Generation of Fullerenes by Circumscribing

Jerry Ray Dias

Department of Chemistry, University of Missouri, Kansas City, MO 64110-2499, USA

An algorithm for the generation of fullerenes with isolated pentagonal rings by successively circumscribing base excised internal structures with a combination of pentagonal and hexagonal rings is detailed. The presence of adjacent bay regions is a necesary and sufficient condition for precluding this circumscribing operation for a polypent/polyhex system.

Introduction

The only two previously known allotropic forms of carbon, diamond and graphite, require the presence of noncarbon end groups or dangling bonds in which the valencies of the terminal carbons are left unsatisfied. However, twelve pentagonal rings in a dodecahedron of carbon atoms (or in fullerene) leads to a geometrically closed polyhedron where the valence of every carbon is satisfied. Thus, any fullerene polyhedron with $n = N_c$ vertices has $r_5 = 12$ pentagonal rings, $r_6 = (n-20)/2$ hexagonal rings, and $q = 3n/2$ edges. Several large carbon polyhedral clusters (C_{60}, C_{70}, C_{76}, C_{78}, C_{82}, C_{84}, C_{90}, C_{94}, and C_{96}) have now been isolated and, at least partially, characterized [1]. Many more fullerenes beyond C_{96} are observed in the mass spectra of soot extract [2]. These fullerenes constitute a new class of polycyclic conjugated compounds, and the enumeration of all their possible structures is an important endeavor [3, 4] which has facilitated the deduction of the probable structures of several experimentally observed fullerene species. In this communication, the circumscribing algorithm, which has been the subject of several papers on the enumeration and generation of other polycyclic conjugated systems [5, 6], will be exploited in the generation of the more stable fullerenes.

The successive circumscribing of qualified conjugated hydrocarbons with hexagonal rings leads to constant-isomer series. Constant-isomer series are infinite polycyclic aromatic hydrocarbon sets of increasing formulas having equal numbers of isomers. Symmetry between the base excised internal structure (EIS) and its successors is preserved when one successively circumscribes with hexagonal rings to generate constant-isomer series. It will be shown that the successive circumscribing of qualified conjugated hydrocarbons with a combination of pentagonal and hexagonal rings terminates at fullerenes when the number of pentagonal rings reaches 12 or terminates at systems that can be capped to give fullerenes with 12 pentagonal rings [7]. Symmetry is not necessarily preserved between the EIS and its successor when circumscribing with a combination of pentagonal and hexagonal rings.

Basic Terminology

A polypent/polyhex system consists of interlocking pentagons and hexagons where the degree-2 vertices correspond to methine ($\geqslant C-H$) units and degree-3 vertices correspond to trivalent ($=C<$) carbon units. The number of degree-2 vertices, degree-3 vertices, edges, and rings are given by N_H, $N_c = n$, q, and r, respectively. Denote the circumscription of a polypent/polyhex (polyene) system by P $\rightarrow$ circum-P = P'. It has been previously shown [8] that $N_{pc} = N_H - 6 + r_5$, $q_p = N_H + N_{pc} = 2 N_H - 6 - r_5$, and $r = (1/2)(N_c - N_H) + 1$ where $N_c = N_{pc} + N_{Ic} + N_H$ and N_{pc} and N_{Ic} and q_p are the number of perimeter and internal degree-3 vertices and perimeter edges, respectively. For P $\rightarrow$ P', $N_c \rightarrow N'_{Ic}$ and $N_H \rightarrow N'_{pc}$. Thus, for circum-P, $N'_{pc} = N'_H - 6 + r'_5$ $= N_H$ giving $N'_H = N_H + 6 - r'_5$ and, similarly, $q'_p = N'_{pc} + N'_H$ and $N'_c = q'_p + N_c$ giving $N'_c = N_c + N'_{pc} + N'_H = N_c + 2 N_H + 6 - r'_5$. These recursive equations are useful for monitoring the progress of successive circumscription.
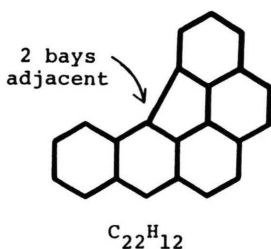
2 bays
adjacent

$C_{22}H_{12}$

Fig. 1. The only structure out of 19 fluoranthenoid isomers of $C_{22}H_{12}$ incapable of being circumscribed.

