A geometric constraint, the head-to-tail exclusion rule, may be the basis for the isolated-pentagon rule in fullerenes with more than 60 vertices

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Carbon atoms self-assemble into the famous soccer-ball shaped Buckminsterfullerene (C_{60}), the smallest fullerene cage that obeys the isolated-pentagon rule (IPR). Carbon atoms self-assemble into larger (n > 60 vertices) empty cages as well—but only the few that obey the IPR—and at least 1 small fullerene (n ≤ 60) with adjacent pentagons. Clathrin protein also self-assembles into small fullerene cages with adjacent pentagons, but just a few of those. We asked why carbon atoms and clathrin proteins self-assembled into just those IPR and small cage isomers. In answer, we described a geometric constraint—the head-to-tail exclusion rule—that permits self-assembly of just the following fullerene cages: among the 5,769 possible small cages (n ≤ 60 vertices) with adjacent pentagons, only 15; the soccer ball (n = 60); and among the 216,739 large cages with 60 < n ≤ 84 vertices, only the 50 IPR ones. The last finding was a complete surprise. Here, by showing that the largest permitted fullerene with adjacent pentagons is one with 60 vertices and a ring of interleaved hexagons and pentagon pairs, we prove that for all n > 60, the head-to-tail exclusion rule permits only (and all) fullerene cages and nanotubes that obey the IPR. We therefore suggest that self-assembly that obeys the IPR may be explained by the head-to-tail exclusion rule, a geometric constraint.

Buckminsterfullerene | buckyball | self assembly | clathrin

Fullerenes are closed cages with an even number n ≥ 20 of three-connected vertices, 3n/2 edges, 12 pentagonal faces, and (n-20)/2 hexagonal faces (1, 2). The soccer ball with n = 60 vertices is the smallest fullerene with all of its pentagons surrounded (“isolated”) by hexagons. It is therefore said to obey the “isolated-pentagon rule” (IPR) (2–5). No cage that obeys the IPR is mathematically possible for 62 ≤ n ≤ 68, but IPR cage isomers are possible for every even n ≥ 70, the number generally growing as n grows (2). In accord with the IPR, carbon atoms self-assemble into the soccer-ball shaped Buckminsterfullerene (C_{60}) (1) and larger fullerene cages, but only those few that obey the IPR, starting with the one IPR isomer of C_{70} (Fig. 1A) (6–9).

Various explanations have been offered for the IPR. Kroto suggested that “strain-related instability” within the network of σ bonds was minimal for cages with isolated pentagons but increased with pairs of adjacent pentagons, even more so with clusters of 3 pentagons, etc (3). Schmalz and colleagues offered a quite different explanation, that adjacent pentagons had “eight-cycles,” in violation of Hückel’s 4n + 2 rule, thus focusing on diminution of π bond interaction by adjacent pentagons (4, 5). Later, because π orbital overlap is also reduced generally by cage curvature (10, 11), they suggested that overlap would be most greatly reduced at the sites of greater (and anisotropic) curvature produced by adjacent pentagons (12). These mechanisms work together for Buckminsterfullerene but not necessarily for larger IPR cages and not for smaller cages with adjacent pentagons, at least 1 of which is also formed by carbon (13, 14).

Here, we propose an alternate explanation for the IPR. Initially focusing on the small fullerene cages (n ≤ 60 vertices) with adjacent pentagons into which the protein clathrin (15) and carbon atoms self-assemble (13, 14) [e.g., 36-15 (the 15th isomer with 36 vertices) and 28-2 (the 2nd isomer with 28 vertices)], we described a geometric constraint, the head-to-tail exclusion rule (16, 17). Among the 5,769 small cages with adjacent pentagons, the head-to-tail exclusion rule permits self-assembly of just 15. It also permits self-assembly of the IPR soccer ball (n = 60).

When we investigated larger cages in the range 60 < n ≤ 84, we were surprised to discover that the head-to-tail exclusion rule permits only (and all of) the 50 cages that obey the IPR in this range of n. Might it permit some larger non-IPR fullerene? There is precedent for such a concern; for example, the pentagon-spiral algorithm (18) produces every 1 of >1 million fullerene cage isomers before missing one with 100 vertices (19, 20). To be regarded as an explanation for the IPR, the head-to-tail exclusion rule would have to be shown to permit only and all IPR cages for all n > 60. Here, by proving that the largest permitted cage with adjacent pentagons is one with n = 60 vertices, we do so. In addition, based on the physical mechanism underlying the operation of the head-to-tail exclusion rule (17), that the head to tail rule identifies fullerenes with severely nonplanar faces that are unlikely to self-assemble and are energetically disfavored, we describe how the head-to-tail exclusion rule promotes production of IPR cages.

