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Combinatorial Construction of Fullerene Structures

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Combinatorial fullerene structures (buckyballs for short) have been introduced as a result of the recent discovery of fullerene molecules in laboratories. The stable forms of these materials appear to depend on the method of production as well as on energetic considerations. To understand the stable forms, one would have to examine the confirmed structures among the theoretical structures. As an alternate route to computerized enumeration (which appears to be expensive and not totally safe), we present a procedure that is geometrically transparent. *Under certain conditions*, our procedure is economical and complete. For example, in the case of buckyballs C_v with $v \leq 84$ satisfying the isolated pentagon rule, our procedure can be carried out by hand. To distinguish the inequivalent structures, we present a procedure that does not involve costly spectral computation. In particular, we show that C_{60} and C_{70} are uniquely characterized as the IPR C_v for the two smallest permissible values of v. Some of our results can be used to study qualitative selection rules as well as the structure of hexagonal cylinders.

1. Basic Definitions.

Definition 1.1. A (topological) buckyball is a convex, closed polyhedral surface in Euclidian 3-space that satisfies the following conditions:

(BB1) Three edges meet at each of the v vertices.

(BB2) Each of the f faces is either a convex pentagon or a convex hexagon so that 2 such faces may have at most one common edge.

Two such buckyballs are *topologically* (or *combinatorially) equivalent* if there is a homeomorphism between the surfaces so that vertices, edges and faces are preserved. The equivalence class is, in fact, completely determined by the combinatorial equivalence defined on the vertices and edges. Chirality reversing homeomorphisms are permitted.

Definition 1.2. A buckydisk is a polygonal disk in 3-space that can be flattened into a planar disk (not necessarily convex) so as to satisfy the following conditions:

(BD1) Each of the v_{in} interior vertices is the end point of 3 edges. On the boundary, each of c_2 vertices is the end point of two edges on the boundary and each of the remaining c_3 vertices is the end point of 2 edges on the boundary and 1 edge from the interior.

(BD2) Each of the polygonal faces is either a convex pentagon or a convex hexagon.

Definition 1.3. A hexagonal cylinder is a polygonal surface in 3-space that can be flattened into a plane so that it is an annulus satisfying the following conditions:

(HC1) Same as (BD1) (but there are two boundary components).

(HC2) Each of the faces is a convex hexagon.

Definition 1.1 is based on the classical experimental results of chemists and physicists, see Ref. 1 for discussions. However, in a recent private communication from M. Dresselhaus, see Ref. 2., it appears that this definition may be too restrictive when dealing with »buckytubes«. Definitions 1.2 and 1.3 are based on a naive mathematical view of the production process for fullerenes. Namely, we consider the shattering of stacked graphite sheets. The results are assumed to be small units in the form of disks (hemispheres), rings (annuli) and carbon atoms. Two such disks together with some rings and carbon atoms can then be assembled to make up buckyballs, as well as buckytubes and hexagonal cylinders. Such a hypothetical viewpoint would surely depend on the laboratory environment. For example, buckytubes are »grown« at a negative electrode.

2. *Cyclic Boundary Valence Code (CBVC) and Euler's Theorem.*

By flattening a buckydisk into a plane, it can be given the usual orientation of the plane. Each combinatorial equivalence class may, therefore, support at most two distinct oriented structures. To the vertices on the boundary, we assign the integer 0 (for out) or 1 (for in) which is 2 less than the valence. The CBVC assigned to the disk is the cyclic sequence of 0's and 1's starting anywhere on the boundary in the counterclockwise direction. For example, $(0,1)^m$ is called a *sawtooth* cycle and $(0,0,1,1)^n$ is called a *square-wave* cycle. In general, a given CBVC may or may not occur as the boundary of a buckydisk. Similarly, a given buckydisk may or may not be completed to a buckyball. A reversal of orientation corresponds to the inversion of the CBVC. If an oriented buckyball is divided into two oriented buckydisks, then the two CBVC's are related by inversion plus complementation (namely, exchange 0 and 1 in the code).

The following result is well known. The first part follows easily from the definition together with Euler's Theorem ($v - e + f = 2$ holds for a spherical 2-complex). The last is due to Grünbaum and Motzkin, see Grübaum [Ref. 3; Theorem 13.4.1, p. 271]. Namely, the existence was based on the construction of buckydisks with CBVC $(0,1)^6$ and $h = 1, 2, 3$ and 4. The exclusion of $f_6 = 1$ can be deduced easily from Theorem 2.2 below.

Theorem 2.1. Let C_v be a buckyball with v vertices. Let e denote the number of edges and let f_m denote the number of m-gon faces, $m = 5$ or 6. Then,

$$\text{(a) } v = 20 + 2f_6; \quad \text{(b) } e = 30 + 3f_6; \quad \text{(c) } f_5 = 12.$$

The number f_6 of hexagons can be any non-negative integer other than 1.

An easy extension of the first part yields the following result.

Theorem 2.2 Let a buckydisk have c_m boundary vertices with valence m (= 2 or 3). Suppose it has h hexagons, p pentagons and v_{in} vertices in its interior. Then,

$$\text{(a) } c_2 = p + 2h - v_{in} + 4; \quad \text{(b) } c_3 = 2p + 2h - v_{in} - 2.$$

In particular, $c_2 - c_3 = 6 - p$.

