Formalized Drawing of Fullerene Nets. 1. Algorithm and Exhaustive Generation of Isomeric Structures

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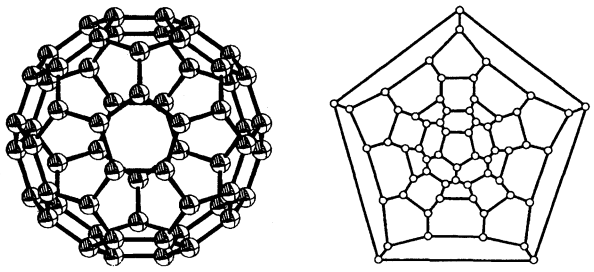
A simple formalism for unfolding the fullerene structure onto a planar lattice is proposed. We recommend using deltahedra containing twelve penta-coordinated vertices as the geometrical precursors of fullerenes, and unfolding them onto a planar lattice according to Dürer's style. This old style has several unique features that allow a priori drawing of diagrams that fold to fullerenes. Combined with the known algorithm for generating approximate atomic coordinates from the connectivity, which can be readily read off from the net diagram, the present method provides an alternative way of exhaustive generation of isomeric fullerene structures.

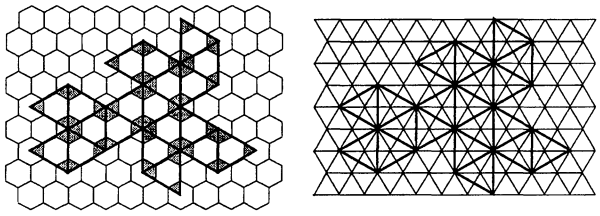
As the impact of fullerene research gains ever greater momentum and spreads over many areas of science and technology,[1—5] the needed for a good representation of the three-dimensional structure of fullerene is becoming acute. Fullerenes have such unusual structural features like the strongly curved and closed network of sp^2-carbon atoms, the hollow inside, and the non-uniform distribution of pentagonal rings that conventional drawing methods are often inadequate. Thus, in the perspective drawing like **1a**, one-half of the structure is hidden behind the front side and even in the front side the periphery is greatly distorted. The Schlegel diagram like **1b** provides a bird's-eye view of the whole structure, but the geometry is badly deformed (Chart 1).

It is desirable to seek other drawing methods to supplement the conventional ones. In this regard, the net diagram[6] method (Fig. 1) offers an attractive alternative, but has so far received only moderate attention.[7—11] This long-practiced art[12] of unfolding three-dimensional polyhedral objects into planar polygons has several advantages when applied to fullerenes: Symmetry and geometrical interrelations among isomers can be clearly displayed, and environment of each carbon atom visualized.



1a **1b**

Chart 1.



(a) (b)

Fig. 1. Unformalized net diagrams of C_{60} (**1**) onto (a) hexagonal and (b) equilateral triangular lattices.

The modest popularity of the net method for representing fullerene structures may have arisen at least partly from chemists' unfamiliarity with this method.[13] In our opinion, however, the main reason for the modestry is the lack of systematization in the net drawing. For any solid, there are a number of ways to unfold it onto a planar lattice. Therefore, for example, it would be hard to extract common structural features among isometric fullerenes by comparing arbitrarily unfolded diagrams. We find that introducing a simple formalism greatly simplifies both drawing process and interpretation.

This paper gives brief accounts on the properties of net diagrams of fullerenes and the new rules that we have devised for systematic drawing. These rules lead

to a new algorithm for producing all possible isomers of fullerenes C_n with any given n.[14]

Background

For simplicity, we treat only those fullerenes which have a closed network of five- and six-membered rings of sp^2-hybridized carbon atoms.[15] Let us take buckminsterfullerene **1** as the first example, which geometrically corresponds to truncated icosahedron. It is more convenient to unfold the untruncated master solid, in this case regular icosahedron, than to open out **1** itself. The net diagram as shown in Fig. 1 (thick lines) can be obtained by cutting open a paper model of large icosahedron (Fig. 2) along the edges through the twelve vertices to give one planar piece.[16] The resulting polygon nicely fits a hexagonal lattice (Fig. 1a), as first shown by Fujita and coworkers.[7] Small shaded triangles at every corner of the polygon shows those parts that are to be truncated to give **1**. In other words, all the corners in this unfolded diagram are the sites of five-membered ring.

For the systematic development of the net method, however, the equilateral triangular lattice (Fig. 1b), first suggested by Caspar,[8] is better suited than the honeycomb lattice. These two typical 'wall paper' lattices are readily convertible into each other by face-dual operation: connecting the centers of hexagons in honeycomb lattice gives the lattice points of triangular lattice and vice versa.[17] Cutting out the net diagram of Fig. 1b from the lattice paper, folding edge-to-edge, connecting the centers of subtriangles (namely taking face-dual) and truncating vertices give back **1** as shown in Fig. 2.[18] The center of each hexagonal ring of Fig. 2 is the meeting place of six subtriangles (hexa-coordinated vertex V_6), while in the center of each pentagonal ring five subtriangles meet (V_5).

