

## FROM BENZENOID HYDROCARBONS TO FULLERENE CARBONS

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

### *Abstract*

While reviewing the circumscribing and leapfrog operations used in the structural studies of polycyclic conjugated hydrocarbons and fullerenes, how these two classes of compounds are related will be demonstrated. Some new insights and observations are noted.

### **Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous compounds. PAHs consist of benzenoids (PAH<sub>6</sub>s) having only fused hexagonal rings, fluoranthenoids having one pentagonal ring among otherwise hexagonal ones, indacenoids having two pentagonal rings among otherwise hexagonal ones, etc. They are present in fossil fuels, automobile exhaust, and cigarette smoke. They are formed in catalytic reforming to produce gasoline and carbonization of hard coal to produce coke. Virtually every combustion/pyrolytic process generates PAHs [1]. The formation of PAHs by geological diagenesis gives rise to a number of intriguing questions concerning their starting structures and the reactions they undergo [2]. The starting structures in turn are

determined by primeval fauna and flora. For example, sterols belonging to ancient living organisms can undergo paleotransformations to first C-ring monoaromatic steranes and then after many steps to A/B/C-ring triaromatic phenanthrene-related steranes and the degree of aromatization can be used as an indicator of the maturity of oils. In this aromatization process, the 18-methyl migrates from the 13-position to the 17-position and the 19-methyl group is lost. Our own work has shown that aromatization of the B-ring of sterols is accompanied by the simultaneous loss of the 19-methyl group [3]. Thus, the presence of specific PAHs can possibly be used as biomarkers.

A number of PAHs are known carcinogens, like benzo[*a*]anthracene, benzo[*a*]pyrene, and dibenzo[*a,l*]pyrene, where the latter is the most potent. The formation and identification of PAH/DNA-adducts is an ongoing area of investigation. Industrial hygienists use the metabolite, 1-hydroxypyrene, as a urine biomarker to measure the exposure of workers to PAHs and benzo[*a*]pyrene-hemoglobin adducts in a population exposed to traffic exhaust. Because PAHs are formed in combustion/pyrolytic processes and many have tumorigenic properties, their presence in environmental samples represents another important area of study. The presence of PAHs, like pyrene, benzopyrenes, benzo[*ghi*]perylene, and coronene, in recent sediments is generally considered to reflect inputs from combustion of wood and fossil fuels. It appears that a recognizable PAH fingerprint can survive over geological time-scales and historical PAHs profiles in polar ice drill-core samples from Greenland have been obtained. While wildfires, initiated by lightning strikes, are probably the most likely source of these PAHs in ancient sediments, metamorphic or volcanic origin can not be excluded. The presence

of large benzenoids have been identified in bitumens from deep-sea hydrothermal vents. Many benzenoids are electroconducting, photoactive (photochromic and photoconductive), and used as starting compounds for dyes, pharmaceuticals, and polymers.

The thermal transformation of organic materials to carbon is called carbonization. Gas phase carbonization in hydrocarbon flames is referred to as soot formation. In profile sampling of flames from hydrocarbon combustion under sooting conditions, the combustion products change sequentially from aliphatic chains, alicyclic rings, polycyclic aromatics, and finally fullerenes as the distance from the flame base increases [4]. The pitch (300-500°C) to coke (500-1000°C) to carbon (1000-2500°C) to graphite (2500-3000°C) transformation processes passes through a liquid crystal-like or mesophase in the first stage ( $\approx 400^\circ\text{C}$ ). The known components of pitch are flat, disc-like polycyclic aromatic hydrocarbon molecules that are devoid of polar substituents. At the onset of mesophase formation, the benzenoid molecules have approximately sixty carbons [4]. It may be no coincidence that the recently discovered new allotrope of carbon, buckminsterfullerene ( $\text{C}_{60}$ ) also has a formula containing sixty carbons.

The only two previously known allotropic forms of carbon, diamond and graphite, requires the presence of noncarbon end groups or dangling bonds in which the valence of the terminal carbons are left unsatisfied. However, twelve pentagonal rings in a dodecahedron of carbon atoms (or the fullerenes) leads to a geometrically closed polyhedron where the valence of all the carbons are satisfied. Thus, any fullerene polyhedron with  $n=N_c$  vertices has  $r_3=12$  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 [5]. Many more fullerenes above  $C_{96}$  are observed in the mass spectra of soot extract [6]. When  $C_{60}$  and  $C_{70}$  fullerenes became readily available [7], they were subsequently found to exist in shungite, a coal-type rock from Russia, in lightning-seared glassy rocks called fulgurites from Colorado, in the massive Sudbury meteorite crater in Ontario, and in the K-T boundary layer which is a sedimentary clay deposit at the end of the Cretaceous period [8]. These fullerenes constitutes a new class of polycyclic conjugated compounds, and the enumeration of all their possible structures has been important endeavor [9,10] which has facilitated the deduction of the probable structures of several experimentally observed fullerene species. Polymerized fullerenes form graphitic microtubules (or nanotubes) that may prove to have far-reaching implications for material science.

Buckminsterfullerene is one isomer out of 1812 possible  $C_{60}$  fullerene structures [11] having a nominal MW of 720 Da. There are  $\approx 133713$  benzenoid  $C_{58}H_{24}$  isomers [12] of the same nominal MW. Similarly, fullerene is one isomer out of 8149 possible  $C_{70}$  fullerene structures [11] having a nominal MW of 840 Da. There are far more than 6000 benzenoid  $C_{68}H_{24}$  isomers [12] of the same nominal MW. The  $C_{98}$  fullerenes correspond to only one  $C_{96}H_{24}$  benzenoid isomer, that is dicircum(42,30)coronene, and higher MW fullerenes have no benzenoid-related MWs. Interestingly,  $C_{50}$  fullerenes have the same nominal MW as  $C_{48}H_{24}$  (i.e., 600 Da) which corresponds to approximately 114326 benzenoids [12]; the four most stable  $C_{48}H_{24}$  benzenoids have been depicted [1, Part A, page 88-89] and are total resonant sextet systems. Thus, mass spectroscopic analysis

alone can not be used to ascertain the presence of a lower MW fullerene in some environmental sample.

