

# Algorithm for Generating Fullerenes by Circumscribing

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The generation of fullerenes by successively circumscribing base excised internal structures is detailed. Successive circumscribing of carbon ring fragments represents one possible growth scenario by which fullerenes can form in carbon vapor.

## INTRODUCTION

If a polycyclic conjugated hydrocarbon is encircled by a ring of carbon atoms and incremented by additional hydrogens in such a way as to form only hexagonal rings, then this process is referred to as circumscribing (with hexagonal rings). If this process is reversed, then one obtains the excised internal structure (EIS).<sup>1</sup> To be circumscribable by hexagonal rings, the EIS must be devoid of adjacent bay regions on its perimeter. On successively circumscribing, a qualified base EIS eventually becomes a first generation member of some constant-isomer series.<sup>2</sup> Constant-isomer series are infinite polycyclic conjugated hydrocarbon sets of increasing formulas having equal numbers of isomers of a given class. Successively circumscribing benzene, naphthalene, and pyrene gives the three respective one-isomer benzenoid series of infinite extent. Symmetry between a base EIS and its successors is preserved when one successively circumscribes it with exclusively hexagonal rings.<sup>3,4</sup> Herein, we present an algorithm for successively circumscribing a base EIS with a combination of pentagonal and hexagonal rings which ultimately terminates at a fullerene with 12 pentagonal rings or terminates at a system that can be capped to give a fullerene with 12 pentagonal rings.<sup>5</sup> In this case, symmetry is not necessarily preserved between an EIS and its generated successors. The smallest fullerene that can have at least one of its isomers with all twelve of its pentagonal rings isolated occurs at  $C_{60}$ . Thus, since fullerene isomers with isolated pentagonal rings are the more stable ones, we will focus our major efforts to these systems for fullerenes larger than  $C_{60}$ . Herein, the term *fullerene* should be understood to be a carbon polyhedral cage structure possessing only pentagonal and hexagonal rings.

## GENERATION OF FULLERENES BY CIRCUMSCRIBING

To generate the Schlegel of a fullerene having a maximum number of its 12 pentagonal rings (sometimes including the outer perimeter) isolated, one must successively circumscribe a given EIS devoid of proximate bay regions until the number of degree-2 vertices are reduced to 6 or less. At each circumscribing step formation of adjacent pentagonal rings, which is always possible for carbon cage clusters of 60 carbons or more, should be avoided. At each step of circumscribing, different arrangements of the pentagonal rings may be possible. Adjacent bay regions should only be allowed in the next to the last step. If there are five or six degree-2 vertices, one should circumscribe a final time; this last step will result in the simultaneous formation of either five or six adjacent bay regions and is equivalent to capping with cyclopentadienyl-

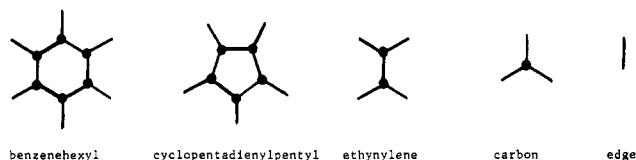


Figure 1. Elementary carbon fragments used in capping per the circumscribing algorithm.

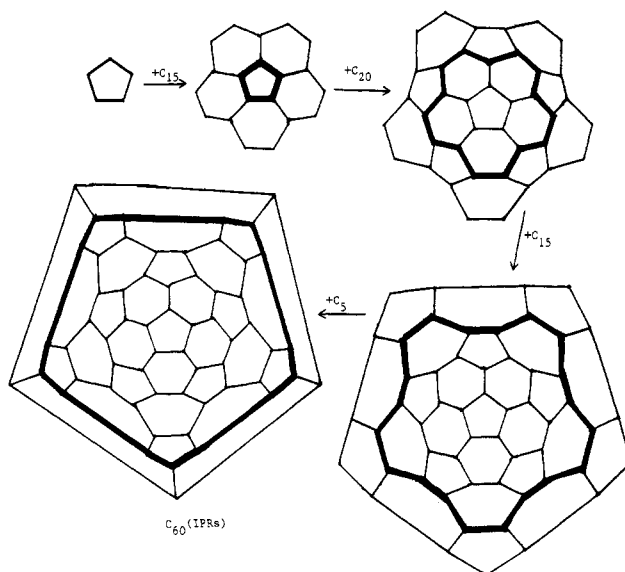
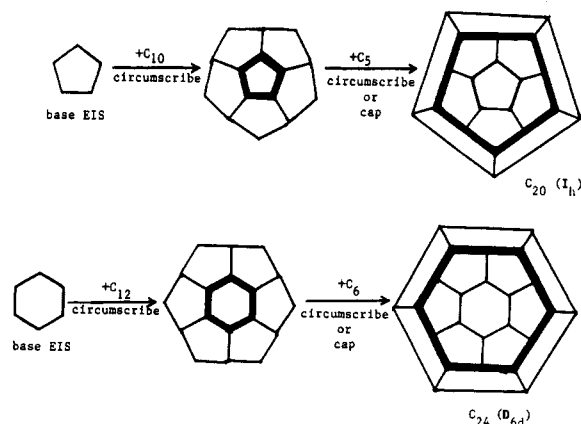