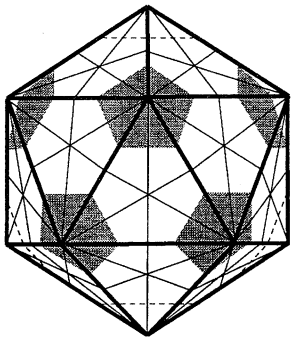


Fig. 2. Final stages of constructing truncated icosahedron back from a triangular-faceted polygon given in Fig. 1b. Thin lines=net of subtriangles, thick lines=20 faces of icosahedron, shade and dotted lines=sites of truncation. Back side is omitted for clarity.

How can we unfold other fullerenes? The facetted triangle (thick lines) appearing in Figs. 1b and 2 is one of the triangular patches (B, Fig. 3) used by Fowler[19] and others[8,20] for the modeling of Goldberg polyhedra[21] to study higher fullerenes having icosahedral symmetry. A vector connecting the lower left corner of a patch to a corner on the right, $(\vec{a}, \vec{b})$, where the vector components are displacements along the two edges of subtriangle as indicated in Fig. 3, gives the area of patch or the number of triangular facets, T, according to a relation a^2+ab+b^2. A Goldberg polyhedron obtained by constructing an icosahedron from twenty patches of the same kind has $20T$ subtriangels, 12 V_5s, and $10(T-1)$ V_6s. Such polyhedra are also called deltahedra (solids whose faces are covered with regular triangles),[8] and it can be readily understood that these solids can be likewise unfolded as illustrated in Fig. 1.

The net diagram of a deltahedron as shown in Fig. 1 always has 22 corners. This number can be derived from the general form of Euler's theorem,

$$v - e + f = K, \tag{1}$$

where v stands for the number of vertices, e for edges and f for faces. K is equal to 1 for planes, 2 for solids and 0 for tori. For a polygon like the one given in Fig. 1, v is the number of corners, and $K=1$. When 20 triangular patches ($e=3\times20$) are combined into one piece, 19 of the edges are shared, and hence ($e=41$, and $v=22$. As a consequence, a net diagram of any Goldberg polyhedron or deltahedron with 12 V_5s is invariably a docosagon.

Formalized Net of the Fullerene Structure

1. Dürer's Design. When we began our work, we soon realized it advantageous to fix the way of unfolding deltahedra to that shown in Fig. 4a. The master

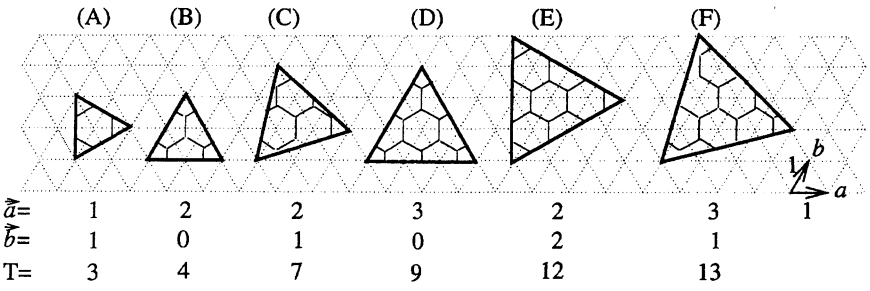


Fig. 3. Seven smallest triangular-faceted patches used in the construction of Goldberg polyhedra.[21] These patches are used to construct low-symmetric deltahedra.

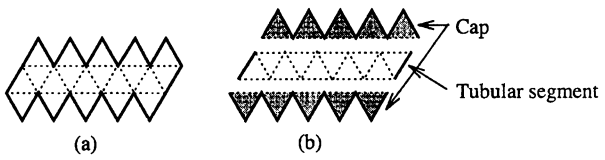
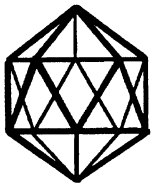


Fig. 4. (a) Net diagram of icosahedron **2** as first done by Dürer (bold line) along a five-fold axis. (b) There are three sections: top and bottom rows of five triangles and a parallelogram in the middle containing ten triangles.