2 bays
adjacent

2 bays
adjacent

$C_{26}H_{14}$
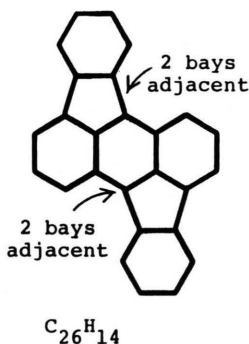
Fig. 2. The indacenoid, rubicene, can not be circumscribed.
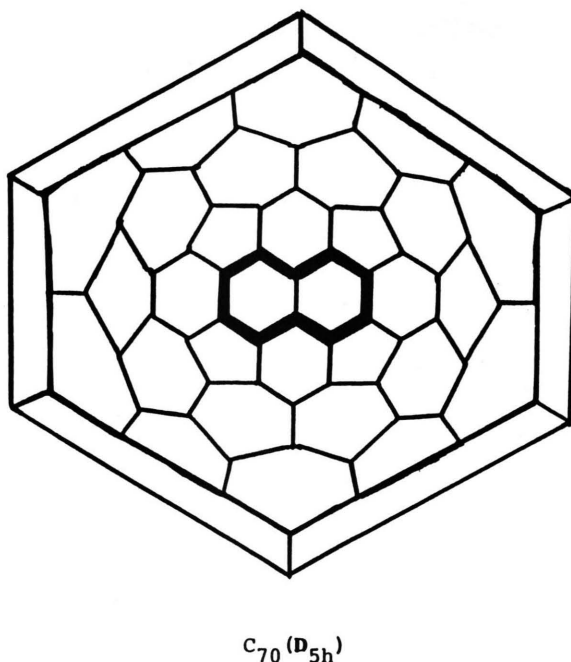

$C_{70}(D_{5h})$

Fig. 3. Circumscribing naphthalenoctyl (C_{10}) four successive times with a combination of pentagonal and hexagonal rings generates the Schlegel diagram of falmerene. The ultimate excised internal structure (EIS) is shown in bold.

Circumscribing with Hexagonal Rings and Constant-Isomer Series

The excised internal structure-circumscribing principle is an extremely important concept which leads to constant-isomer benzenoid series. The EIS is the subgraph spanned by the internal vertices of a benzenoid system. The circumscription of ethene (C_2H_4) with a perimeter of 14 carbon atoms and addition of 6 hydrogen atoms in such a way as to generate only hexagonal rings with each atom fulfilling proper valence leads to pyrene ($C_{16}H_{10}$). Conversely, excising the connected internal carbon vertices of pyrene with simultaneous transfer of 4 hydrogen atoms leads to ethene. Since there is only one isomer of ethene, there can only be one benzenoid isomer of the formula of $C_{16}H_{10}$, namely pyrene. Circumscribing pyrene with a 26 carbon atom perimeter and supplementing with 6 more hydrogens gives the only $C_{42}H_{16}$ benzenoid possible, called circum(26)pyrene. Continuation of this process leads to the infinite one-isomer circumpyrene series. Note that pyrene and all its circumscribed successors have the same D_{2h} symmetry.