For a prescribed CBVC, Theorem 2.2 does not impose any a priori restriction on h and v_{in}. For a buckydisk to be part of a buckyball, it is clearly necessary (but not always sufficient) that $|c_2 - c_3| \leq 6$. The following result is not difficult.

Theorem 2.3. (Finiteness Criterion). For a prescribed CBVC with $c_2 - c_3\rangle$ 0, there are at most a finite number of topologically distinct buckydisks (possibly none). The bound can be expressed in terms of c_2 and c_3.

Sketch of the proof. We proceed by induction on $c_2 + c_3$ and begin from the boundary by drawing short inward pointing edges from the c_3 boundary vertices with code 1. Some of these edges may coincide (to form a 1-bridge) or have a common interior vertex (to form a 2-bridge). We then assign 5- or 6-gons in all possible ways between successive inward pointing edges. There are at most a finite number of possibilities. It is important to note that each 1- and 2-bridge divides the given CBVC into two. To smooth out the argument, we also consider 0-bridges that arise from the identification of 2 boundary vertices (one must have code 1 while the other may have code 0 or 1). In organizing the proof, when an i-bridge is formed, i = 0, 1, and 2, we immediately consider the resulting two CBVC separately by induction. When there is no i-bridge, i = 0, 1 or 2, we treat the remaining case by first considering the case where the assignment leads to a new CBVC and show that $c_2 + c_3$ decreased. The possibility of a 3-bridge or 4-bridge is then subsumed by the inductive treatment of 0-bridges. One may extract a crude bound on the number of possibilities in terms of c_2 and c_3. The main point is that the assigned 5- and 6-gons may reach across in the form of pontoon bridges. We omit further details. This result motivates the following definition.

Definition 2.4. Let H be a buckydisk with CBVC having $c_2 = c_3$. H is called *minimal* if there is at least one pentagon along the boundary.

Evidently, for any prescribed CBVC with $c_2 = c_3$, there are at most a finite number of topologically distinct minimal buckydisks. For small c_2 and c_3, we can perform classification of the minimal buckydisks by hand. The imposition of IPR will, of course, speed up the process by a large factor. In general, by paying attention to 0-, 1- and 2-bridges, the task can be accomplished by using a super-computer.

3. IPR Buckydisks with CBVC $(0,1)^m$ and $(0,0,1,1)^n$ and Magic Numbers.

Based on the qualitative idea of minimizing »steric strain«, chemists, see Ref. 1, have proposed the following selection rule for fullerenes:

(IPR) *Isolated Pentagon Rule*: No two pentagon faces are adjacent. (IPR) is confirmed by the long-lived fullerene molecules C_v, v = 60, 70, 76 and 78. In fact, the first observed cases correspond to v = 60 and 70. For small v, (IPR) cuts down the number of possible buckyball structures by a large factor. The following table (from computer enumeration) is taken from Ref. 4. and Ref. 5.

60	70	72	74	76	78	80	82	84	86	88	90
1	1	1	1	2	5	7	9	24	19	35	45

Our procedure will in fact produce at least these numbers for $v \leq 84$ (see Tables I through IV). In contrast, the total number of C_{60} buckyball structures has been reported to be 1760 in Ref. 4., 1790 in Ref. 5. and revised upward to 1812 by both algorithms, see the comment and reply (listed at the end of Ref. 5. about these algorithms.

TABLES

In the following tables, the name of the fullerenes structures is denoted in the form of $G{-}C_v$. G denotes the symmetry group of the graph. We follow the point group notation in Ref. 12. Apostrophes on group G in the case of $v = 78$ follows the convention in Refs. 6 and 7. In Tables II through IV, superscripts of the form (t) or ⟨t⟩ signify the number of isolated sites in the pyrene subcomplex. Additional letters appear as superscripts in Table IV to signify certain distinguishing features in the pyrene subcomplex. These are not standard. The additional column in Table IV sets up the distinction between the present Table and Table in Ref. 12. The type column describes the construction of the fullerene structures in terms of buckydisks and hexagonal cylinders. The notation is of the form $(h_1,h_2;k)_m$ or $\langle h_1,h_2;k\rangle_n$. In the first case, there are two buckydisks with h_i hexagons each and CBVC $(0,0,1,1)^m$ joined by k hexagonal necklaces each with m hexagons so that $f_6 = h_1 + h_2 + km$. In the second case, the buckydisks have CBVC $(0,1)^n$ and they are joined by k hexagonal band bracelets with n hexagons each, so that $f_6 = h_1 + h_2 + kn$. A rotation angle is appended to indicate the different ways of attaching the disks to each other. This angle is measured in terms of our graph and has no quantitative physical significance. Column $H(C_v)$ gives the structure of the pyrene subcomplex in terms of the shape of the connected components and their multiplicities (as exponents). The remarks column provides an alternate type description as well as chirality and stability in experimental work.