Model

Dihedral Angle Discrepancy (DAD). The head-to-tail exclusion rule relies on appreciation of “dihedral angle discrepancy” (DAD) (16). As shown in Fig. 1B, a DAD is a vector that we draw along an edge that abuts a pentagon at one end and a hexagon at the other. Depending on the faces to the sides of the edge, we color the DAD “green” (two side hexagons), “red” (a hexagon and a pentagon), or “blue” (two pentagons). The dihedral angles about an edge with a green DAD are 138.2° at its pentagon end and 180° at its hexagon end, so the green DAD corresponds physically to an increase (or broadening) of dihedral angle of 41.8° (17). This broadening requires that one or usually both of the faces on either side of such an edge—the two hexagons marked with asterisks in Fig. 1B in the case of a green DAD—cannot be planar.

In the three-dimensional IPR 70 fullerene cage shown in Fig. 1A, we mark just one green DAD, with its tail at the pentagon end of the edge and its head at the hexagon end. In the corresponding two-dimensional “Schlegel diagram” representation shown in Fig. 1C, we mark all 20 of the green DADs. In Fig. 1A, the nonplanar side faces (hexagons) are evident along the cinched “waist” of the IPR 70 cage.

Edges with “red” and “blue” DADs have adjacent pentagons...
self-assembly of a fullerene.

For this reason, although from the point of view of graph theory some edges with a DAD, and thus some nonplanar faces (16). As noted above, most of the different fullerenes that have been isolated and identified have DADs and thus nonplanar faces (e.g., Fig. 1). The nature—DAD or no DAD—of all of the edges of a face can be assigned if the identities—pentagons and hexagons—of all of its surrounding faces are known. We call such arrangements Rings. Fig. 2A shows all 8 pentagon-centered Rings (“pent-Rings”) and all 13 hexagon-centered Rings (“hex-Rings”) from (16). In a fullerene cage, every pentagonal face can be regarded as the central face of a pent-Ring, and every hexagonal face can be regarded as the central face of a hex-Ring. We can therefore label every pentagon or hexagon with its pent-Ring type (e.g., 521) or hex-Ring type (e.g., 611). As can be seen in Fig. 2A, the edges of the central face of a Ring can have 0, 2, or 4 DADs. What is new in Fig. 2A is how the Rings are grouped for the purpose of this article’s proof, a critical advance over the corresponding figure in ref. 16.

**Head-to-Tail Exclusion Rule.** As noted above, most of the different fullerenes that have been isolated and identified have DADs and thus nonplanar faces (e.g., Fig. 1). The head-to-tail exclusion rule specifically excludes just the Rings that have DADs arranged head-to-tail, namely, the 2 pent-Rings (521 and 531) and 4 hex-Rings (621, 631, 632, and 642) grouped together in Fig. 2A Left.

Fig. 2B illustrates the physical basis for the head-to-tail exclusion rule. Edges $c$ and $a$ in that figure are examples of “external edges” because they are external to the central face of a Ring, and edge $b$ is an example of a “central edge” because it is an edge of the central face. “External rotation” refers to the rotation (in a surrounding face of a Ring) of external edges from one another, for example, edge $c$ from external edge $a$ about central edge $b$. In Rings with head-to-tail DADs, the magnitude of the external rotation about a central edge with DAD is equal to nearly the entire DAD about that edge, for example, 41.8° for an edge with a green DAD, and the resulting nonplanarity of the surround face is very severe. In Rings without head-to-tail...
DADs, the external rotation due to the DAD is shared among surrounding faces, and the resulting nonplanarity of the surrounding faces is much less severe (17).