2
Chart 2.

solid in this case is icosahedron **2** made from twenty unit triangles patches (A, Fig. 3). This small solid also is a geometrical precursor of C_{20} fullerene,[22] which can be obtained by taking face-dual. The stylized design of Fig. 4a had been drawn by Albrecht Dürer, a German painter in the sixteenth century noted for geometrical objects, in his classical textbook of surveying.[23] When Dürer obtained this diagram, he must have held an icosahedron before him with the two farthest vertices at the top and bottom (see Chart 2. the drawing of **2**), cut along the ten slant edges extending from these vertices, and finally severed an edge in the middle. The resulting diagram consists of two caps[24] in top and bottom, each containing six V_5s, and a tubular segment in the middle (Fig. 4b). Advantages of using Dürer's design will soon become clear.[25]

Three net drawings of **1** according to Dürer's design are shown in Fig. 5 (thick lines). A few general characteristics in the net diagrams are mentioned here. First, all the corners (site of pentagons) are equidistant, $\sqrt{3}$ in the unit of base vector, from the nearest corners.[26] If the distance between any pair of corners is equal to 1 as in Fig. 4, then its face-dual gives two pentagonal rings fused to form a partial structure of 'pentalene' (**3**) (Chart 3). Hence a statement that 'all the corner-to-corner distances must be greater than 1 on an equilateral triangular lattice' is the necessary condition

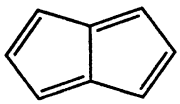


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Chart 3.

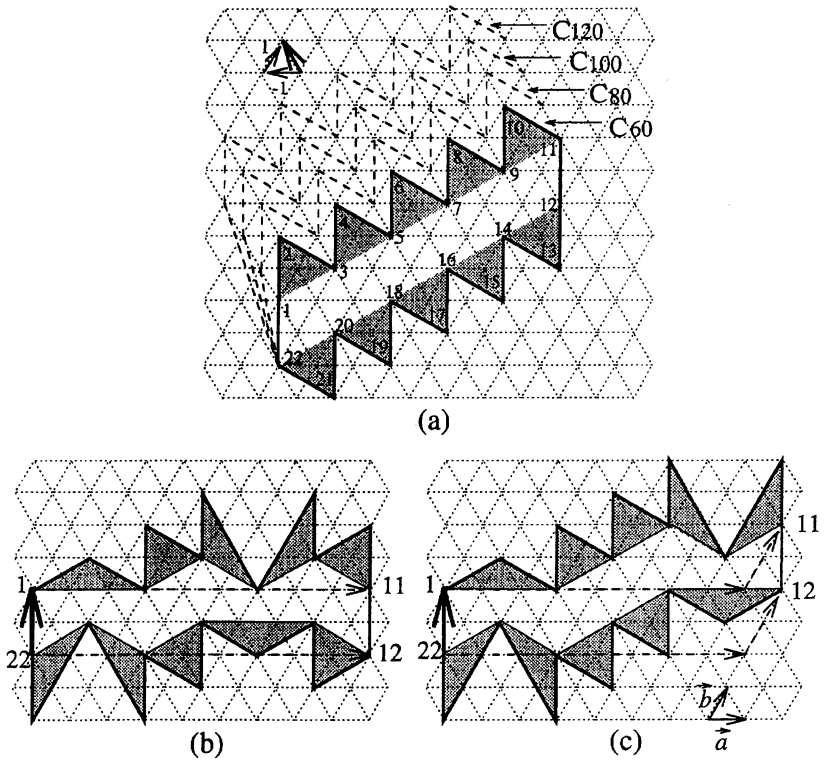

Fig. 5. (a) Net diagram of **1** according to Dürer's style. Dotted lines show a series of C_{60+20n} (n=0, 1, 2$\cdots$) fullerenes. (b,c) Two additional net diagrams of **1** in Dürer's design, opened along C_3 (b) and C_2 (c) rotation axes, respectively. Tubule vector $\vec{w}$ is shown by a broken arrow: (b) (9, 0), (c) (8, 2). Height vector $\vec{h}$ is shown by a solid arrow.

for the isolated pentagon rule (IPR) to hold.

As mentioned above, net diagrams of 12-V_5 deltahedra always produce docosagons. We temporarily make it a rule to number the corners starting from the left end of the upper cap and continue clockwise as shown in Fig. 5a. Corner 1 is taken as the origin (0,0) of the triangular coordinates, and other 21 corners are designated by displacement vectors (m,n) from the origin, for example $(-1,2)$ for corner 2, (1,1) for corner 3, etc. Such a set of vectors, or triangular coordinates, is the simplest possible numerical representation of a structure of fullerene.[27] The displacement vector of corner 11 (5,5) in the example of Fig. 5a, corresponds to the circumference of a tubular segment, or the width of cap, and it is specially designated as a *tubule vector*.[28] We will come back to this vector in the next section.