TABLE I

IPR—C_{60} to C_{78}

Name	Type (rot. angle)	$H(C_v)$	Remarks
$I_h{-}C_{60}$	$(5,5;2)_5$	empty	$\langle 10,10;0\rangle_9$, stable
$D_{5h}{-}C_{70}$	$(5,5;3)_5$	$(\vert)^5$	$\langle 11_2,14;0\rangle_{10}$, stable
$D_{6d}{-}C_{72}$	$(7,7;2)_6$	$(\text{hex})^2$	not observed
$D_{3h}{-}C_{74}$	$\langle 13,14;0\rangle_{10}$	$(\cdot)^2(\vert)^6$	$\langle 11_2,16;0\rangle_{10}$, absent
$D_2{-}C_{76}$	$\langle 14,14;0\rangle_{10}(3\pi/20)$	$(\vert)^2(\text{S})^2$	chiral, stable
$T_d{-}C_{76}$	$\langle 14,14;0\rangle_{10}$ $(5\pi/20)$	$(\cdot)^4(\vert)^6$	$(14_2,14_2;0)_6$, absent
$D_3{-}C_{78}$	$\langle 10,10;1\rangle_9(2\pi/9)$	$(\text{S})^3$	chiral, minor Ref. 6, Ref. 7.
$D_{3h}{-}C_{78}$	$(7,10_v;2)_6$	$(\text{hex})^3$	$\langle 10,10;1\rangle_9(0)$, absent
$C_{2v}{-}C_{78}$	$(7,10_h;2)_6$	$(\vert)^2(\text{U})^2(\text{hex})$	major Ref. 6, minor Ref. 7
$C'_{2v}{-}C_{78}$	$(10_v,13_2;1)_6$	$(\cdot)^2(\vert)^4(\text{U})^2$	$(14_1,15_t;0)_6$, $\langle 13,16;0\rangle_{10}$, absent Ref. 6, major Ref. 7
$D'_{3h}{-}C_{78}$	$(10_h,13_2;1)_6$	$(\cdot)^6(\vert)^6$	$(14_2,15_t;0)_6$, absent

TABLE II

IPR—C_{80} (none observed)

Name	Type (rot. angle)	H(C_v)	Remarks
D_{5d}–C_{80}	$(5,5;4)_5$	$(0,0,1,1)^5$	$(12_1,12_1;1)_6(\pi)$
D_{5h}–C_{80}	$\langle 10,10;1\rangle_{10}(0)$	$(\cdot)^{10}(\vert)^5$	$(10_h,14_2;1)_6$
I_h–C_{80}	$\langle 10,10;1\rangle_{10}(\pi)$	$(\cdot)^{20}$	$(12_3,12_3;1)_6$
D_3–C_{80}	$\langle 14,16;0\rangle_{10}(3\pi/20)$	$(\vert)^3$(7–pinwheel)^2	
D_{2h}–$C_{80}^{(2)}$	$\langle 14,16;0\rangle_{10}(5\pi/20)$	$(\cdot)^2(\vert)^1(U)^4$	$(10_v,14_1;1)_6$, $(14_2,16_1;0)_6$
D_{2h}–$C_{80}^{(6)}$	$(10_h,14_1;1)_6$	$(\cdot)^6(\vert)^3(U)^2$	$(10_v,14_1;1)_6$, $(14_2,16_1;0)_6$, $(15_t,15_t;0)_6$
D_2–C_{80}	$(12_1,12_1;1)_6(2\pi/3)$	(10-sq-wave)^2	

TABLE III

IPR—C_{82} (observed in Ref. 7)

Name	Type (rot. angle)	H(C_v)	Remarks
$C_s-C_{82}^{\langle 6\rangle}$	$\langle 10,11_1;1\rangle_{10}(0)$	$(\cdot)^6(\vert)^2(U)^3$	$(10_h,15_t;1)_6$, $(12_3,13_{1t;}1)_6$
$C_{3v}-C_{82}^{\langle 10\rangle}$	$\langle 10,11_1;1\rangle_{10}(\pi)$	$(\cdot)^{10}(U)^3$	$(12_3,13_3;1)_6$, $(12_3,13_{1v;}1)_6$
$C_{2v}-C_{82}^{\langle 8\rangle}$	$\langle 10,11_2;1\rangle_{10}$	$(\cdot)^8(\vert)^3(U)^2$	$(12_3,13_{1h};1)_6$
C_2-C_{82}	$\langle 11_1,20;0\rangle_{10}$	$(U)^2$(14-sq-wave)^1	$(12_1,13_{1v};1)_6$, $(12_1,13_{1t;}1)_6(\pi/6)$
C_s-C_{82}	$\langle 11_2,20;0\rangle_{10}$	$(\vert)^2$(hex)^1(12-sq-wave)^1	$(7,12_1;1)_6$, $(12_1,13_{1h};1)_6$
$C_{3v}-C_{82}^{(4)}$	$(7,12_3;2)_6$	$(\cdot)^4(U)^3$(hex)^1	$(10_v,15_t;1)_6$
$C_s-C_{82}^{(2)}$	$(12_1,13_2;1)_6$	$(\cdot)^2(\vert)^2(U)^2$(8-sq-wave)^1	$(15_t,16_2;0)_6$
$C_2-C_{82}^{b}$	$(12_1,13_{1t};1)_6(\pi/2)$	$(\vert)^2(U)^2$(10-sq-wave)^1	
$C_2-C_{82}^{(4)}$	$(15_t,16_1;0)_6$	$(\cdot)^4(\vert)^2(U)^2(S)^1$	