In this review, the circumscribing algorithm which has been the subject of several papers on the enumeration and generation of polycyclic conjugated systems [13], including fullerenes [14], will be discussed and related to one fullerene growth scenario. Further aspects of protofullerene enumeration will be investigated. 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) [15] and its successors is preserved when one successively circumscribes with hexagonal rings to ultimately generate constant-isomer series. It has been 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 where the outer perimeter of a Schlegel may comprise of one of the pentagonal rings [14]. Symmetry is not necessarily preserved between the EIS and its successor when circumscribing with a combination of pentagonal and hexagonal rings. Also, the properties of the circumscribing and leapfrog operations will be contrasted and compared [16-17].

#### **Basic terminology**

A polypent/polyhex system consists of interlocking pentagons and hexagons where

the degree-2 vertices correspond to methine >C-H units and degree-3 vertices correspond to =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. In going from a 3-dimensional polyhedron to a corresponding 2-dimensional Schlegel, faces become rings where the number of rings ( $r$ ) is one less than the number of faces because the outer perimeter of the 2-dimensional Schlegel which corresponds to one of the polyhedron faces is not counted as a ring. Denote the circumscription of a polyent/polyhex (polyene) system by  $\mathbf{P} \rightarrow \text{circum-}\mathbf{P} = \mathbf{P}'$ . It has been previously shown that  $N_{pc} = N_H - 6 + r_s$ ,  $q_p = N_H + N_{pc} = 2N_H - 6 - r_s$ , 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  $\mathbf{P} \rightarrow \mathbf{P}'$ ,  $N_c \rightarrow N_c'$  and  $N_H \rightarrow N_{pc}'$ . Thus, for circum- $\mathbf{P}$ ,  $N_{pc}' = N_H' - 6 + r_s' = N_H$  giving  $N_H' = N_H + 6 - r_s'$  and, similarly,  $q_p' = N_{pc}' + N_H'$  and  $N_c' = q_p' + N_c$  giving  $N_c' = N_c + N_{pc}' + N_H' = N_c + 2N_H + 6 - r_s'$ . These recursive equations are useful for monitoring the progress of successive circumscription.

### Graph theoretical operations

The graph theoretical operations that will be used in this review are dual, inner dual, circumscribing, and leapfrogging. Two polyhedra are duals when the vertices of one corresponds to the face centers of the other. The tetrahedron is self-dual and the cube and octahedron are duals, as are the dodecahedron and icosahedron. The dual of a 3-connected spherical polyhedron with  $n$  vertices, twelve pentagonal faces, and remaining hexagonal faces ( $r = r_5 + r_6 = n/2 + 2$ ,  $q = 3n/2$ ) is a deltahedron composed of triangular faces

with twelve 5-coordinate and  $r_6$  6-coordinate vertices. Exactly 12 pentagons or 6 tetragons are required to give a geometrically closed polyhedron. Inner dual differs from dual in that it is applied to planar polygonal systems and a vertex belonging to the infinite outer region is omitted.

The circumscribing operator is a construction process in which a starting conjugated polyene is encircled by a chain of carbon atoms in such a way as to form a perimeter of pentagonal and/or hexagonal rings to give a successor conjugated polycyclic polyene [1,13-14]. In this construction process, the initial number of carbons  $N_c$  and hydrogens  $N_H$  are increased to give  $N_c'$  carbons and  $N_H'$  hydrogens

$$N_c' = N_c + 2N_H + 6 - r_5'$$

$$N_H' = N_H + 6 - r_5'$$

where  $r_5'$  is the total number of pentagonal rings after circumscribing. Reversing this process is called excising. The excised internal structure (EIS) is the subgraph spanned by the internal vertices of a polycyclic system [1,15]

The leapfrog operation is a geometrical construction process in which a starting fullerene is capped on every face [16] or a benzenoid is capped on every ring [17] and then dualized to give a successor fullerene cage or total resonant sextet (TRS) benzenoid [18] of the same symmetry. Successor fullerenes have three times as many carbon atoms, isolated pentagons, and closed shell  $\pi$ -electronic systems [16] and successor TRS benzenoids have closed shell  $\pi$ -electronic systems [17]. Leapfrog fullerenes are spherical with  $n = 60 + 6k$  ( $k = 1, n = N_c$ ) carbon atoms (vertices). Fullerenes, in general, have  $n = 20 + 2k$  ( $k = 1$ ) vertices,  $3n/2$  bonds (edges),  $n/2 + 2$  faces, 12 pentagonal faces, and

$n/2 - 10$  hexagonal faces; note that the number of polyhedral faces equals the number of rings in a Schlegel plus one because the outer perimeter in the Schlegel corresponds to the back face in the polyhedral system.

The circumscribing and leapfrog algorithms are based on operations which transform planar and polyhedral 3-connected structures into other structures with well defined characteristics. The ultimate outcome when each operation is successively applied to a given initial set of structures have opposite consequences which will be compared and contrasted in this paper. The leapfrog operation on dodecahedron ( $C_{20}$ ) gives buckminsterfullerene ( $C_{60}$ ). Since fullerenes with four-membered rings have been recently studied [19-21], we will now illustrate the Schlegel version [17] of the leapfrog operation on the hexahedron (cube) and hexagonal prism in Figures 1 and 2.

The successive circumscribing of qualified conjugated hydrocarbons with hexagonal rings generates an infinite series of symmetry-related conjugated polycyclic polyenes called constant-isomer series [1,13]. Successive circumscribing with a combination of pentagonal and hexagonal rings leads to a terminating series of polypent/polyhex systems that increasingly curl upon themselves until the last structure finally closes up with the simultaneous formation of the twelfth pentagonal ring and (5 or 6) proximate bay regions [14]. In comparison, successive leapfrogging of a 3-connected polyhedral carbon cage generates an infinite series of symmetry-related, closed-shell polyhedra,  $C_n \rightarrow C_{3n} \rightarrow C_{9n} \rightarrow \dots$  [16]. One should note that successive leapfrogging of a (planar) benzenoid is terminated at a polyphenyl substituted TRS system [17].