In the net diagrams of **1** of Figs. 5b and 5c, the cap-triangles are not necessarily regular and the tubular segments are no longer parallelogram. These diagrams are prepared by first dividing the 12 V_5s into two groups each containing six of them, in these cases along appropriate rotational axis, and following the method mentioned above with **2**. As a matter of fact, finding the rotational axis is not a necessary condition to divide V_5s into two groups, but the only requirement is that the two caps do not overlap on the diagram. Dürer's procedure is generally applicable to any fullerene (12-V_5 deltahedron), even to those having no symmetry element.

We wish to achieve the reverse of the unfolding process. In other words, we like to draw the net first and fold it to a fullerene, so that we can design fullerene structures on paper. For this purpose, we must figure out the conditions for a docosagon in Dürer's design to close to a solid deltahedron. Let us analyze the conditions separately, first for the tubular segment and then for the caps.

2. Tubule and Height Vectors. The condition for the closure of a tubular segment can be readily worked out: Both sides of the segment must be parallel and of equal length. A more convenient way to characterize this condition is to state that a pair of vectors connecting corners, 1→11 and 22→12 (Figs. 5b and 5c) must be equal for the closure to take place. These are the tubule vectors defined above and are denoted hereinafter by $\boldsymbol{w}(i,j)$, wherein i and j are the vector components. In this paper we consider only those diagrams in which $i \geq j \geq 0$, in order to avoid duplications due to chirality. For this reason, in all the net diagrams depicted in this paper following Dürer's design, tubule vectors point either to the right, or into the upper right quadrant.

The tubule vector is also a measure of increments in the number of subtriangular facets (or the number of carbon atoms) that would accompany the translation of cap (see Fig. 5a). Every translation along the direction of the $\vec{a}$-axis by one unit increases or decreases the number of atoms by $2j$ and each translation in the $\vec{b}$ direction by $2i$. Translation in the $(-1, 1)$ direction as shown in Fig. 5a increases the number of atoms by $2(i+j)$. In this case $(i=j=5)$, successive unit translations give rise to a series of D_{5d} fullerenes C_{60+20n} $(n=0,1,2\cdots)$,[29] which Saito called 'armchair fibres'.[30] It is quite obvious that our formalism is suited for unfolding simple nanotubes.[31,32] Similarly, a unit move of the net shown in Fig. 5b would involve $2(9+0)=18$ atoms and succession of such moves produces a series of fullerenes $D_{3d/h}$-C_{60+18n} $(n=0,1,2\cdots)$ called 'zigzag fibers'.[30]

Another convenient index in a net diagram is the height vector $\vec{h}$ which connects corner 22 with 1 (thick arrow in Figs. 5b and 5c) and corresponds to the height of cylindrical portion of a fullerene (vide infra).

3. Property of Cap. What are the conditions for a cap to close to a cone? In the first place it is necessary that two nearer edges between adjacent cap-triangles (thick lines) must be of equal length (Fig. 6). Furthermore, the angle made by these edges must be equal to 60° according to Descartes' theorem.[33] These considerations lead to an interesting fact that the area between adjacent cap-triangles (lightly shaded) is a *regular triangle*. Because this rule applies to any pair of neighboring cap-triangles, it leads to a useful property that *the complementary structure of a cap is a row of five regular triangles*. The edge lengths of these reverse triangles may be varied, but must be greater than $\sqrt{3}$ if the IPR is to be observed.

The novel property of the cap structure mentioned above makes it possible to produce a 'closable' cap from a row of regular triangles that fit the equilateral triangular lattice. Such triangles are the Goldberg patches, the smaller members of which have already been given in Fig. 3. The general procedure for preparing a Dürer cap is as follows:

1. Align five regular triangles, selected from Goldberg patches in random order and allowing duplication, on a triangular lattice in succession through one-point contacts. The lightly shaded area of Fig. 6 is an example of such row.

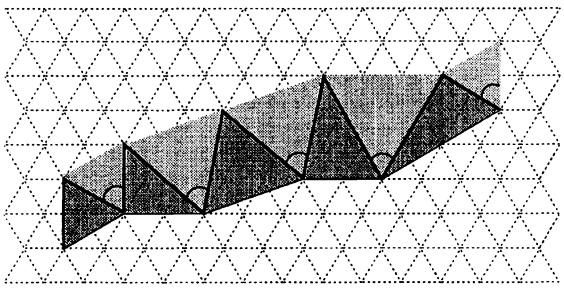

Fig. 6. A cap structure with low symmetry. While cap-triangles (shaded) vary in shape and size, the space to be removed (painted) between two adjacent cap triangles is always a *regular triangle*.

2. Move the far-right edge to the far-left. Then a cap has been already completed as the complementary row (dark shaded). Figure 6 corresponds to this stage.

3. Check if the tubular vector of the cap satisfies the condition that $i \geq j \geq 0$ (when duplication by chirality is to avoided). Otherwise rotate the cap to fill the condition.

4. Represent the cap structure by a set of 11 pairs of displacement vectors relative to the lower left corner, or better, by a set of five vectors connecting the five 'tips' of cap-triangles.