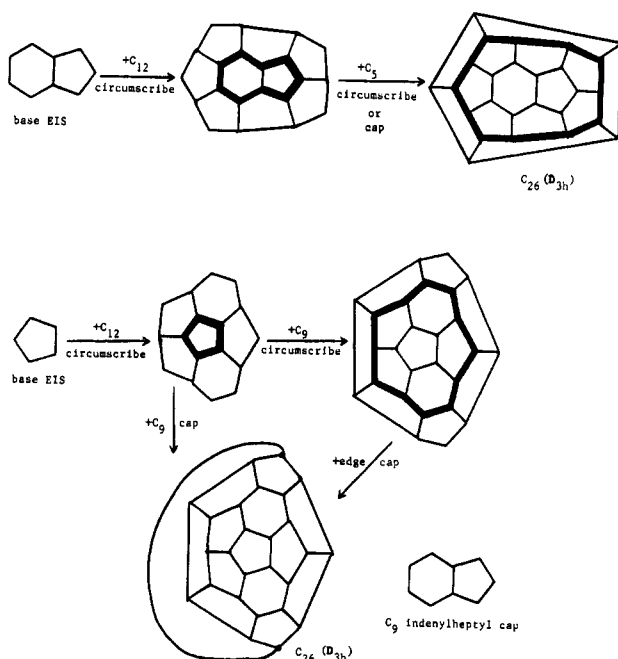
Figure 2. Successive circumscribing of  $C_5$  cyclopentadienylpentyl, generating a  $C_{60}$  (IPRs) buckminsterfullerene. Each prior EIS is shown in bold outline.

pentyl or benzenehexyl, respectively. If there are four degree-2 vertices, capping is done with a  $C_2$  unit or, on rare occasions, with two noncrossing edges. If there are three degree-2 vertices, capping is done with a carbon atom. If there are two degree-2 vertices, an edge (bond) is connected from one to the other. Figure 1 presents these five elementary capping units. All the circuits formed in the last step are hexagonal or nonadjacent pentagonal rings. At each step of this algorithm,  $N_c' = N_c + 2N_H + 6 - r's$ ,  $N_H' = N_H + 6 - r's$ , and  $-n_0 + n_2 = 6 - r_s$  are applicable. The  $C_{60}$ (IPRs) fullerene can be generated by each of the above five different elementary capping processes. Figure 2 fully illustrates the generation of buckminsterfullerene by successive circumscribing of cyclopentadienylpentyl where each prior EIS is shown by the bold outline. One may be able to stop the successive circumscribing process before the number of degree-2 vertices is reduced to six or less and cap with a larger carbon fragment to generate appropriate fullerenes. While these cases might more closely represent actual carbon vapor elementary reactions, from an algorithmic point of view these larger carbon

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**Figure 3.** Generation of the Schlegels for the  $C_{20}$  and  $C_{24}$  fullerenes by successive circumscribing. Each prior excised internal structure is shown in bold outline.

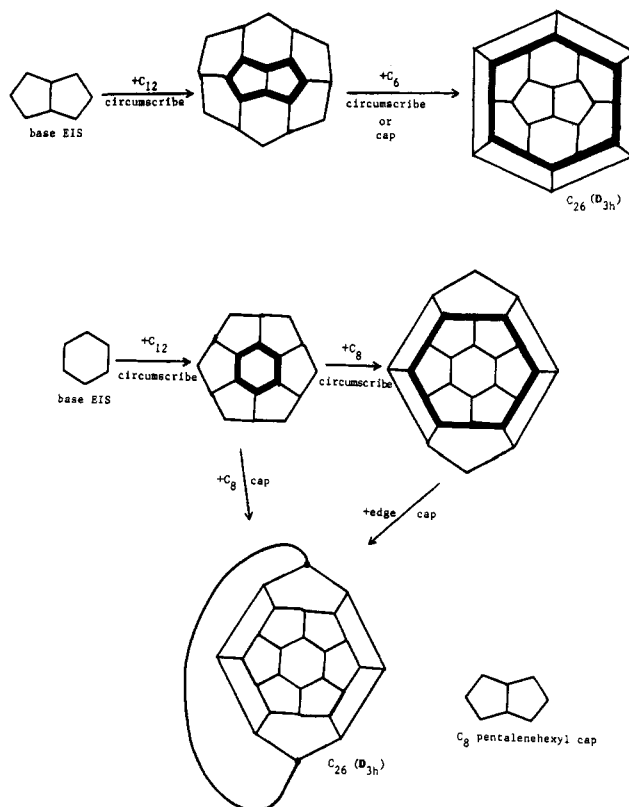


**Figure 4.** Generation of the  $C_{26}$  fullerene by circumscribing and capping.

fragment cappings can always be reduced to the above five *elementary* cappings. These five elementary capping units arise quite naturally from the definition of fullerene which is restricted to pentagonal and hexagonal rings; these elementary units represent the smallest distinct substructures used in the construction of fullerenes. The largest circumscribing carbon ring gives a measure of the circumference of the corresponding fullerene. For example, from Figure 2 one can immediately see that the circumference of buckminsterfullerene is 20 carbon atoms.