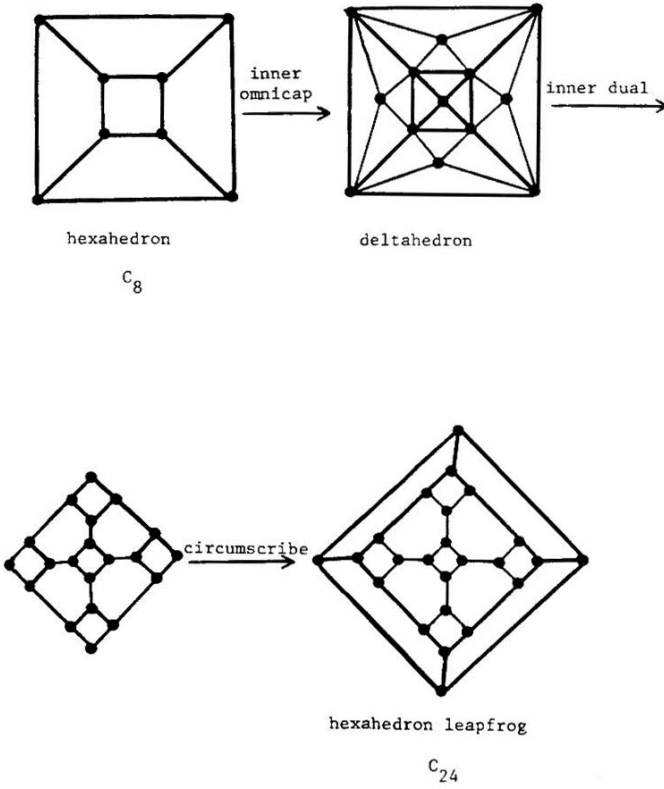


Figure 1. The Schlegel version of the leapfrog operation on hexahedron.

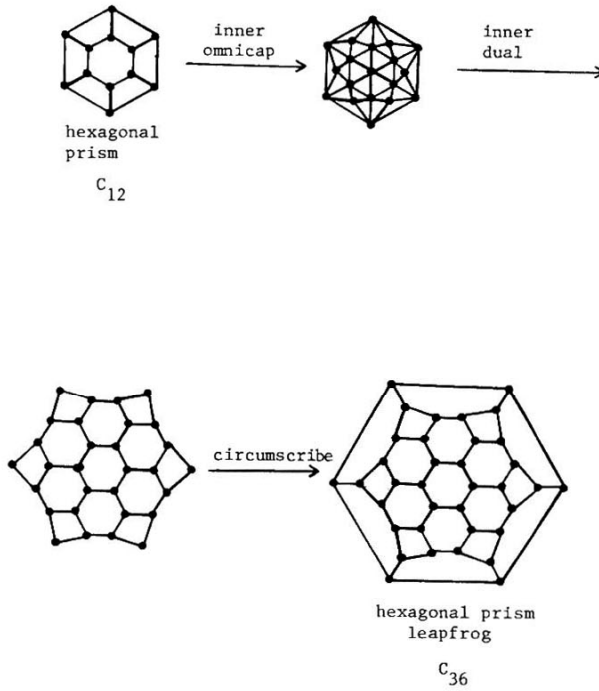


Figure 2. The Schlegel version of the leapfrog operation on the hexagonal prism.

### **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 excised internal structure (EIS) is the subgraph spanned by the internal vertices of a benzenoid system. The circumscribing of ethene ( $C_2H_4$ ) with a perimeter of 14 carbon atoms and supplementing with 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 out 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 give the only  $C_{42}H_{16}$  benzenoid possible, called circum(26)pyrene. Continuing this process leads to the infinite one-isomer circumpyrene series. Note that pyrene and all its circumscribed successors have the same  $D_{2h}$  symmetry, one selective lineation, and no bays.

The hexagonal-ring circumscribing of fluorenoids/fluoranthenoids, indacenoids [13], and biphenylenoids (contains one four-membered ring among otherwise hexagonal ones) [22] with a perimeter of hexagonal rings also lead to constant-isomer series. To be circumscribable by a perimeter of hexagonal rings, an EIS must be devoid of adjacent bay rings. The presence of adjacent bay regions is a necessary and sufficient condition to preclude the circumscription of any polypent/polyhex system.

### **Circumscribing with a combination of pentagonal and hexagonal rings**

Dodecahedron ( $C_{20}$ ) has only 12 pentagonal faces. For any polypent/polyhex system, exactly 12 pentagonal rings are required for it to be able to form a geometrically closed shape. Thus, the process of successive circumscribing with a combination of pentagonal and hexagonal rings must necessarily terminate once 12 pentagonal rings are formed. A necessary and sufficient requirement to preclude circumscription of a polycyclic structure is the presence of proximate bay regions. The formation of the 12th pentagonal ring during successive circumscribing will always be associated with the simultaneous formation of proximate bay regions. To generate the Schlegel diagram of a fullerene, successively circumscribe a given EIS devoid of proximate bay regions until the number of degree-2 vertices is reduced to 6 or less. If this penultimate structure has 5 or 6 degree-2 vertices, circumscribe a final time; this latter step is equivalent to a  $C_5$  or  $C_6$  capping, respectively [14]. The EIS selected should be a substructure possessed by the target fullerene. Figure 3 gives a representative example which shows how one can generate a  $C_{30}$  fullerene starting with acenaphthalenoctyl. If the penultimate structure has 4 degree-2 vertices, cap it with a  $C_2$  ethylenyl unit. Figure 4 gives one of two different  $C_2$  capping modes of the same  $C_{76}$  carbon fragment produced by successive circumscribing to generate one of the five possible  $C_{78}$  fullerenes with isolated pentagonal rings; this same  $C_{78}$  fullerene can be generated by capping the antecedent carbon fragment with pyracylenoctyl. If it has 3 degree-2 vertices, cap it with a carbon atom. If the penultimate structure has 2 degree-2 vertices, cap it with an edge by connecting a bond from one to the other. These elementary capping units ( $C_6$ ,  $C_5$ ,  $C_2$ ,  $C_1$ , and edge) simulate actual carbon vapor chemical reactions.