4. Construction of the Net Diagram and Generation of Atomic Coordinates Therefrom. Having clarified conditions for closure, we first exercised the drawing of several familiar fullerenes on the net. The results reveal a few new properties of nets. Take C_{70} as an example. The structure of C_{70} (a) has been interpreted typically as C_{60} (**1**) cut into two halves at the five-fold rotational axis, one half of the ball rotated by 36°, five C_2 fragments inserted and the two halves rejoined.[34] In accordance with this interpretation, its net diagram has been derived from that of C_{60} depicted in Fig. 5a by shifting the upper cap along $\vec{a}$ axis by -1 (Fig. 7a). Thus, the translation of a cap on the diagram is equivalent to the rotation of half of the molecule and the insertion (or removal) of carbon atoms in the tubular segment.

As a matter of fact, the parallel shift of cap, in any direction over any distance, is a useful means of generating an infinite number of analogous nets. Figure 8 illustrates how to reproduce as many fullerene nets (but smaller than C_{100}) as possible from one cap structure using the height vector $\vec{h}$ as the variable guide. One can naturally use any pair of two caps as long as they have identical tubular vector. High capability of a cap in generating diverse fullerene structures is a strong advantage of the present formalism and will be utilized below for the exhaustive generation of fullerene isomers.

Once a net diagram of a fullerene structure is drawn, it contains information on the atomic connectivities, which allow us to derive Hückel molecular orbitals of the fullerene. According to Manolopoulos and Fowler,[35] eigenvectors of the three, low-energy HMO's having only one nodal plane may be approximated to Cartesian coordinates of carbon atoms. The so-called topological Cartesian coordinates thus obtained usually give too small interatomic distances. Hence we scaled them with an empirical factor, f_s, derived from the computed relation between diameters of icosahedral fullerenes and the number of atoms (n):[20]

$$f_s = 2.2(\sqrt{n} + 3.218)/4.889. \quad (2)$$

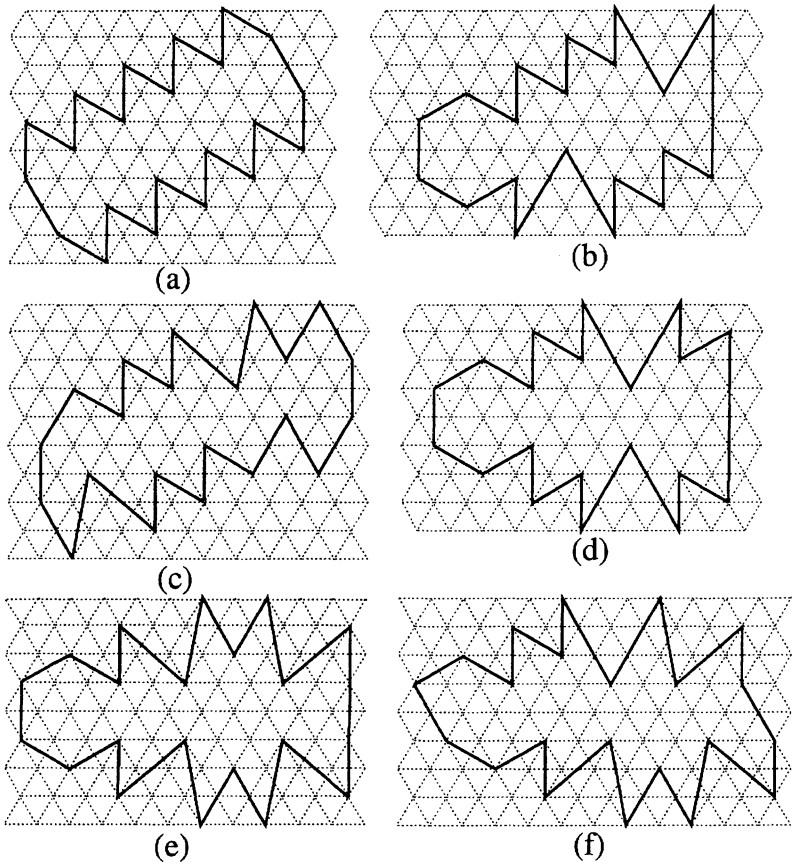

Fig. 7. Examples of net diagrams of several known fullerenes. (a) D_{5h}–C_{70}, (b) D_{6d}–C_{72}, (c) T_d–C_{76}, (d) D_{3h}–C_{78}, (e) D_{6h}–C_{84}, (f) C_1–C_{84}.