TABLE IV

IPR—C_{84} (observed in Ref. 7, FM # as in Ref. 12)

FM #	Name	Type (rot. angle)	H(C_v)	Remarks
#18	$C_{2v}-C_{84}$	$\langle 11_1,11_1;1\rangle_{10}(0)$	$(\vert)^2(U)^2$(hex)^2	$(7,13_{1h;}2)_6$, $(10_h10_v;2)(\pi/2)$, $(13_3,13_{1t};1)_6$
#13	$C_2-C_{84}^{\langle 4\rangle}$	$\langle 11_1,11_1;1\rangle_{10}(\pi/5)$	$(\cdot)^4(U)^2(S)^2$	
#11	$C_2-C_{84}^{b}$	$\langle 11_1,11_1;1\rangle_{10}(2\pi/5)$	$(\vert)^1(U)^4(S)^1$	$(13_{1v},13_{1t};1)_6(2\pi/3)$, $(13_{1t},13_{1t};1)_6(\pi/3)$
#17	$C_{2v}-C_{84}^{\langle 2\rangle}$	$\langle 11_1,11_1;1\rangle_{10}(3\pi/5)$	$(\cdot)^2(U)^4$(hex)^1	$(7,13_2;2)_6$, $(13_3,13_{1v};1)_6$
#9	$C_2-C_{84}^{\langle 2\rangle}$	$\langle 11_1,11_1;1\rangle_{10}(4\pi/5)$	$(\cdot)^2(U)^4(S)^1$	
#19	$D_{3d}-C_{84}$	$\langle 11_1,11_1;1\rangle_{10}(\pi)$	$(U)^6$	$(13_{1v},13_{1v};1)_6$, $(13_{1t},13_{1t};1)(\pi)$
#10	$C_s-C_{84}^{\langle 4\rangle}$	$\langle 11_1,11_2;1\rangle_{10}(0)$	$(\cdot)^4(\vert)^2(U)(S)^{\pm}$	

Table IV (continued)

FM #	Name	Type (rot. angle)	$H(C_v)$	Remarks
#16	C_s–C_{84}	$\langle 11_1,11_2;1\rangle_{10}(\pi/5)$	$(\vert)^3(U)^3(\text{hex})^1$	$(7,13_{1t};2)_6$, $(13_3,13_{1h};1)_6$,
				$(13_{1v},13_{1h};1)_6$, $(13_{1h},13_{1t};1)_6(2\pi/3)$
#12	C_1–$C_{84}^{\langle 2\rangle}$	$\langle 11_1 11_2;1\rangle_{10}(2\pi/5)$	$(\cdot)^2(\vert)^2(U)^3(S)^1$	$(13_2,13_1t;1)_6$
#24	C_{6h}–C_{84}	$\langle 11_2,11_2;1\rangle_{10}(0)$	$(\vert)^6(\text{hex})^2$	$(7,7;3)_6$ $(13_{1h},13_{1h};1)_6$
#21	D_2–$C_{84}^{\langle 4\rangle}$	$\langle 11_2,11_2;1\rangle_{10}(\pi/5)$	$(\cdot)^4(\vert)^4(S)^2$	
#22	D_2–C_{84}^{cb}	$\langle 11_2,11_2;1\rangle_{10}(2\pi/5)$	$(\vert)^4(U)^4$	$(13_{1t},13_{1t};1)(\pi/6)$, chiral baseball
#5	D_2–C_{84}	$\langle 16,16;0\rangle_{10}(3\pi/20)$	$(\vert)^4(\text{open hex glass})^2$	$(10_h,10_h;2)_6(\pi/6)$
#4	D_{2d}–C_{84}	$\langle 16,16;0\rangle_{10}(5\pi/20)$	$(S)^{\pm 2}$	$(14_1,18;0)_6$ $(16_2,16_2;0)_6$
#20	T_d–C_{84}	$(7,13_3;2)_6$	$(\text{hex})^4$	$(10_v,10_v;2)_6(\pi/2)$
#14	C_s–C_{84}^{s}	$(7,13_{1v};2)_6$	$(\vert)^1(U)(S)^{\pm}(\text{hex})^1$	$(13_{1h},13_{1t};1)_6(\pi)$
#23	D_{2d}–C_{84}^{bb}	$(10_h,10_h;2)_6(\pi/2)$	$(\vert)^4(U)^4$	$(13_{1h},13_{1t};1)_6$ baseball
#2	C_2–C_{84}^{bg}	$(10_h,10_v;2)_6(\pi/6)$	$(\vert)^2(1/2\ \text{open hex glass})^2$	broken glass frames
#1	D_2–C_{84}	$(10_v,10_v;2)_6(\pi/6)$	$(\text{hex glass})^2$	glass frames
#3	C_s–$C_{84}^{(2),sw}$	$(12_1,14_1;1)_6(0)$	$(\cdot)^2(\vert)^1(S)^{\pm}(\text{8-sq-wave})^1$	$(14_2,18;0)_6$, $(16_2,16_1;0)_6$,
#6	C_{2v}–C_{84}	$(12_1,14_1;1)_6(\pi)$	$(U)^2(\text{8-sq-wave})^{\pm}$	hour glass
#7	C_{2v}–$C_{84}^{(4)}$	$(12_1,14_2;1)_6$	$(\cdot)^4(\vert)^2(\text{8-sq-wave})^{\pm}$	$(13_2,13_{1v};1)_6$, track
#15	C_s–$C_{84}^{(2),u}$	$(13_{1v},13_{1t};1)_6(0)$	$(\cdot)^2(\vert)^3(U)^1(S)^{\pm}$	$(13_2,13_{1h};1)_6$, bottle
#8	C_2–$C_{84}^{(2)}$	$(16_2,16_1;0)_6$	$(\cdot)^2(\vert)^2(S)^3$	