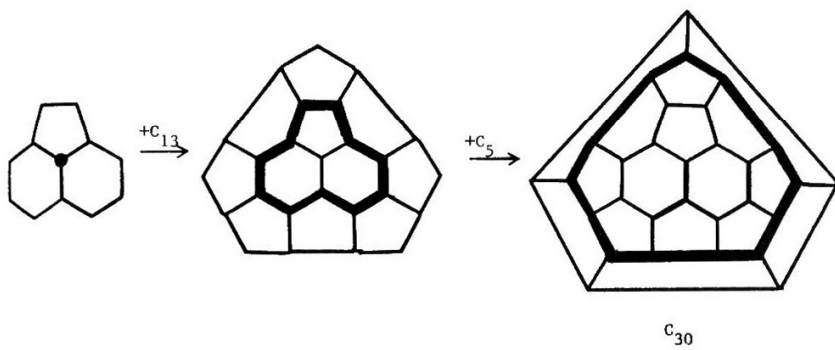
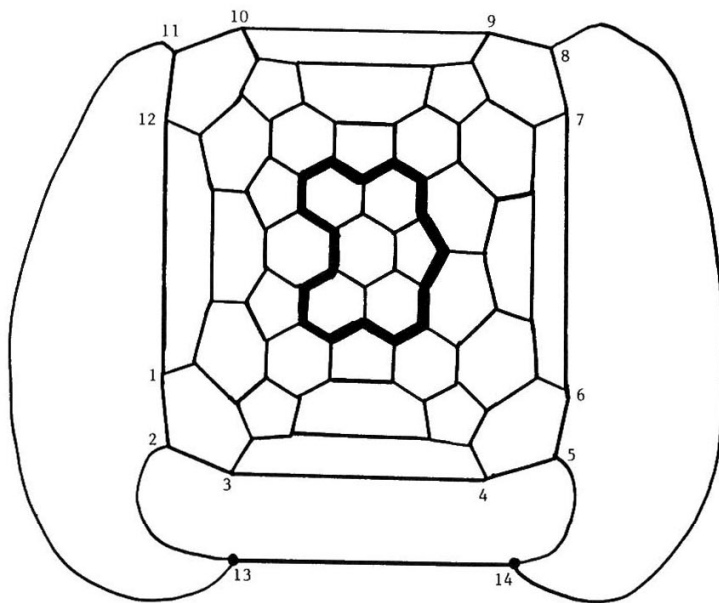
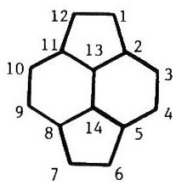


Figure 3. Successive circumscribing of acenaphthaleneoctyl gives a  $C_{30}$  fullerene. The excised internal structures (EISs) are shown in bold.



$C_{78}$  (IPRs)



$C_{14}$  capping  
carbon fragment

Figure 4. Successive circumscribing of the structure shown in bold and capping with a  $C_2$  unit gives one of five possible  $C_{78}$  (IPRs) fullerenes. Here 13 is connected to 2 and 11, but alternatively could be connected to 2 and 5.

By circumscribing the elementary capping carbon fragments, one can generate larger carbon fragments which may also serve as capping units. The EIS and capping structures can be interchanged and the order of successive circumscribing reversed without materially altering the above circumscribing algorithm.

### **Leapfrogging polyhedral cage structures**

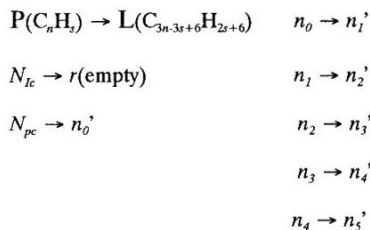
The leapfrog transformation has been described by Fowler [16] a number of times. We will describe here the equivalent process for the leapfrogging on Schlegel representations. It consists of the following three successive operations on the Schlegel of a smaller polyhedron cage having only pentagonal and hexagonal rings - form the inner omnicap, transform it into the inner dual, and circumscribe with either a  $C_5$  or  $C_6$  perimeter; this latter additional step compensates for the "inner" constraint. The distinction between omnicap and dual and inner omnicap and inner dual is that the former each have an additional point in the outer infinite region. Figures 1 and 2 illustrate the Schlegel version of leapfrogging on polyhedral systems having four-membered rings.

### **Leapfrogging benzenoid structures**

The leapfrogging of any benzenoid leads to a total resonant sextet benzenoid (TRS) which has a maximum number of Clar sextets (disjoint hexagon rings with three mutually permutable  $p\pi$  bonds) [17]. Total resonant sextet benzenoid (TRS) systems (called fully benzenoid systems by Clar) have formulas divisible by six and are totally

covered by Clar sextets. The leapfrog transformation is of fundamental importance here because it allows us to identify the essentially strain-free benzenoid isomers predicted to be among the more kinetically stable (largest HOMO values) and with highest Huckel  $p\pi$  electronic energy without requiring one to have knowledge of the remaining isomers [17]. All known TRS benzenoids are colorless crystals that do not react with concentrated sulfuric acid and are the isomers with the largest Huckel  $E_\pi$  and HOMO values. From an experimental and HMO point of view, TRS benzenoids represent a distinctive subset of benzenoids in general.

Our previous work [17] demonstrated that there exists a one-to-one matching between strictly peri-condensed and total resonant sextet constant-isomer series. In going from the parent P to its leapfrog L, the following correspondences hold:



where  $N_{jc}$ ,  $N_{pc}$ ,  $r(\text{empty})$ , and  $n_i$  are the number of internal degree-3, peripheral degree-3, rings without Clar sextets, and perimeter units ( $i=0$  for bay region,  $i=1$  for solo,  $i=2$  for duo,  $i=3$  for trio,  $i=4$  for quarto, and  $i=5$  for phenyl), respectively.

### Circumscribing and the Mechanism of Fullerene Formation

The carbon vapor phase growth of fullerenes must proceed via the involvement of



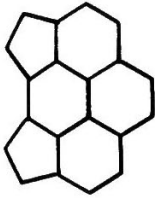
monocyclic and polycyclic carbon species. In the carbon/flame plasma, the formation of monocyclic and then polycyclic carbon clusters have an enthalpic advantage over the entropic content of chainlike carbon clusters after a critical size is reached [20,23]. The ring-stacking model proposed by Achiba and coworkers [23] has a strong resemblance to our circumscribing algorithm for generating fullerenes [14]. The recent retro-synthetic analysis of falmerene  $C_{70}$  [24] is tantamount to our circumscribing algorithm [14] in reverse. A recently published method [25] for the systematic computation of the cartesian coordinates of buckminsterfullerene  $C_{60}$  is equivalent to successively circumscribing indeneheptyl ( $C_9$ ) with monocyclic carbon rings of  $C_{17}$ ,  $C_{19}$ , and  $C_{13}$  followed by a  $C_2$  capping in numerical sequence.