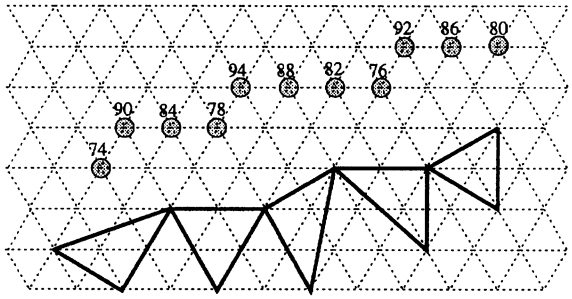

Fig. 8. When the lower cap shown is rotated by 180° and translated upwards so that its left-end (corner 1) is placed on one of the small circles (●, the end point of height vector $\vec{h}$) to make an upper cap, and two parallel lines are drawn to connect the both sides of caps to define the tubular segment, a net diagram of C_n fullerene (n given at the right shoulder of the small circle) is obtained. Only those giving n smaller than 100 are shown.

This factor works well for spherical to nearly spherical fullerenes, but less well for oblong fullerenes.[36]

A program FULLER[37] was written which outputs the scaled atomic coordinates of a fullerene from the input of a net diagram, namely a set of 22 triangular coordinates. The atomic coordinates of a fullerene thus obtained may be used as the input for more sophisticated calculations.

Exhaustive Generation of Isomeric Structures of C_{20} to C_{100}—A Test

The capabilities of systematically generating cap structures and of producing an infinite number of analogous fullerenes from a pair of caps having identical tubule vector can be applied advantageously to the exhaustive generation of isomeric fullerenes. We checked this possibility. For this test, a standard is already available: The list of all possible of C_{20} to C_{60} fullerenes and all IPR isomers of C_{60} to C_{100} fullerenes prepared by Manolopoulos and Fowler using spiral algorithm.[11,35,38]

We first performed trial-and-error experiments to determine how many patches are necessary to achieve complete reproduction of all the known IPR isomers for C_{60} to C_{100}. A small program CAP[37] was written to prepare the IPR cap structures from the Goldberg patches B to G (Fig. 3). Table 1 gives the number of unique caps constructed by using three to six Goldberg patches.

For every pair of matched caps, net diagrams of fullerenes smaller than C_{100} are generated by changing $\vec{h}$ vectors and those conforming to IPR rule are supplied to the program FULLER. This process produces numerous duplications, therefore three criteria are used here to distinguish and remove duplicates: HMO eigenvalues for HOMO and LUMO, as well as the total HMO energy.[39]

As shown in Table 2, when 3980 cap structures generated from the six Goldberg patches are used, the isomer counts agree perfectly with those of Manolopoulos and Fowler. It is evident from Table 2 that the efficiency of isomer generation increases sharply when the number of patches is increased from 3 to 4. The poor performance when only 3 patches are used (109 caps) is probably due to insufficient number of narrow caps, those having small i component in tubule vector and are believed to be important for efficient production of new isomeric structures.[40]

Table 1. Number of Unique Cap Structures Obtained by Using Three to Six Subtriangulated Triangular Patches of Fig. 3 in Random Order and Allowing Duplication

Goldberg patches used	Number of cap structures generated
B, C, D	109
B, C, D, E	603
B, C, D, E, F	2251
B, C, D, E, F, G	3980

Table 2. Dependence of Isomer Counts for the C_{60} to C_{100} IPR Fullerenes on the Number of Caps Used

	No. of caps used[a]					No. of caps used			
n	109	603	2251	3980	n	109	603	2251	3980
60	1	1	1	1	84	18	24	24	24
70	1	1	1	1	86	16	19	19	19
72	0	1	1	1	88	26	35	35	35
74	1	1	1	1	90	26	46	46	46
76	2	2	2	2	92	62	85	86	86
78	3	5	5	5	94	73	134	134	134
80	7	7	7	7	96	86	185	187	187
82	6	9	9	9	98	109	251	258	259
					100	196	437	449	450
					Rate(%)[b]	50.0	98.0	99.8	100.0

a) See Table 1. b) Rate of reproducing the standard results obtained by ring spiral algorithm.[38]

Table 3. Number of Cap Structures (Including anti-IPR Types) Generated from Goldberg Patches A to E and Classified According to Tubular Vectors

Vector[a)]	N[b)]	Vector	N	Vector	N	Vector	N
5,0	2	4,4	40	10,1	104	11,2	7
6,0	22	9,0	232	9,2	145	10,3	17
5,1	8	8,1	226	8,3	168	9,4	32
4,2	2	7,2	118	7,4	173	8,5	44
3,3	1	6,3	143	6,5	155	7,6	48
7,0	92	5,4	106	12,0	8	11,3	1
6,1	51	10,0	161	11,1	25	10,4	4
5,2	25	9,1	205	10,2	51	9,5	8
4,3	13	8,2	218	9,3	79	8,6	12
8,0	193	7,3	201	8,4	102	7,7	14
7,1	145	6,4	172	7,5	109	10,5	1
6,2	95	5,5	138	6,6	99	9,6	1
5,3	58	11,0	58	12,1	2	8,7	2

a) Components of tubular vector $w(i,j)$. b) Number of unique caps.