We now explain the terminology and notation in the following results.

A *hexagonal band bracelet* is obtained by attaching m hexagons in a cyclic manner so that j-th hexagon is attached to the (j-1)-th and (j+1)-th along opposite edges, j mod m. (See Figure 3.1). This leads to two CBVC of the form $(0,1)^m$. It is evident that k such band bracelets can be used in conjunction with two buckydisks with CBVC $(0,1)^m$ to form a buckyball. If both buckydisks satisfy IPR, then we will automatically have an IPR buckyball when $k > 0$. In some cases, we can get a few IPR buckyballs even when $k = 0$. The notation $\langle h_1, h_2; k\rangle_m$ denotes the type of buckyball that is obtained by joining two minimal buckydisks with CBVC $(0,1)^m$ and k hexagonal band bracelets. h_1 and h_2 denote the number of hexagons in the two buckydisks so that the total number f_6 of hexagons is $h_1 + h_2 + km$. There are only a finite number of topologically distinct buckyballs of each type. A given buckyball may belong to several different types.

Similarly, a *hexagonal necklace* is obtained by taking n hexagons so that the j-th is joined to the (j-1)-th and (j+1)-th along two opposite vertices by means of edges, j mod n. (See Figure 3.2). The result is a degenerate cylinder with two CBVC of the form $(0,0,1,1)^n$. We can clearly use k of these hexagonal necklaces in conjunction with two minimal buckydisks with CBVC $(0,0,1,1)^n$ to form a buckyball. If the minimal buckydisks satisfy IPR, then the resulting buckyball will satisfy IPR whenever $k > 1$. In special cases, we could have IPR buckyballs for $k = 0$ or 1. The resulting buckyball will be of the type denoted by $(h_1,h_2;k)_n$. As before, h_1, and h_2 denote the number of hexagons in each of the two minimal buckydisks. The total number f_6 of hexagons will then be $h_1 + h_2 + kn$.

Since $v = 20 + 2f_6$, the above examples create buckyballs with v belonging to suitable arithmetic progressions of the form: $2v_0 + 2\ell k$, $k \geq 0$, where $\ell = m$ or n and $v_0 = 10 + h_1 + h_2$. Such sequences have been called »magic numbers«, see Ref. 6.

Theorem 3.1. Consider minimal IPR buckydisks with CBVC $(0,1)^m$. Then $m \geq 9$ is the only restriction. All such IPR buckydisks can be embedded in IPR buckyballs (and used to cap off suitable hexagonal cylinders). When $m = 9$, there is a unique one (and $h = 10$). When $m = 10$, there are 7 with $h = 10$, 11_1, 11_2, 13, 14, 16, 20 (see Figure 3.3).

Theorem 3.2. Let C_v be an IPR buckyball containing a minimal buckydisk with CBVC $(0,1)^m$, $m = 9$ or 10.

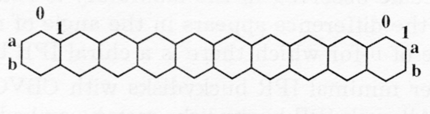

Figure 3.1. Hexagonal Band Bracelet. (Edges ab are identified.)

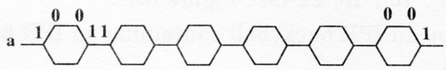

Figure 3.2. Hexagonal Necklace. (Edges a are identified.)

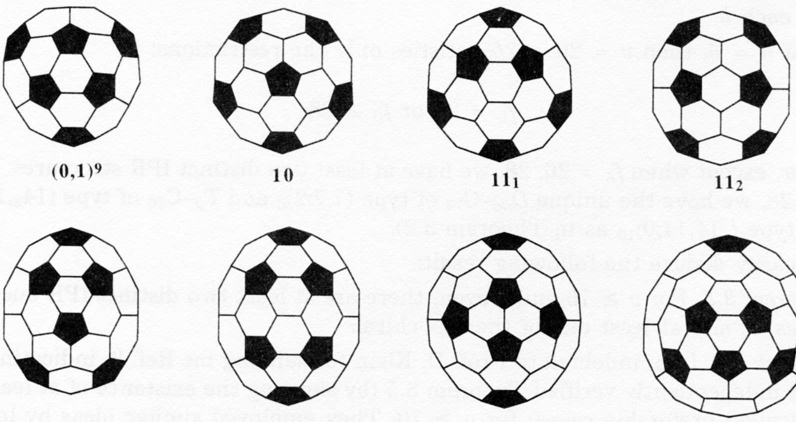

Figure 3.3. IPR Buckydisks with CBVC $(0, 1)^m$, $m = 9$, 10.