### **Protofullerenes**

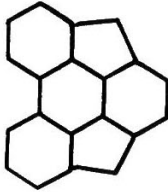
An active area of investigation involves the study of model protofullerene patches. Naphthalene has been studied from various points-of view in this regard [26]. Corannulene ( $C_{20}H_{10}$ ) has been synthesized by flash vacuum pyrolysis (FVP) [27] and was subsequently identified in flames also producing fullerenes [28]. The corannulene  $C_{20}$  skeleton (corannulenedecyl) has been widely hypothesized to be a fullerene precursor [28-29]; in this regard, the reader may wish refer to the successive circumscribing of corannulenedecyl by  $C_{20}$ ,  $C_{15}$ , and  $C_5$  monocyclics to give buckminsterfullerene [30]. Also, it may be noted here that the successive circumscribing of corannulene with only hexagonal rings leads to the one-isomer fluoranthenoid series [13]. Direct pyrolysis of corannulene has been shown to lead to the formation of  $C_{60}$  fullerene via a complicated

pathway [31]. Two recent reports on the FVP synthesis of 3 of the 19 possible  $C_{20}H_{10}$  indacenoid isomers of corannulene have appeared [32]. These  $C_{20}H_{10}$  dicyclopentapyrenes are structures **1**, **5**, and **9** in Figure 5. The fluoranthenoid, corannulene, and its 19 different indacenoid isomers can not be distinguished solely by mass spectrometry in environmental samples, and the availability of these  $C_{20}H_{10}$  PAH isomers will be important in future pyrolytic studies.

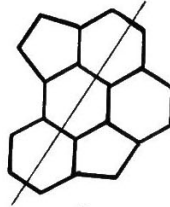
Indacenoids have antiaromatic annulene perimeters, whereas all benzenoids have aromatic annulene perimeters. Per the interpretation of Scott and Necula [32], indacenoids **9**, **10**, **18** and **19** should have  $^1H$  NMR chemical shifts that are relatively more deshielded than the other  $C_{20}H_{10}$  indacenoids in Figure 5 because their trimethylenemethane EISs prevent the antiaromatic perimeter ring current from participating. Thus, **9** which has a trimethylenemethane diradical EIS was observed to have resonances of all its hydrogens shifted downfield by 0.4-0.7 ppm relative to the corresponding hydrogens in **1** and **5** which have a closed-shell 1,3-butadiene EIS [32]. We will now summarize some other topological characteristics of the indacenoids in Figure 5. The structure count (SC) for each indacenoid isomer is given below. SC is an approximate measure of the  $p\pi$  electronic energy, assuming identical strain energies. The structures in Figure 5 marked with a line (selective lineation) have HMO eigenvalues of  $\pm 1$  and **18** contain the eigenvalues of styrene. Isomers **1-10** have IPRs. The isomeric pairs **2**  $\equiv$  **10**, **4**  $\equiv$  **7**, and **6**  $\equiv$  **6** are interconvertible to each other by the Stone-Wales transformation. Interestingly, as shown in Figure 6, indacenoid **1** can be converted to corannulene by rotating the bay region carbons (dots) and corannulene can be converted



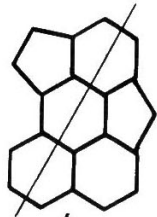
1  
SC = 7



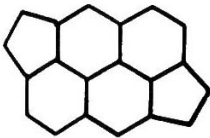
2  
SC = 6



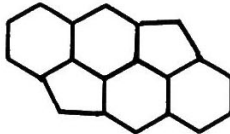
3  
SC = 5



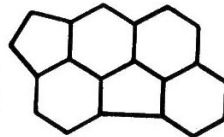
4  
SC = 7



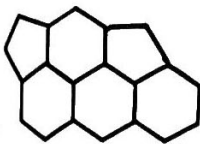
5  
SC = 7



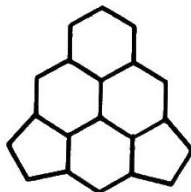
6  
SC = 2



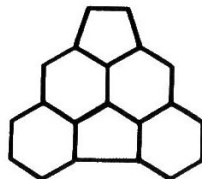
7  
SC = 9



8  
SC = 5

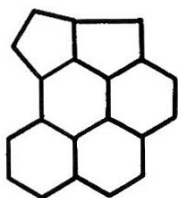


9  
SC = 6



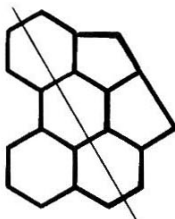
10  
SC = 8

Figure 5



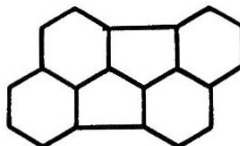
**11**

SC = 9



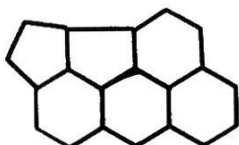
**12**

SC = 8



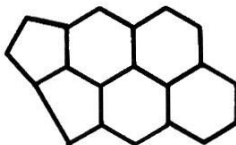
**13**

SC = 10



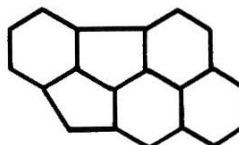
**14**

SC = 7



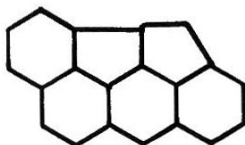
**15**

SC = 7



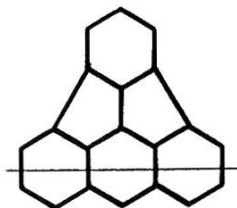
**16**

SC = 5



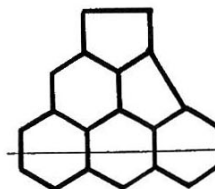
**17**

SC = 8



**18**

SC = 8



**19**

SC = 4

Figure 5. All 19  $C_{20}H_{10}$  indacenoid isomers possible.