The circumscription of fluorenoids/fluoranthenoids [6], indacenoids [9], and biphenylenoids [10] with a perimeter of hexagonal rings also leads to constant-isomer series. To be circumscribable by a perimeter of hexagonal rings, an EIS must be devoid of adjacent bay rings. Since the presence of adjacent bay regions is a necessary and sufficient condition ot preclude the circumscription of any polypent/polyhex system, the $C_{38}H_{22}$, $C_{42}H_{24}$, and $C_{46}H_{26}$ benzenoids in Fig, 4 of [10] are erroneously claimed by S. J. Cyvin et al. as being examples of systems which can not be circumscribed [11]. Figure 1 gives an example (fluoranthenoid) and Fig. 2 gives an example (indacenoid), neither of which can be circumscribed.

Circumscription with Pentagonal and Hexagonal Rings to Generate Fullerenes

The present work gives an algorithm in which successive circumscription of a base EIS (carbon fragment) with a combination of pentagonal and hexagonal rings ultimately terminates at a fullerene because
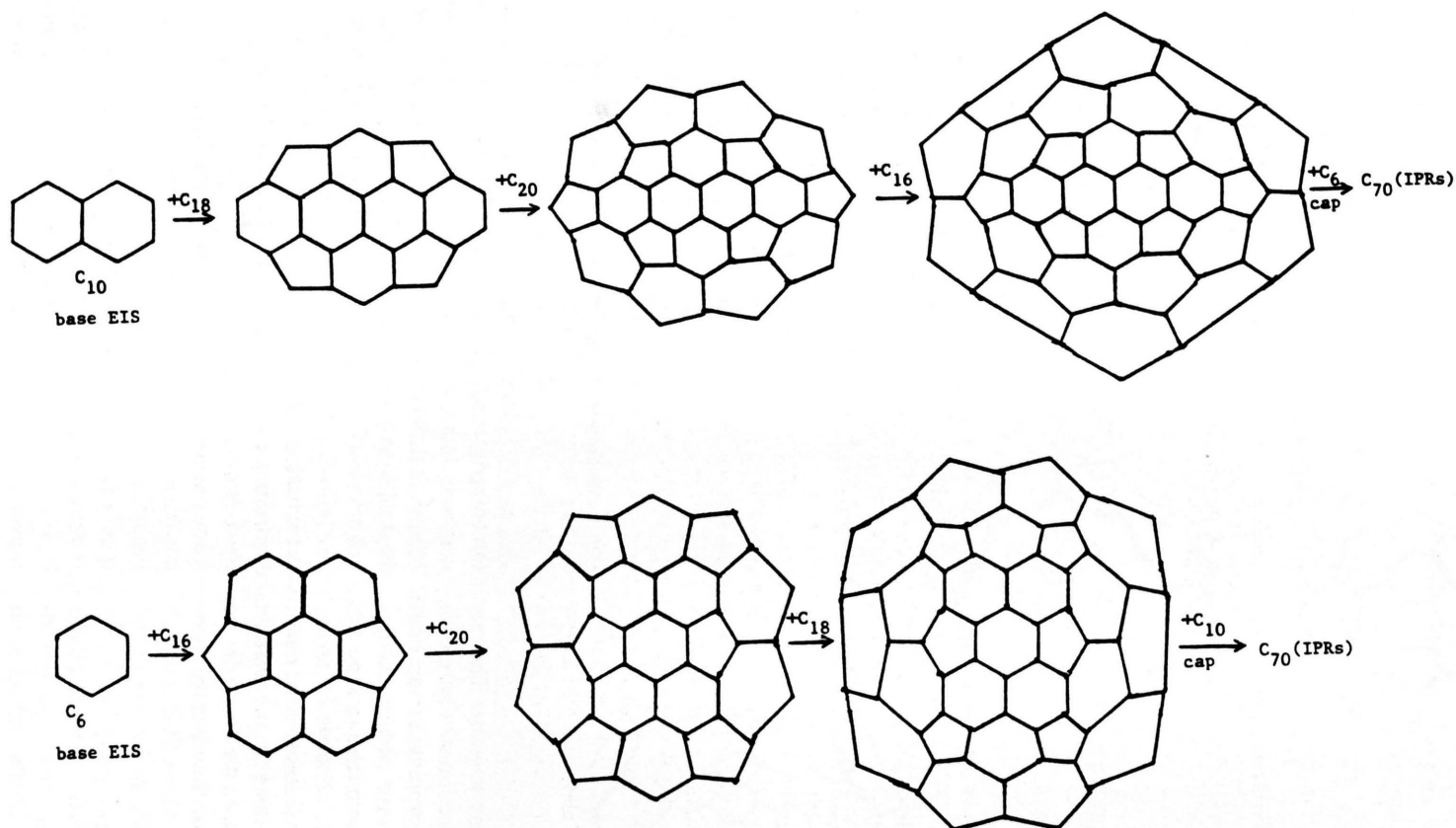
Fig. 4. Generation of the Schlegel diagrams of falmerene by successive circumscribing and capping in two reverse directions. In the top example, naphthalenoctyl is the base EIS and benzenehexyl is the cap. In the bottom example, benzenehexyl is the base EIS and naphthalenoctyl is the cap.
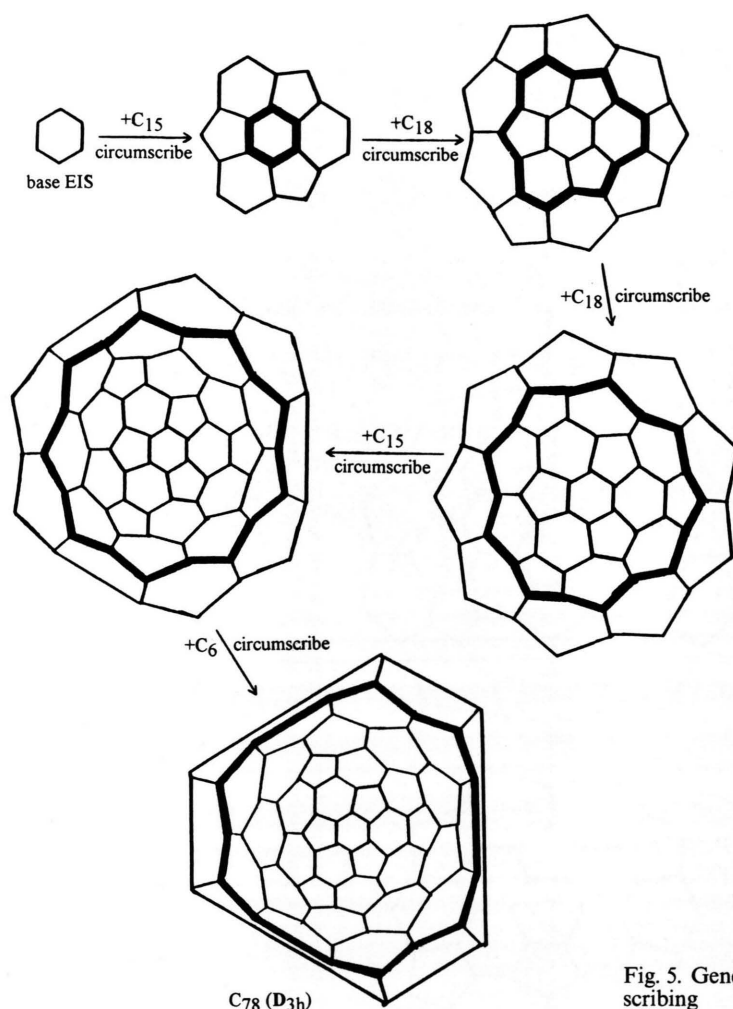
Fig. 5. Generation of the C_{78} (IPRs) fullerenes by circumscribing