(a) If $m = 9$, then C_v must be made up of two such buckydisks which are joined together by k hexagonal band bracelets, $k \geq 0$. It is denoted by $\langle 10,10;k \rangle_9$, $k \geq 0$. $v = 60 + 18k$. If $k = 0$, we have the unique I_h–C_{60}. For $k > 0$, the symmetry group is D_{3d} or D_3 (k odd) and D_{3h} or D_3 (k even). Thus, there are two distinct structures for $k > 0$ (one chiral, the other not).

(b) If $m = 10$, then $v = 20 + 2f_6$ satisfies only the restrictions:

$$f_6 \geq 25, \qquad f_6 \neq 26.$$

Moreover, except when $f_6 = 25, 27$ ($v = 70, 74$), there are at least 2 distinct IPR buckyballs. When $f_6 = 25, 27$, we have the unique D_{5h}–C_{70} (of type $\langle 11_2,14;0 \rangle_{10}$ or $(5,5;3)_5$), and D_{3h}–C_{74} (of type $\langle 13,14;0 \rangle_{10}$). When $f_6 = 28$, we have T_d–C_{76} and D_2–C_{76} both of the type $\langle 14,14;0 \rangle_{10}$, (see Table I).

Remark. The case of $f_6 = 28$ in the preceding Theorem is especially interesting. There are actually three ways of gluing the two buckydisks to make up an IPR buckyball and the stable molecule observed in the laboratory is chiral, see Refs. 7 and 8. In terms of our pictures, the difference appears in the angle of rotation before gluing. This is the smallest value of v for which there is a chiral IPR buckyball.

Theorem 3.3. Consider minimal IPR buckydisks with CBVC $(0,0,1,1)^n$. Then $n \geq 5$ is the only restriction. All such IPR buckydisks may be embedded in IPR buckyballs (and used to cap off suitable hexagonal cylinders). When $n = 5$, there is a unique one (and $h = 5$). When $n = 6$, there are: $h = 7$, 10_h, 10_v, 12_1, 12_3, 13_3, 13_2, 13_{1v} 13_{1h}, 13_{1t}, 14_1, 14_2, 15_w, 15_t, 16_2, 16_1, 18, 22 (see Figure 3.4).

Theorem 3.4. Let C_v be an IPR buckyball containing an IPR buckydisk with CBVC $(0,0,1,1)^n$, $n = 5, 6$. Then,

(a) If $n = 5$, then, in order to satisfy IPR, C_v must contain two such buckydisks which are joined together by $k + 2$ hexagonal necklaces, $k \geq 0$. It is denoted by $(5,5;k+2)_5$. $v = 60 + 10k$. When $k = 0$, we have the unique I_h–C_{60}. For $k > 0$, the symmetry group is D_{5h} or D_{5d} (for k odd or even, respectively) and there is just one structure for each k.

(b) If $n = 6$, then $v = 20 + 2f_6$ satisfies only the restrictions:

$$f_6 = 26 \text{ or } f_6 \geq 28.$$

Moreover, except when $f_6 = 26, 28$, we have at least two distinct IPR structures. When $f_6 = 26, 28$, we have the unique D_{6d}–C_{72} of type $(7,7;2)_6$ and T_d–C_{76} of type $(14_2,14_2;0)_6$ (also of type $\langle 14,14;0 \rangle_{10}$ as in Theorem 3.2).

We easily deduce the following result:

Theorem 3.5. For $v \geq 76$ and v even, there are at least two distinct IPR buckyball structures C_v and at least one of them is chiral.

Remark 3.6. I am indebted to Prof. D. Klein for sending me Ref. 9, indicating that they had independently verified Theorem 3.5 (by showing the existence of at least one IPR C_v (called preferable cages) for $v \geq 70$. They employed similar ideas by looking at a selected (incomplete) list of minimal IPR buckydisks (called buckybowls), with CBVC $(0,0,1,1)^6$. In the present work, Theorem 3.5 is a by-product of Theorems 3.1 through 3.4 where a complete classification of IPR buckydisks with 4 different CBVC is obtained by hand.