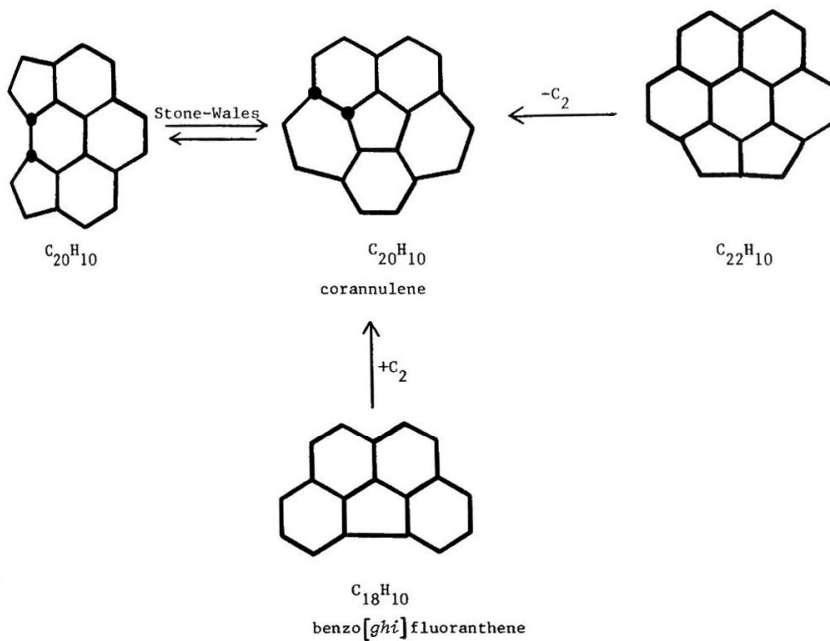


Figure 6. The above reactions can occur on the indicated hydrocarbons and their corresponding carbon cluster skeletons. Fluoranthenoids have one and indenoids have two pentagonal rings in addition to hexagonal ones.

to 1 by rotating two hexagonal ring fusion carbons (dots) via the Stone-Wales transformation. Recall that corannulene is the first generation member of the one-isomer fluoranthenoid constant-isomer series and benzo[*ghi*]fluoranthene is a first generation member of the three-isomer fluoranthenoid constant-isomer series [13]; thermal induced insertion of a  $C_2$  at the bay region of the latter will give the former. The  $C_{22}H_{10}$  PAH given in Figure 6 is a first generation member of the seven-isomer indacenoid constant-isomer series; thermal extrusion of  $C_2$  from the pentalene ring fusion carbons also gives corannulene.

The FVP synthesis of  $C_{30}H_{12}$  buckybowl (circofulvalene) [33] has stimulated a number of works [34-36]. There are 45  $C_{30}H_{12}$  indacenoid isomers [35]. Fowler and Mitchell have shown that placing the pentagonal rings on the perimeter tends to minimize their strain energy of these protofullerenes [36]; this also coincides with a preference for naphthalene EISs and an aversion for pentalene EISs. The first non-Kekulean (a graph devoid of any 1-factor subgraph) indacenoid has been identified as occurring in the  $C_{30}H_{12}$  isomer set and was predicted by the EIS concept. Achiba and coworkers enumerated all 13  $C_{30}$  indacenoid skeletons with the naphthalene EIS in their paper [37] on the ring stacking fullerene growth model with pentagon migration.

## Summary

This paper has reviewed within the context of experimental work the contributions directed toward a unified structure theory of PAHs. As this review has demonstrated, the formation of PAHs and fullerenes are intricately related [38].

## References

1. Dias, J.R. "Handbook of Polycyclic Hydrocarbons - Parts A and B"; Elsevier: New York, 1987 and 1988.
2. Shetty, R.; Stoilov, I.; Watt, D.S.; Carlson, R.M.; Fago, F.J.; Moldowan, J.M. Synthesis of Biomarkers in Fossil Fuels. *J. Org. Chem.* 1994, 59, 8203-8208.
3. Dias, J.R. Ejection of the 19-Methyl Group in Tetracyclic Triterpenes. *J. Org. Chem.* 1974, 39, 1767-1769.
4. Diederich, F.; Whetten, R.L. Beyond C<sub>60</sub>: The Higher Fullerenes. *Acc. Chem. Res.* 1992, 25, 119-126; Pope, C.J.; Marr, J.A.; Howard, J.B. Chemistry of Fullerenes C<sub>60</sub> and C<sub>70</sub>: Formation in Flames. *J. Phys. Chem.* 1993, 97, 11001-11013; Schwarz, H. The Mechanism of Fullerene Formation. *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1412-1415; Lafleur, A.L.; Howard, J.B.; Marr, J.A.; Yadav, T. Proposed Fullerene Precursor Corannulene Identified in Flames Both in the Presence and Absence of Fullerene Production. *J. Phys. Chem.* 1993, 97, 13539-13543; Crowley, C.; Kroto, H.W.; Taylor, R.; Walton, D.R.M.; Bratcher, M.S.; Cheng, P.-C.; Scott, L.T. Formation of [60]Fullerenes by Pyrolysis of Corannulene, 7,10-bis(2,2'-Dibromovinyl)fluoranthene, and 11,12-Benzofluoranthene, *Tetrahedron Lett.* 1995, 36, 9215-9218; Lewis, I.C. Chemistry of Carbonization. *Carbon* 1982, 20, 519-529.
5. Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Honda, M.; Matsumiya, H.; Moriwaki, T.; Suzuki, S.; Shiromaru, M.; Saito, K.; Yamauchi, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* 1992, 188, 177.
6. Ben-Amotz, D.; Cooks, R.G.; Dejarne, L.; Gunderson, J.C.; Hoke II, S.H.; Kahr, B.;