of the formation of adjacent bay regions. This algorithm involves three steps: Selection of a base EIS, successive circumscribing, and capping in the final step. Because listing all combinatorial circumscribings of all possible EISs is an overwhelming task, we will limit ourselves to the generation of those fullerenes above C_{60} believed to be the most stable. Some general rules for qualitatively determining the more stable fullerene isomer structures have been put forward and will be incorporated into our algorithm. Isolated pentagonal rings (IPRs) are more favorable than adjacent ones because they minimize both antiaromatic and strain contributions. Since it is desirable to derive structures where strain is distributed as uniformly as possible, an ancillary rule involves the "neighbor index" of a ring which gives the number of adjacent 6-membered rings [12]. For systems with IPRs, the neighbor index (NI) for each pentagon is 5. If we require that the local environments of all hexagons be as similar as possible, the optimal hexagon arrangement for any C_n fullerene is to have an average NI of $\overline{NI} = 2(q - 60)/r_6 = (6n - 240)/(n - 20)$, where those hexagons of the same NI value are distributed as far from each other as possible in order to minimize local strains. From example, consider the C_{84} $\mathbf{D}_{6h}$ isomer which possesses two opposing (graphite-like) coronene caps. The presence of two graphite-like hexagons (NI = 6) makes the local curvature around them relatively flat, resulting in an oblate spheroidal geometry. The remaining 30 hexagonal rings $[r_6 = (n - 20)/2]$ each have an NI = 4. The optimal arrangement for C_{84} is to have 28 hexagons with NI = 4

+C_{20} circumscribe

+C_{24} circumscribe

+C_{18} circumscribe

base EIS

+C_6 circumscribe

C_{78} (C_{2v})

Fig. 5b.