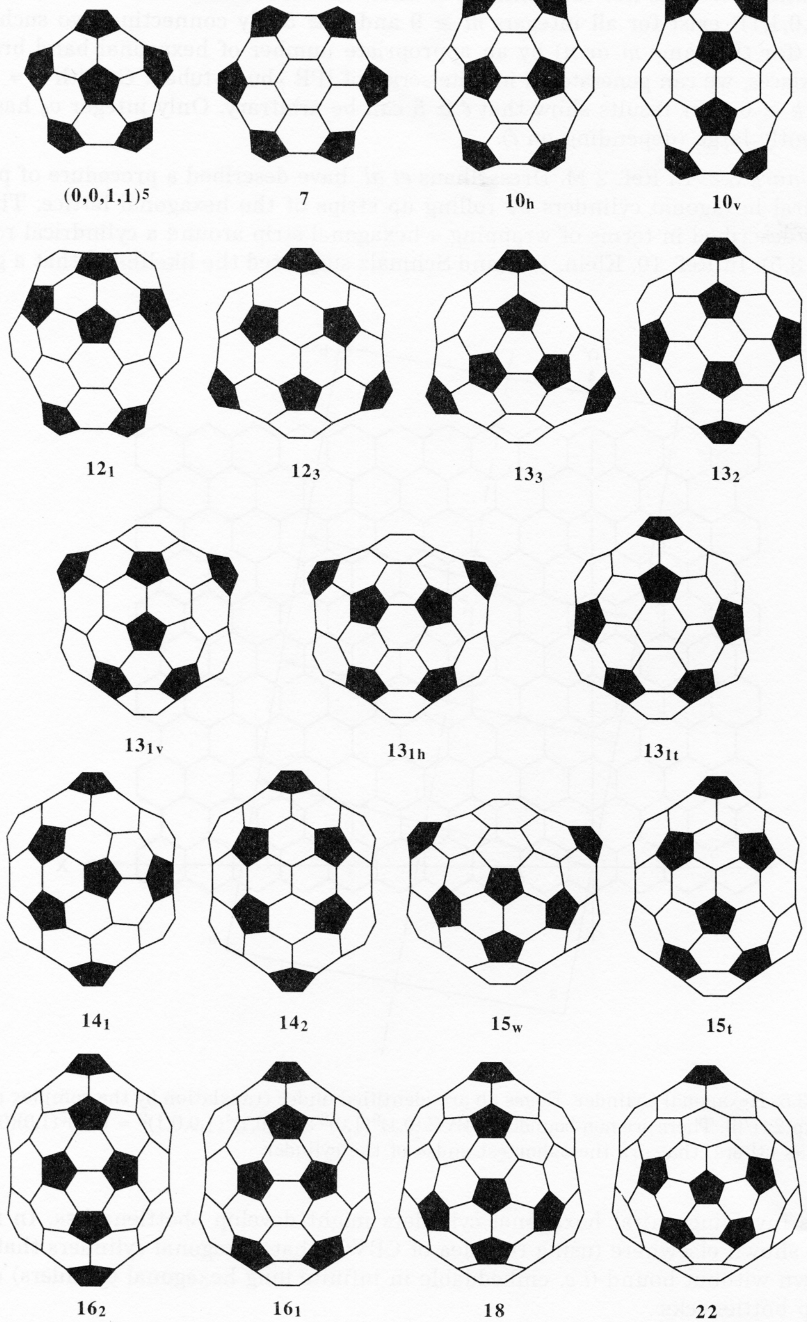

Figure 3.4. IPR Buckydisks with CBVC $(0, 0, 1, 1)^n$, $n = 5, 6$.

Remark 3.7. It is not very difficult to show that IPR buckydisks with CBVC $(0,1)^m$ and $(0,0,1,1)^n$ exist for all integers $m \geq 9$ and $n \geq 5$. By connecting two such buckydisks (for the same m or n) by an appropriate number of hexagonal band bracelets or necklaces, we can generate an infinite series of IPR »buckytubes« C_v with $v = 2v_0 + 2\ell k$, $k \geq 0$. Our results show that $\ell \geq 5$ can be arbitrary. Only integer v_0 has to be sufficiently large (depending on ℓ).

Remark 3.8. In Ref. 2 M. Dresselhaus *et al.* have described a procedure of producing chiral hexagonal cylinders by rolling up strips of the hexagonal lattice. This can also be described in terms of wrapping a hexagonal strip around a cylindrical rod (see Figure 3.5). In Ref. 10, Klein, Liu, and Schmalz suggested the likelihood that a growth

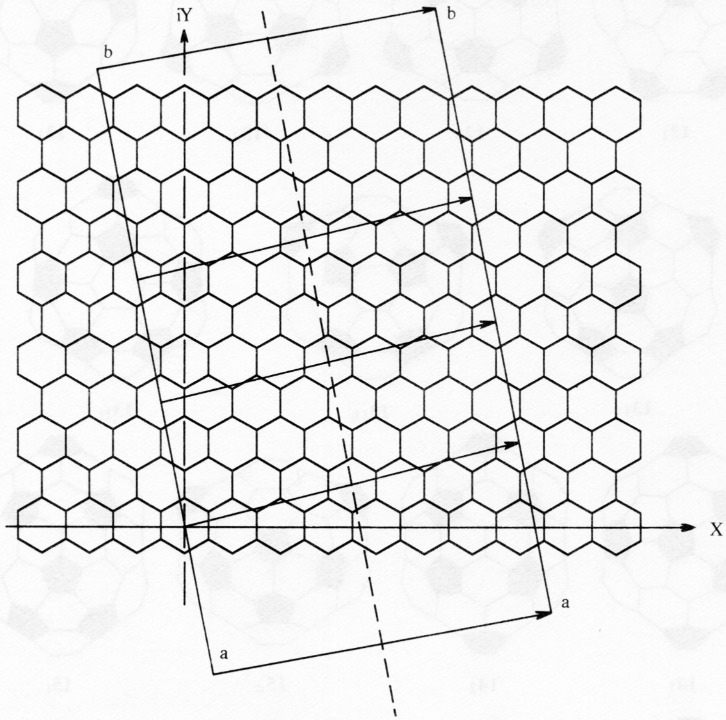

Figure 3.5. Hexagonal Cylinder. Edges ab are identified under translation by the complex number $6 + 2.\exp(2\pi i/6)$. There are non-bounding CBVC $(0,1)^6(1,0)^2$ and $(0,1)^4(1,0,0,1)^2 = (0,1)^5(1,0)(0,1)(1,0)$, as well as others, that are the »shortest ends« of the cylinder.