Table 4. Number of Unique Isomers (I) of Small Fullerenes C_n (n=20—60) Generated by the Net-Based Method

n	I	n	I	n	I	n	I
20	1	32	6	42	45	52	437
24	1	34	6	44	89	54	580
26	1	36	15	46	116	56	924
28	2	38	17	48	199	58	1205
30	3	40	40	50	271	60	1812

For fullerenes smaller than C_{60}, no IPR isomer exists. Hence, the programs FULLER and CAP are modified for the enumeration of C_{20} to C_{60} isomers that contain abutting pentagons. Based on the experience given above, caps are generated by using five patches, A to E, to give a total of 4206 unique structures (Table 3). Table 4 shows the isomer counts, which agree with those of previous authors.[35,41] The count of C_{60} isomers (1812) is confirmed.

About 6800 C_n isomers (n=20—100) thus obtained have been subjected to geometry-optimization with MM3.[42] SCF π-MO cycles converge for 96.5% of these structures.[43] Complete analysis of energetics and other aspects of these calculations will be described elsewhere, but some of the results will be referred to in the succeeding paper.

The test mentioned above had two purposes: To validate the methodology and to confirm the generality of our formalized net drawing algorithm. While these goals have been achieved, we should note that our methodology cannot be applied to higher fullerenes C_n (n>100) as it is. This is because there is no efficient way to remove duplication[44] which is supposed to increase exponentially. Another problem is that the appropriate number of caps must be decided on empirical basis. For these reasons, our net diagram method is not necessarily the most versatile in the exhaustive generation of isomeric fullerene structures. Rather, the advantage of our method resides in its potential to address various chemical problems as will be mentioned in the succeeding paper.[45]

Conclusions

(1) The net drawing on an equilateral triangular lattice is well suited for representing the disposition of twelve pentagonal rings in fullerenes.

(2) A formalized net drawing algorithm based on Dürer's old net design of icosahedron turned out to be suitable to the net drawing of fullerenes. In the final algorithm, a deltahedron (master solid for a fullerene) is unfolded into a net consisting of two caps and a tubular segment.

(3) This algorithm has been successfully applied to the exhaustive generation of all possible isomers of smaller fullerenes, C_{20} to C_{100}.

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12) See for example: A. Dürer, "Underweysung der Messung," in "The Printed Sources of Western Art," ed by T. Besterman, Colleguim Graphicum, Portland, Oregon (1972), Vol. 4.

13) We realize that even the terminology for this old geometrical operation is uncertain. Fujita et al.[7] used a term 'projection', which in our opinion does not exactly fit the unfolding operation but basically means a light-projected shadow. The term projection is adopted by at least one author [J. S. Rutherford, *Inorg. Chem.*, **32**, 3579 (1993)]. Caspar never employed any term in his paper on this topic[8] but instead used verbs like 'unfold' and 'open-out'.

14) Preliminary communication: M. Yoshida and E. Ōsawa, in "Advanced Materials '93, I/B: Magnetic, Fullerene, Dielectric, Ferroelectric, Diamond and Related Materials," ed by S. Somiya, M. Doyama, M. Hasegawa, and S. Yamada, Elsevier Sci. Publ. B. V. (North Holland), Amsterdam (1994), pp. 1223—1226.

15) Whereas the original definition of fullerene is restricted to C_n carbon cages with any number of six-membered rings and twelve five-membered rings, modifications containing seven- and higher-membered rings have been suggested: M. Fujita, M. Yoshida, and E. Ōsawa, *Fullerene Sci. Technol.*, **3**, 93 (1995). Extension of the net diagram method to those containing seven-membered rings will be shortly described elsewhere.

16) For an alternative method, see: F. Chung and S. Sternberg, *Am. Sci.*, **81**, 56 (1993).

17) I. Grossman and W. Magnus, "Groups and Their Graphs," Mathematical Association of America, Washington, D.C. (1964).

18) Net diagrams drawn on the hexagonal lattice have an advantage of showing up six-membered rings of fullerenes directly. The second paper of this series contains several net drawings of fullerenes on honeycomb lattice.

19) P. W. Fowler, *Chem. Phys. Lett.*, **131**, 444 (1986).

20) M. Yoshida and E. Ōsawa, *Fullerene Sci. Technol.*, **1**, 55 (1993).