Fig. 2. Rings may be grouped according to their arrangements of edges with DAD. (A) Each pent-Ring (or hex-Ring) has a particular arrangement of the 5 (or 6) faces surrounding a pentagon (or a hexagon). These may be grouped as follows: the Left has Rings with head-to-tail DADs, all excluded; the Middle has permitted Rings with no adjacent pentagons, thus IPR; the Right has permitted Rings with adjacent pentagons, thus non-IPR. (B) A DAD like a green one in hex-Ring 611 or in hex-Ring 631 produces rotation of edge a (external to the central face) from edge c (also external to the central face) about the green central edge (b), more so for a Ring with head-to-tail DADs (e.g., 631). This “external rotation” of edge a from edge c is equal to the (dihedral) angle between the two shaded planes in the surround face. (C) Sighting down edge b in B shows clearly this external rotation and the resultant nonplanarity of a surrounding face that would contain edges a and c.

Because we follow An Atlas of Fullerenes (2) in numbering isomers (e.g., isomer 1784 with 60 vertices), the highest numbered isomers have the most dispersed pentagons. With 1812 isomers for $n = 60$, isomer 1784 is close to having the most dispersed isomers, but 60–1812—the soccer ball—wins that distinction.

Results

First, we review why the head-to-tail exclusion rule permits any fullerene cage that is IPR. Then we prove that the largest permitted cage with adjacent pentagons is 60–1784, thus showing that the head-to-tail rule permits only as well as all IPR cages for all $n > 60$, not just for $60 < n \leq 84$.

All IPR Cages Are Permitted. By definition, an “isolated” pentagon has no adjacent pentagons. Fig. 2 A Middle groups together all of the Rings that have no adjacent pentagons, that is, “IPR Rings.” There is just one IPR pent-Ring (501), but there are 5 IPR hex-Rings (601, 611, 622, 623, and 633). Therefore, IPR cages can contain only the 501 type of pent-Ring, a pentagon surrounded by 5 hexagons, and these 5 types of hex-Ring. None of
these Rings have head-to-tail DADs; therefore, none of these IPR Rings are excluded by the head-to-tail exclusion rule; therefore, all IPR fullerenes are permitted (16).

60–1784 Is the Largest Permitted Cage with Adjacent Pentagons. Permitted non-IPR Rings. Fig. 2A Right groups together all of the permitted pent-Rings with adjacent pentagons (511, 522, 532, 541, and 551) and all of the permitted hex-Rings with adjacent pentagons (642, 643, 651, and 661). Of particular note, each of the central hexagons in the latter non-IPR hex-Rings “anneals” surrounding pentagons on one side of the Ring to pentagons on the other side, thus limiting dispersal of pentagons. For example, among its surrounding faces, hex-Ring 642 has 2 pentagons on one side and 2 pentagons on the other side. Without the second set of pentagons, the hexagon would have been hex-Ring 621 (Fig. 2A Left), which has head-to-tail DADs and would be excluded.

Pentagon doublets. We showed that among fullerenes with \(20 \leq n \leq 60\) vertices, the head-to-tail exclusion rule permits only these 15 isomers with adjacent pentagons and the IPR soccer ball (data not shown). The isomers are represented by Schlegel diagrams produced by the Carbon Generator (CaGe) program (available at www.mathematik.uni-bielefeld.de/~CaGe) (36). For any given \(n\) (e.g., 50 vertices), isomers are specified by number—the highest numbered one (e.g., the 271st isomer, thus 50–271) having the most dispersed pentagons (2)—and also by symmetry point group (e.g., \(D_{3h}\)). Hex-Rings are numbered as in Fig. 2A. Strings and rings of pentagons are outlined by thick edges.

![Image of fullerenes and rings](image.png)

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Pentagon clusters. Extended clusters of pentagons are found in very small \((n \leq 32)\) permitted cages, but there are no independent clusters (e.g., 3 pentagons) in any of the permitted cages (Fig. 3). Moreover, in larger cages, independent clusters would be surrounded by hexagons, and the pentagons at the interface would be an excluded type of ring are labeled. Caps (containing 6 pentagons) are taken from all of the permitted cages with adjacent pentagons shown in Fig. 3. One such carbon cage, \(60-1784\), which has no adjacent pentagons, but only a subset of 12 pentagons and thus obey the IPR.

**Nanotubes with Non-IPR Caps.** Proof that the largest fullerene with adjacent pentagons permitted by the head-to-tail exclusion rule is \(60–1784\) also means that the caps on nanotubes must be IPR. The most likely challenge to this claim would come from the caps extracted from the permitted small fullerenes in Fig. 3, a cap being defined as a region with 6 pentagons. However, we need only to add a single additional ring of hexagons—the very beginning of the tube portion of the nanotube—at the circumference of each cap to demonstrate excluded rings (Fig. 4B).