+C_{15} circumscribe

+C_{18} circumscribe

+C_{18} circumscribe
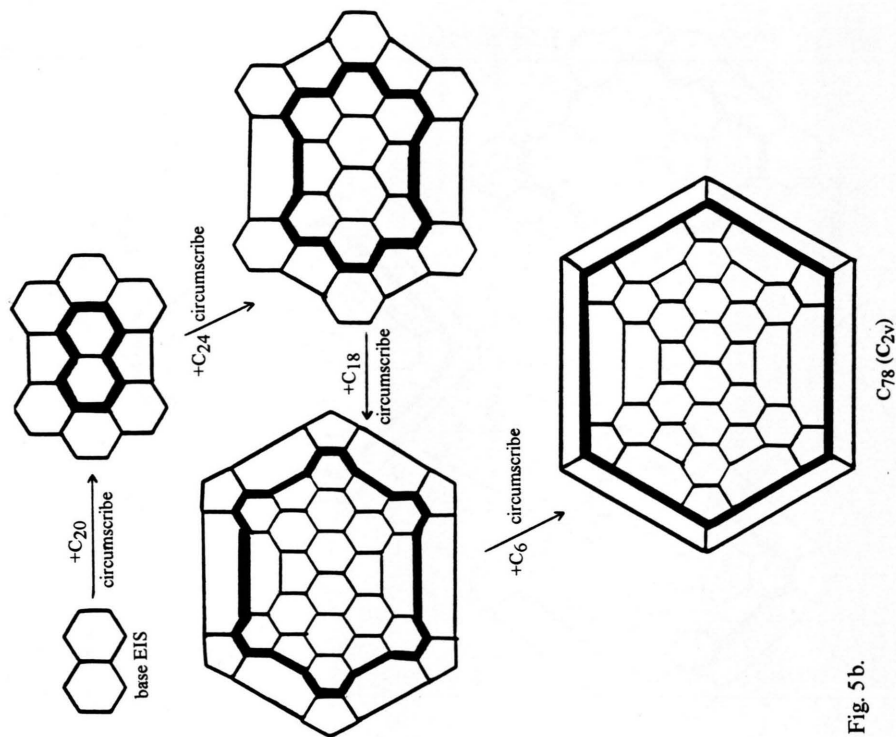
base EIS

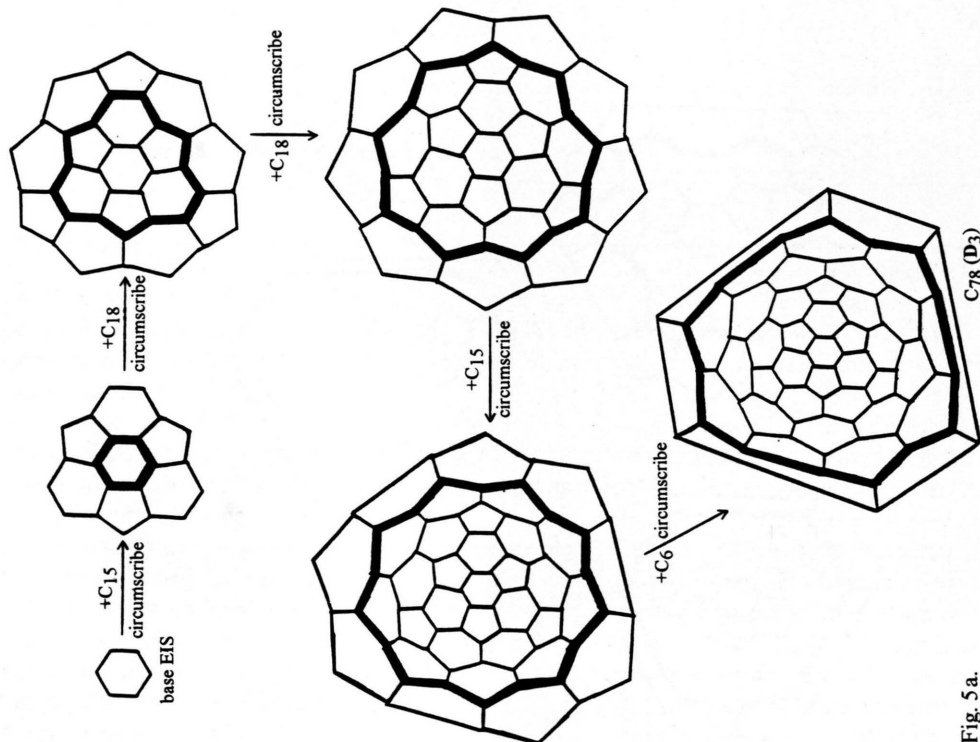+C_{15} circumscribe
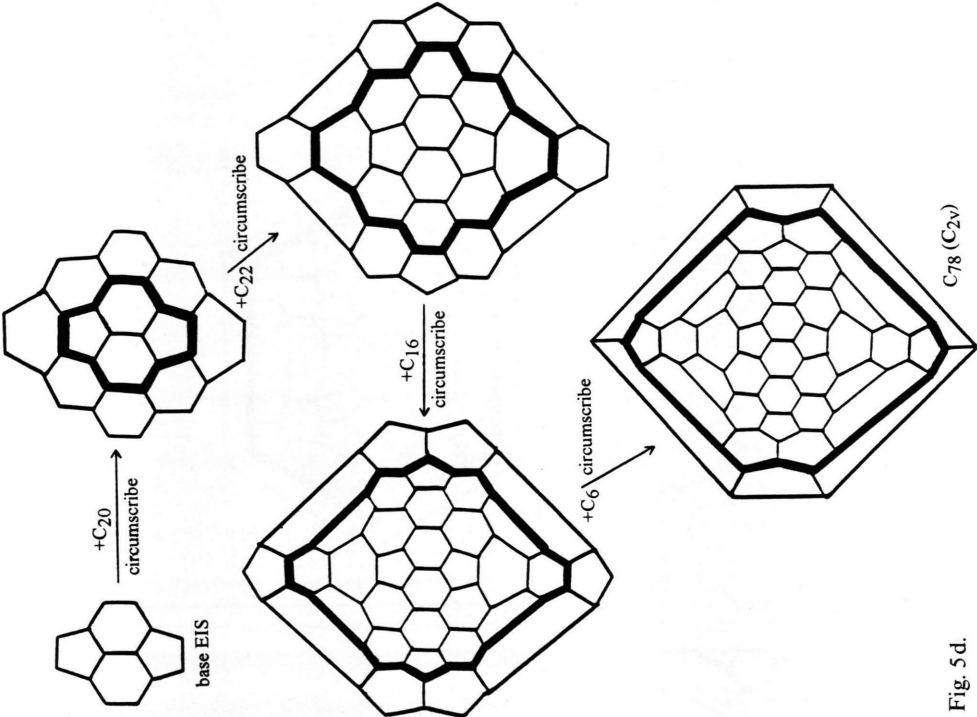
+C_6 circumscribe

