*-icosahedral cage, Figs 1 and 2.
- (2) Small fullerenes with many different cage symmetries, Figs 3–5.
- (3) Giant fullerenes with quasi-icosahedral polyhedral shape, Fig. 7.
- (4) The icospiral shell, Fig. 6.

It is interesting to conjecture that the icospiral shell may well be *the* primordial particle. It is highly likely that the first particle to form was carbonaceous and must have done so in the gas phase. If so our new observations point unequivocally to this structure. Indeed this icospiral structure may have even wider applicability in that it provides a way to form globular materials from sheets involving hexagonally packed entities by occasionally introducing defects. Another interesting possible rôle exists for this quasi-icosahedral, quasi-single-crystal particle, which is essentially a giant molecule; it is feasible that under isotropic pressure it will be an ideal embryo which with a minimal rearrangement serves as a growth nucleus for the diamond crystal.

The curious icospiral shell structure proposed here has C_s symmetry in its most symmetric form. The initial embryo is seen from the side in Fig. 6. It is effectively a spiral constructed from essentially triangular segments, more-or-less smoothly connecting the pentagonal cusps in such a way that the interlayer separation is as close to the graphitic distance of *ca* 3.4 Å as possible. As successive segments form, the size must increase and in the case of the more symmetric structures a more or less icosahedral particle results. The spiral shell will have two helical edges which spiral away in opposite directions. It is intriguing to note that in one-and-the-same object one can have both of the highly bioemotive features, the helix and icosahedron.

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