- Payne, G.L.; Wood, J.M. *Chem Phys. Lett.* 1991, 183, 149.
7. Scrivens, W.A.; Cassell, A.M.; North, B.L.; Tour, J.M. Single Column Purification of Gram Quantities of  $C_{70}$ . *J. Am. Chem. Soc.* 1994, 116, 6939-6940; Khemani, K.C.; Prato, M.; Wudl, F. A Simple Soxhlet Chromatographic Method for the Isolation of Pure  $C_{60}$  and  $C_{70}$ . *J. Org. Chem.* 1992, 57, 3254-3256.
  8. Buseck, P.R.; Tsipursky, S.J.; Hettich, R. Fullerenes in Nature:  $C_{60}$  and  $C_{70}$  Found in Ancient Russian Rock. *Science* 1992, 257, 215-217; Heymann, D.; Smalley, R.E. Ancient Fullerenes: Extensive Natural  $C_{60}$  Deposits Discovered. *Science* 1994, 265, 642-644; Allamandola, L.J.; Tielens, A.G.G.M.; Barker, J.R. Interstellar Polycyclic Aromatic Hydrocarbons. *Astrophys. J. Suppl. Series*, 1989, 71, 733-775; Hare, J.P.; Kroto, H.W. A Postbuckminsterfullerene View of Carbon in the Galaxy. *Acc. Chem. Res.* 1992, 25, 106-112; Becker, L.; Bada, J.L. *Science* 1994, 265, 645-647; Becker, L.; Bada, J.L.; Winans, R.E.; Bunch, T.E. Fullerenes in Allende Meteorite. *Nature* 1994, 372, 507.
  9. Liu, X.; Klein, D.J.; Schmalz, T.G.; Seitz, W.A. *J. Comput. Chem.* 1991, 12, 1252; Schmalz, T.G.; Seitz, W.A.; Klein, D.J.; Hite, G.E. *J. Amer. Chem. Soc.* 1988, 110, 1113; Liu, X.; Schmalz, T.G.; Klein, D.J. Favorable Structures for Higher Fullerenes. *Chem. Phys. Lett.* 1992, 550-554 .
  10. Fowler, P.W.; *Chem Phys. Lett.* 1986, 131, 444; Manolopoulos, D.E.; Woodall, D.R.; Fowler, P.W. *J. Chem. Soc. Faraday Trans.* 1992, 88, 2427.
  11. Babić, D.; Klein, D.J.; Sah, C.H. Symmetry of Fullerenes. *Chem Phys. Lett.* 1993, 211, 235-241; Manolopoulos, D.E. Comment on "Favorable Structures for Higher



- Fullerenes". *Chem. Phys. Lett.* 1992,192, 330; Liu, X.; Schmalz, T.G.; Klein, D.J. Reply to Comment on "Favorable Structures for Higher Fullerenes". *Chem Phys. Lett.* 1992, 192, 331.
12. Dias, J.R. The Formula Periodic Table for Benzenoid Hydrocarbons and the Unifying Theory of a Periodic Table Set. *Polycycl. Aromat. Comp.* 1994, 4, 87-106.
13. Dias, J.R. Notes on Constant-Isomer Series. *J. Chem. Inf. Comput. Sci.* 1993, 33, 117-127; Cyvin, B.N.; Cyvin, S.J.; Brunvoll, J. A New Picture for Constant-Isomer Series of Benzenoids and Related Species. *J. Chem. Inf. Comput. Sci.*, 1993, 33, 745-749; Dias, J.R. Series of Fluorenoïd/Fluoranthenoïd Hydrocarbons having a Constant Number of Isomers. *Chem. Phys. Lett.* 1991,185, 10-15; Dias, J.R. Chemical and Structural Characteristics and Enumeration of Indacenes. *J. Chem. Inf. Comput. Sci.* 1992, 32, 203-209.
14. Dias, J.R. From Benzenoids to Fullerenes and the Circumscribing Algorithm. *Chem. Phys. Lett.* 1993, 209, 439-444; Dias, J.R. Generation of Fullerenes by Circumscribing. *Z. Naturforsch.* 1993, 48a, 1009-1016.
15. Brunvoll, J.; Cyvin, B.N., Cyvin, S.J.; Gutman, I. Some Benzenoid Hydrocarbons with Extremal Properties. *Z. Naturforsch.* 1988, 43A, 889-894; Dias, J.R. A Formula Periodic Table for Benzenoid Hydrocarbons and the Aufbau and Excised Internal Structure Concepts in Benzenoid Enumerations. *Z. Naturforsch.* 1989, 44A, 765-771.
16. Fowler, P.W. How Unusual is  $C_{60}$ ? Magic Numbers for Carbon Clusters. *Chem. Phys. Lett.* 1986, 131, 444-450; Manolopoulos, D.M.; Woodall, D.R.; Fowler, P.W. Electronic Stability of Fullerenes: Eigenvalue Theorems for Leapfrog Carbon

- Clusters. *J. Chem. Soc. Faraday Trans.* 1992, 88, 2427-2435; Fowler, P.W.; Redmond, D.B. *Symmetry Aspects of Bonding in Carbon Clusters: The Leapfrog transformation.* *Theor. Chim. Acta* 1992, 83, 367-375.
17. Dias, J.R. *Fullerenes to Benzenoids and the Leapfrog Algorithm.* *Chem. Phys. Lett.* 1993, 204, 486-490; Dias, J.R. *Benzenoids and Fullerenes and the Circumscribing and Leapfrog Algorithms.* *New J. Chem.* 1994, 18, 667-673.
18. Dias, J.R. *Benzenoid Series Having a Constant Number of Isomers. 3. Total Resonant Sextet Benzenoids and Their Topological Characteristics.* *J. Chem. Inf. Comput. Sci.* 1991, 31, 89-96; Cyvin, B.N.; Brunvoll, J.; Cyvin, S.J. *Notes on Fully Benzenoid Hydrocarbons and Their Constant-Isomer Series.* *J. Chem. Inf. Comput. Sci.* 1992, 32, 72-78.
19. Gao, Y.-D.; Herndon, W.C. *Fullerenes with Four-Membered Rings.* *J. Am. Chem. Soc.* 1993, 115, 8459-8460.
20. Raghavachari, K.; Zhang, B.; Pople, J.A.; Johnson, B.G.; Gill, P.M.W. *Isomers of C<sub>24</sub>. Density Functional Studies Including Gradient Corrections.* *Chem. Phys. Lett.* 1994, 220, 385-390.
21. Aihara, J. *Kinetic Stability of Fullerenes with Four-Membered Rings.* *J. Chem. Soc. Faraday Trans.* 1995, 91, 4349-4353.
22. Cyvin, S.J.; Cyvin, B.N.; Brunvoll, J. *General Formulations for Some Polycyclic Hydrocarbons. Constant-Isomer Series and a Formula Index.* *Chem. Phys. Lett.* 1993, 201, 273-277.
23. Wakabayashi, T.; Achiba, Y. *A Model for the C<sub>60</sub> and C<sub>70</sub> Growth Mechanism.*