C_{78} (D_3)
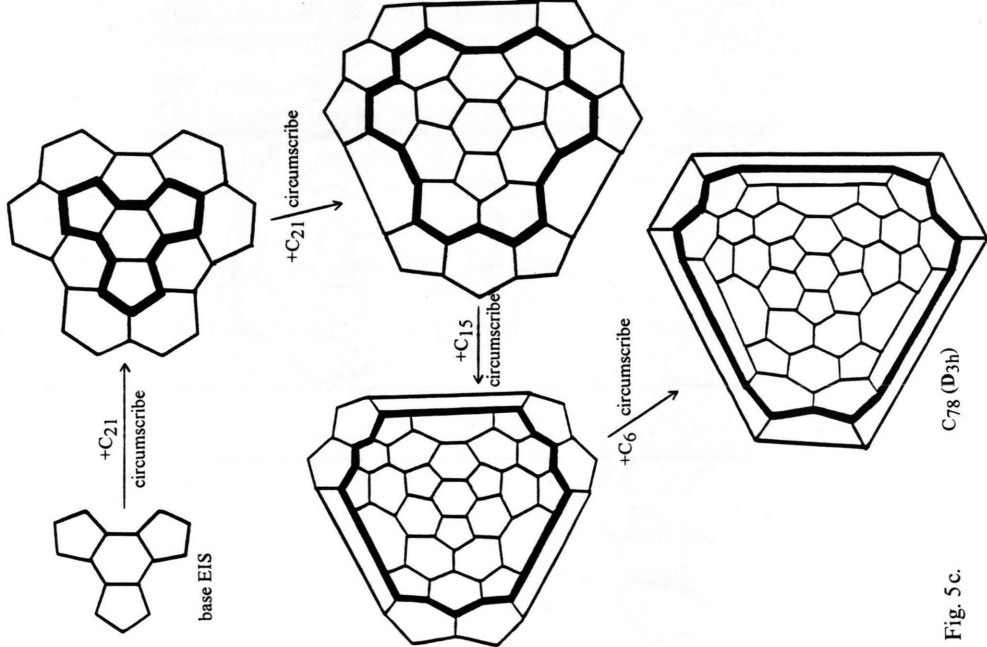
Fig. 5a.

Fig. 5d.

Fig. 5c.

and 4 hexagons with NI = 5, preferably with the latter 4 hexagons as far as possible. One of the C_{84} D_2 isomers with this optimal arrangement is likely to be more stable than the D_{6h} isomer and can be formed from the latter by two Stone-Wales pyracylene transformations [12].