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22) K. Balasubramanian, *Chem. Phys. Lett.*, **202**, 399 (1993); H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, **214**, 353 (1993); Z. Slanina and L. Adamowicz, *J. Mol. Struct.*, **281**, 33 (1993); M. T. Bowers, P. R. Kemper, G. von Helden, and P. A. M. van Koppen, *Science*, **260**, 1446 (1993); G. von Helden, M. T. Hsu, N. G. Gotts, P. R. Kemper, and M. T. Bowers, *Chem. Phys. Lett.*, **204**, 15 (1993).

23) Plate No. 31 of Ref. 12, we are indebted to Professor K. Miyazaki for indicating this reference to us.

24) For a different usage of the term cap, see: D. M. P. Mingos, *Acc. Chem. Res.*, **17**, 311 (1984). We are indebted to Professor J. Aihara for indicating this literature to us.

25) In this seminal paper[8] on the deltahedral view of fullerene polymorphism, Caspar attempted to formalize the unfolding drawing of 12-V_5 deltahedra. While many features of his method are common to ours, there is an important and critical difference between Casper and us regarding the structure of cap. Casper's cap is made by cutting along the vectors between the nearest neighbor V_5s, whereas we chose one V_5 from a group of six V_5s and always cut from this central V_5 to the rest five V_5s.

26) This relation is most clearly seen in Fig. 5a. On the other hand, Figs. 5b and 5c contains adjacent corners separated by more than $\sqrt{3}$, but they are not the *nearest* ones.

27) Because a fullerene structure can be opened out in many ways, the relation between the set of vectors and the structure is redundant.

28) N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.*, **68**, 1579 (1992). Caspar named $\boldsymbol{w}(i, j)$ a circumference vector in Ref. 8.

29) This series has also been mentioned by Fowler and his group: P. W. Fowler, J. E. Cremona, and J. I. Steer, *Theor. Chim. Acta*, **73**, 1 (1988).

30) R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B*, **46**, 1804 (1992).

31) P. M. Ajayan and S. Iijima, *Nature*, **361**, 333 (1993).

32) E. G. Gal'pern, I. V. Stankevich, A. L. Chistyakov, and L. A. Chernozatonskii, *JETP Lett.*, **55**, 483 (1992).

33) Sum of cut-in angles in the net diagram of any polyhedral solid is 720°.

34) P. W. Fowler, R. C. Batten, and D. E. Manolopoulos, *J. Chem. Soc., Faraday Trans.*, **87**, 3103 (1991).

35) D. E. Manolopoulos and P. W. Fowler, *J. Chem. Phys.*, **96**, 7603 (1992).

36) A better scaling would be to calculate bond orders P_{mn} from HMO and estimate bond lengths R_{mn} therefrom by using the relationship between R_{mn} and P_{mn}.

37) M. Yoshida and E. Ōsawa, "FULLER, PYRA, and C2," JCPE Program No. P074, obtainable from the Japan Chemistry Program Exchange, Japan Association for International Information, Nakai Bldg., 6-25-4 Honkomagome, Bunkyo-ku, Tokyo 113 (Fax x-81-3-5978-3600).

38) a) B. L. Zhang, C. Z. Wang, K. M. Ho, C. H. Xu, and C. T. Chan, *J. Chem. Phys.*, **98**, 3095 (1993); b) T. G. Schmalz, D. J. Klein, and X. Liu, *Mat. Res. Soc. Symp. Proc.*, **270**, 129 (1992); c) D. Babić, D. J. Klein, and C. H. Sah, *Chem. Phys. Lett.*, **211**, 235 (1993).

39) These HMO-based criteria may not be completely safe because it is not known whether isospectral fullerenes exist. At least up to C_{100}, our criteria proved satisfactory. However, new criteria may have to be derived for higher fullerenes for which the HMO energies become hardly indistinguishable.

40) An attempt has been made to increase the efficiency by using patches in different orientations on the triangular lattice from those in Fig. 3. This test led to substantial increase in the number of unique caps (ca. 10000 when more than 6 patches were used), but the rate of production of unique fullerenes did not increase as much as expected. We maintain that the use of six caps (B—G) in the limited orientation is enough for generating IPR isomers up to C_{100}.

41) D. Babigč and N. Trinajstić, *Comput. Chem.*, **17**, 271

(1993).
42) N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, **111**, 8551 (1989).
43) Net diagrams and perspective drawings of the global minimum structures of C_{20}, C_{24}—C_{60} and C_{70}—C_{100} are available upon request to the correspondence author. Each drawing is accompanied by the HMO informations (eigenvalues of HOMO and LUMO, HOMO-LUMO energy gap and total energy, all in β unit) and a set of 22 triangular coordinates.
44) We have developed a graphical method to select those fullerenes having stable electronic configurations and tested this method to C_{101}—C_{120} fullerenes. The results will be reported shortly elsewhere.
45) M. Yoshida and E. Ōsawa, *Bull. Chem. Soc. Jpn.*, **68**, 2083 (1995).