- Chem. Phys. Lett. 1992, 190, 465-468; Hutter, J.; Luthi, H.P.; Diederich, F. Structures and Vibrational Frequencies of Carbon Molecules  $C_2$ - $C_{18}$  Calculated by Density Functional Theory. J. Am. Chem. Soc. 1994, 116, 750-756; Taylor, P.R.; Bylaska, E.; Weare, J.H.; Kawai, R.  $C_{20}$ : Fullerene, Bowl, or Ring?. New Results from Coupled-Cluster Calculations. Chem. Phys. Lett. 1995, 235, 558-563; Plattner, D.A.; Houk, K.N.  $C_{18}$  Is a Polyynes. J. Am. Chem. Soc. 1995, 117, 4405-4406; Wang, Z.; Day, P.; Pachter, R. Ab Initio Study of  $C_{20}$  Isomers. Chem. Phys. Lett. 1996, 248, 121-126.
24. Jemmis, E.D.; Sastry, G.N.; Mehta, G. Synthetic Strategies towards  $C_{70}$ . J. Chem. Soc. Perkin Trans. 2 1994, 437-441.
25. Senn, P. Computation of the Cartesian Coordinates of Buckminsterfullerene. J. Chem. Educ. 1995, 72, 302-303.
26. Goeres, A.; Sedmayr, E. On the Nucleation Mechanism of Effective Fullerite Condensation. Chem. Phys. Lett. 1991, 184, 310-317; Taylor, R.; Langley, G.J.; Kroto, H.W.; Walton, D.R.M. Formation of  $C_{60}$  by Pyrolysis of Naphthalene. Nature 1993, 366, 728-731; Bachmann, M.; Griesheimer, J.; Homann, K.-H. The Formation of  $C_{60}$  and its Precursors in Naphthalene Flames. Chem. Phys. Lett. 1994, 223, 506-510; Hepp, H.; Siegmann, K.; Sattler, K. New Aspects of Growth Mechanisms for Polyaromatic Hydrocarbons in Diffusion Flames. Chem Phys. Lett. 1995, 233, 16-22.
27. Scott, L.T.; Hashemi, M.; Meyer, D.; Warren, H. Corannulene: A Convenient New Synthesis. J. Am. Chem. Soc. 1991, 113, 7082-7084.
28. Lafleur, A.L.; Howard, J.B.; Marr, J.A.; Yadav, T. Proposed Fullerene Precursor Corannulene Identified in Flames Both in the Presence and Absence of Fullerene

- Production. *J. Phys. Chem.* 1993, 97, 13539-13543.
29. Chang, T.-M.; Naim, A.; Ahmed, S.N.; Goodloe, G.; Shevlin, P.B. On the Mechanism of Fullerene Formation. *J. Am. Chem. Soc.* 1992, 114, 7603-7604.
30. Dias, J.R. Algorithm for Generating Fullerenes by Circumscribing. *J. Chem. Inf. Comput. Sci.* 1994, 34, 248-251.
31. Crowley, C.; Kroto, H.W.; Taylor, R.; Walton, D.R.M.; Bratcher, M.S.; Cheng, P.-C.; Scott, L.T. Formation of [60]Fullerene by Pyrolysis of Corannulene, 7,10-bis(2,2'-Dibromovinyl)fluoranthene, and 11,12-Benzofluoranthene. *Tetrahedron Lett.* 1995, 36, 9215-9218.
32. Sarobe, M.; Flink, S.; Jenneskens, L.W.; van Poecke, B.L.A.; Zwikker, J.W. Cyclopent[fg]acepyrylene, Cyclopent[jk]acepyrylene, Cyclopent[mn]acepyrylene: Novel C<sub>20</sub>H<sub>10</sub> Cyclopenta-fused Polycyclic Aromatic Hydrocarbons. *J. Chem. Soc., Chem. Commun.* 1995, 2415-2416; Scott, L.T.; Necula, A. Synthesis and Characterization of the three Dicyclopentapyrenes. *J. Org. Chem.* 1996, 61, 386-388.
33. Rabideau, P.W.; Abdourazak, A.H.; Folsom, H.E.; Marcinow, Z.; Sygula, A.; Sygula, R. Buckybowls: Synthesis and ab Initio Calculated Structure of the First Semibuckminsterfullerene. *J. Am. Chem. Soc.* 1994, 116, 7891-7892.
34. Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. From 4,4'-Bi-4*H*-cyclopenta[def]phenanthrenylidene towards [5,5]Circulene. *Tetrahedron Lett.* 1994, 35, 7013-7014; Hagen, S.; Christoph, H.; Zimmermann, G. From 4-[9*H*-Fluorenylidene-(9)]-4*H*-cyclopenta[def]phenanthrene to Fluoreno[1,9,8-*abcd*]corannulene and Difluoreno[1,9,8,7-*cdefg*:2',1',9',8'-*klmno*]anthracene.

Tetrahedron 1995, 51, 6961-6970.

35. Dias, J.R. Indacenooid Isomers of Semibuckminsterfullerene (Buckybowl) and Their Topological Characteristics. *J. Chem. Inf. Comput. Sci.* 1995, 35, 148-151.
36. Fowler, P.W.; Mitchell, D. Electronic and Steric Factors in the Stability of a Prot fullerene Framework: Indacenooid Isomers of  $C_{30}H_{12}$ . *J. Chem. Inf. Comput. Sci.* 1995, 35, 874-878.
37. Wakabayashi, T.; Shiromaru, H.; Kikuchi, K.; Achiba, Y. A Selective Isomer Growth of Fullerenes. *Chem. Phys. Lett.* 1993, 201, 470-474.
38. Dias, J.R. Deciphering the Information Content of Polycyclic Conjugated Hydrocarbon Formulas - From Benzenoids to Fullerenes. *Tetrahedron*, 1993, 49, 9207-9220.