A valence bond approach for explaining fullerene stabilities has been offered by Taylor [13]. A factor governing electron distributions in fullerene cages is the need to minimize the π-bond order in pentagonal rings. If a fullerene structure can have all single bonds assigned to its pentagonal rings and all its conjugated double bonds to the hexagonal rings, then the corresponding fullerene will be more stable than an isomer where this is not possible. Hexagonal rings in which three double bonds are located are said to be benzenoid. Only for the I_h isomer of C_{60} is it possible to locate all the double bonds in the hexagonal rings with none in the pentagonal rings. This minimization of double bond orders in pentagonal rings occurs with the *meta* orientation of two pentagonal rings about the hexagonal ring in *as*-indacene substructures [13]. The decacylene moiety in fullerenes contain ten hexagonal rings (after fusion) which are all benzenoid and three pentagonal rings to which the double bonds are exocyclic [14]. All C_{3n} leapfrogs have n benzenoid rings [15]. Thus, in the implementation of our circumscribing algorithm for generating the more stable intermediate carbon fragments and fullerenes, systems with IPRs will only be considered, *meta* oriented pentagonal rings will be preferred, and coronene-related substructures will be placed as widely separated as possible.

Generation of the Schlegel Diagram of Falmerene by Circumscribing

Figure 3 presents the Schlegel diagram of C_{70} (IPR) falmerene with its ultimate EIS shown in bold. Figure 4 shows two different circumscribing pathways for the generation of falmerene, one starting with the naphthalenoctyl carbon fragment as the base EIS and the other starting with benzenehexyl as the base EIS. Starting with the C_{10} naphthalenoctyl carbon fragment, one circumscribes three successive times and then caps with the C_6 benzenehexyl carbon fragment; note that this last capping step is equivalent to circumscribing a fourth time. Starting with C_6 benzenehexyl, one circumscribes three successive times and then caps

with the C_{10} naphthalenoctyl carbon fragment. It should now be evident to the reader that the first circumscribing sequence is the reverse of the second one, and vice versa. That is, these two pathways are growing the same C_{70} fullerene from opposite directions. This circumscribing example is equivalent to the ring-stacking growth model proposed by Achiba and coworkers [16]. This model assumes the isolated-pentagon rule and that even carbon rings prevail in the carbon vapor reaction medium in which fullerenes are formed. At each step of circumscribing (ring-stacking), the isomeric set of carbon fragmets is culled of the less stable isomers. Thus, the ring-stacking model leads to kinetic predictions of relative fullerene abundances.

Generation of the Schlegel Diagrams for the five C_{78} (IPRs) Fullerene Isomers by Circumscribing

While there are 21822 C_{78} fullerene structures, there are only five isomers with IPRs [17]. While calculations suggest that one C_{78} isomer with D_{3h} symmetry is the more stable one, Diederich and Whetten [18] have shown that the major experimental isomer has C_{2v} symmetry. Figure 5 presents the generation of the five C_{78} IPRs isomers by circumscribing appropriate EISs with a combination of pentagonal and hexagonal rings. These Schlegel diagrams have been previously published by Balasubramanian [19]. The kinetic ring-stacking model of Achiba and coworkers predicts that the C_{2v} isomers should be preferred. The reverse pathways for formation of the C_{2v} isomers, where the base EISs shown in Fig. 4 become capping carbon fragments, should be equally plausible [7].

Conclusion

The circumscribing algorithm for the generation of fullerenes has been detailed. The connection of our circumscribing algorithm [5, 20] and the ring-stacking model of Achiba and coworkers [16] has been made explicit. From this paper one can gain further appreciation of the generality of our excised internal structure/circumscribing principle [20]. The absence of adjacent bay regions is a necessary and sufficient condition to allow circumscription of any polypent/polyhex system. During successive circumscribing each successor polypent/polyhex system increasingly curls

upon itself and finally close up with the simultaneous formation of the twelfth pentagonal ring and (5 or 6) adjacent bay regions. Thus, successive circumscribing with a combination pentagonal and hexagonal rings eventually terminates. Successive circumscribing with exclusively hexagonal rings eventually leads to infinite

constant-isomer series. For the circumscribing algorithm to reach its full potential, the problems of selecting the given set of EISs that will generate the target set of fullerenes and the development of a rapid method of descerning isomorphic Schlegel diagrams must be solved.

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