Moreover, two exceptions prove the rule: The cap from cage \(50-271\) is IPR; it is also the pentagon-centered half of the IPR soccer ball and IPR nanotubes with caps composed of half of a Buckminsterfullerene cage. The cap from cage \(60-1784\) is IPR as well; it is also the hexagon-centered half of the one IPR cage with 72 vertices and corresponding nanotubes. Thus, only nanotube caps that obey the IPR are permitted by the head-to-tail exclusion rule.

**Discussion**

By exhaustive examination of the 216,739 large cages with \(60 < n \leq 84\) vertices, we had shown that the geometric constraint embodied by the head-to-tail exclusion rule permitted only the 50 IPR fullerenes for this range of \(n\) (16). Here, we have shown why and proven that for all even \(n > 60\), the head-to-tail exclusion rule permits only and all IPR cages. Therefore, we suggest that the head-to-tail exclusion rule could (and does) explain the isolated pentagon rule (IPR). In addition, the head-to-tail exclusion rule—but not the isolated-pentagon rule—permits self-assembly of the small group of small fullerene cages with adjacent pentagons shown in Fig. 3. One such carbon cage, \(C_{36}-15\), has already been isolated and identified (13, 14), and some assembly conditions have favored unspecified carbon cages with \(32, 44\) and \(50\) carbon atoms (21, 22), numbers of vertices represented among the small permitted cages in Fig. 3.

The IPR itself does not allow cages with \(< 60\) vertices, cages that necessarily have adjacent pentagons, whereas the originators of the IPR (3–5) pointed out that 2 isomers with 50 carbons (50–270 and 50–271) were special in having no adjacent-pentagon configurations larger than a doublet. This line of thinking was formalized by the suggestion that for every even \(n\) without IPR cages, that is, in the ranges \(20 \leq n \leq 58\) and \(62 \leq n \leq 68\), favored isomers could be identified as those with fewest pentagon neighbors (2). Likewise, it would be possible to identify lowest-energy isomers for any \(n\), perhaps by measuring curvature energy (23), and likely produce the same list of fewest-pentagon-neighbor isomers.

By contrast, the head-to-tail exclusion rule permits isomers with adjacent pentagons, but only a subset of \(n\), the ones shown in Fig. 3. It permits no isomers with \(30, 34, 46,\) and \(48\) vertices, and of particular note, no isomers with \(52–58\) and \(62–68\) vertices.
Indeed, we have proposed that the abundance of C₆₀ could be due to these large gaps on both sides of n = 60, gaps that leave no nearby smaller or larger cages into which assembly could settle (16). (Similarly, the abundance of the IPR C₉₀, second only to C₆₀, may be related to the gap from 62 to 68.) Thus, the head-to-tail exclusion rule explains not only the IPR but also why Buckminsterfullerene is the most abundant of the IPR carbon fullerences.

Prior models for IPR fullerene production, including the Pentagon Road (24, 25), the Hexagon Road (26), and fusion of large carbon cycles (27–29), invoke cage growth and internal reorganization to eliminate pentagon adjacencies (30). Together, these processes are supposed to come into play when a stable structure like Buckminsterfullerene or larger IPR cage is reached (31). Based on the head-to-tail exclusion rule, we proposed the “Probable Road”: Carbon atoms would more probably complete Rings with planar faces or Rings with modest nonplanarity than the excluded Rings with head-to-tail DADS, the severely nonplanar ones (16). We have now shown that the only large fullerences that could self-assemble, those with none of the excluded Rings, would be the IPR ones.

We suppose that 4 mechanisms could contribute to the operation of the Probable Road. As suggested by Fig. 2C, 2 carbon atoms would be unlikely to bridge the gap between the ends of edge e and edge a in an excluded hex-Ring, and 1 carbon atom would be unlikely to bridge the gap between such disparate ends in an excluded pent-Ring. Such a kinetic barrier could operate during growth (i) and reorganization (ii). In addition, higher order (resonant and double) bonds, which enforce planarity, tend to point away from pentagons (32–35) and thus locate along edges with a DAD (e.g., edge b in Fig. 2B). The severe rotation out of planarity of edges e from a about edge b in Fig. 2B would thus incur a high energy cost. Such a thermodynamic barrier could also operate during both growth (iii) and reorganization (iv).