process involving chiral hexagonal cylinders might develop »bottlenecks«. In fact, it will be shown elsewhere (using the idea of CBVC) that hexagonal cylinders that could be grown without bound (*i.e.* embeddable in infinite long hexagonal cylinders) cannot develop bottlenecks.

In a private discussion, Prof. M. Dresselhaus described a flaring-out mechanism involving pentagon-septagon pairs so that one could have »bottlenecks«, see also Ref. 10.

4. Pyrene Subcomplex in IPR Buckyball.

Throughout this section, we consider only IPR-buckyballs C_v. The main goal is to describe a procedure that will distinguish non-equivalent structures in an efficient manner when v is not too large. For example, in comparison with the computer generated list for $v \leq 84$, we have the curious result that our construction procedure (which is, a priori, only complete under the assumption of the existence of suitable buckydisks) manages to generate all such IPR buckyballs. We make no effort to produce a rigorous proof. In Table IV, we present the distinction between our list and the list generated by computers in Ref. 12.

We begin by noting that the vertices of any IPR C_v are of two types. A vertex common to 1 pentagon and 2 hexagons is called a *corannulene* site. There are 60 such sites. A vertex common to 3 hexagons is called a *pyrene* site. There are $v - 60$ such sites. We define the *pyrene subcomplex* $H(C_v)$ by retaining all the faces, edges and vertices spanned by these $v - 60$ pyrene sites. Clearly, equivalent buckyballs will have equivalent pyrene subcomplexes (the reverse is not true, see Table IV, D_2–$C_{84}{}^{cb}$ and D_{2d}–$C_{84}{}^{bb}$). Each hexagonal face of an IPR C_v can be classified into 4 types according to the number of its pentagon neighbors. Evidently, each hexagon must have an even number of pyrene vertices. These must either occupy consecutive sites or appear at exactly one pair of opposite sites. By looking at $H(C_v)$, it is therefore trivial to see that there is no IPR buckyball C_{62}. With a little more work, it is not difficult to prove:

Theorem 4.1. Let C_v be an IPR buckyball. Then $v \geq 60$. If $v > 60$, then $v \ \geq 70$. For $v = 60$, 70, 72 and 74, there is just one IPR buckyball structure.

Remark. Theorem 4.1 was proved independently by Klein and Liu in Ref. 8 apparently, as a by-product in constructing their computer algorithm.

Sketch of the proof. Let f_{6j} denote the number of hexagons with j adjacent pentagons. Under IPR, we must have $0 \leq j \leq 3$. When $j = 2$, we can subdivide the case in two and define $f'_{6,2}$ and $f''_{6,2}$ according to whether the two pyrene vertices are opposite or adjacent. By counting the hexagons adjacent to pentagons in two different ways, we have the equation:

$$60 = 3f_{6,3} + 2f_{6,2} + f_{6,1}$$

Using $f_6 = f_{6,3} + f_{6,2} + f_{6,1} + f_{6,0}$, we obtain the equation:

$$3f_6 - 60 = f_{6,2} + 2f_{6,1} + 3f_{6,0} \geq 0.$$

With additional work and some case analysis (involving the IPR buckydisks surrounding appropriate pentagons and hexagons), the proof can be completed.

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SAŽETAK

Kombinatorna konstrukcija fullerenskih struktura

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Kombinatorne strukture fullerena (skraćeno – buckylopte) javljaju se kao posljedica nedavnog otkrića fullerena u laboratoriju. Raspodjela stabilnih formi, osim o energijskim svojstvima, izgleda zavisi i o postupku proizvodnje. Za razumijevanje stabilnih oblika, potvrđene strukture treba sagledati među ostalima teorijski mogućim strukturama. Kao alternativa računalskom prebrojavanju (koje se pokazuje skupim i ne sasvim sigurnim) ovdje je prikazan jednostavan geometrijski postupak. U određenim uvjetima ovaj postupak je ekonomičan i potpun. Npr. za buckylopte C_v, uz $v \leq 84$, koje zadovoljavaju uvjet odvojenih pentagona, ovaj postupak se može provesti ručno. Razlikovanje neekvivalentnih struktura ostvareno je bez skupog proračuna spektra. U radu je naročito pokazano da su C_{60} i C_{70} jedinstveno karaterizirani kao C_v molekule s odvojenim pentagonima za dvije najmanje moguće vrijednosti v. Neki rezultati korisni su za proučavanje kvalitativnih izbornih pravila i strukture heksagonskih cilindara.