#### GENERATION OF ALL THE SMALLEST ( $<C_{30}$ ) FULLERENES BY SUCCESSIVE CIRCUMSCRIBING WITH A COMBINATION OF PENTAGONAL AND HEXAGONAL RINGS

Circumscribing cyclopentadienylpentyl with pentagonal rings twice generates  $C_{20}$  ( $I_h$ ), the smallest fullerene,<sup>6</sup> with the dodecahedron structure (Figure 3). Circumscribing benzenehexyl with pentagonal rings twice gives  $C_{24}$  ( $D_{6d}$ ) shown in Figure 3. Note that for a polyhedral  $C_n$  ( $n = N_c$ ), the number of hexagonal rings is given by  $r_6 = (n - 20)/2$  [ $r_6 = 2$ ] and the number of edges by  $q = 3n/2$ . In the generation

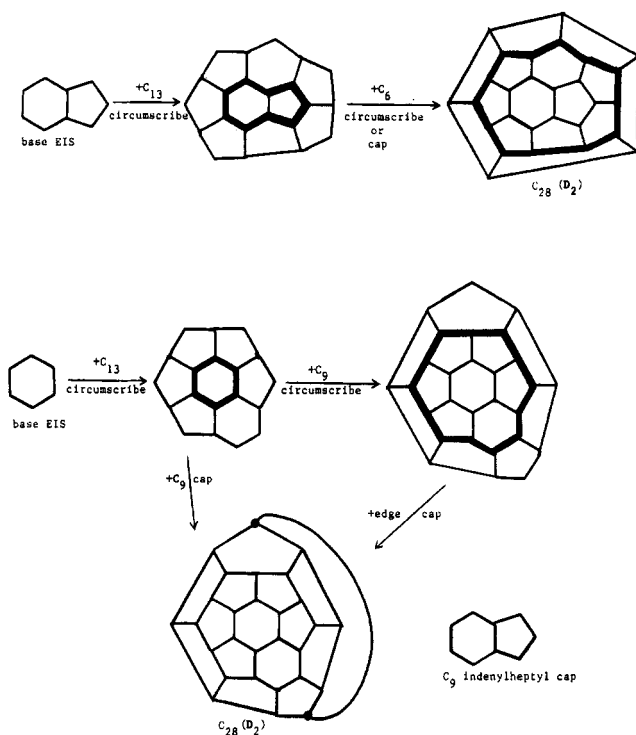


**Figure 5.** Generation of  $C_{26}$  via a second pathway.

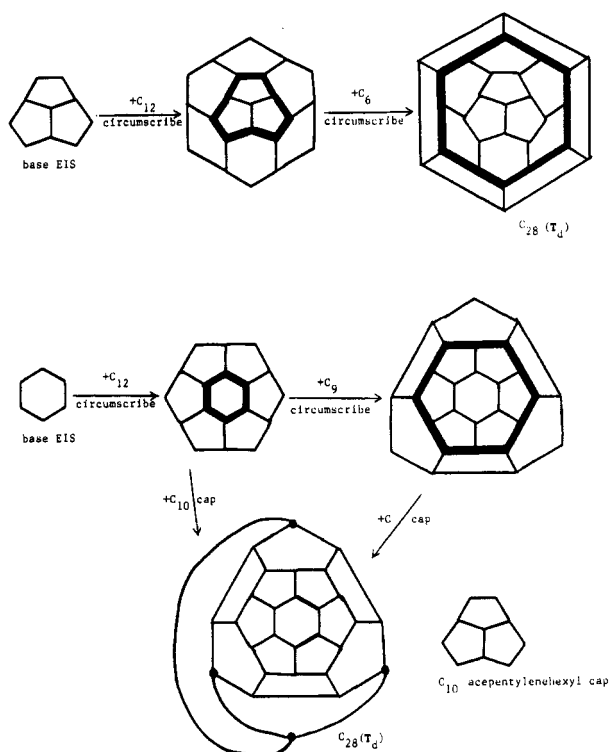
of  $C_{20}$  and  $C_{24}$ , one starts with a  $C_5$  or  $C_6$  base EIS, circumscribes, and ends with a  $C_5$  or  $C_6$  cap, respectively (Figure 3). Figure 4 shows that starting with the indenylheptyl EIS, one can circumscribe twice to obtain  $C_{26}$  ( $D_{3h}$ ), where the second circumscribing step is equivalent to capping with a  $C_5$  cyclopentadienylpentyl. If this sequence is reversed, the  $C_5$  cap becomes the base EIS and indenylheptyl becomes the cap. It should be evident here that a  $C_9$  circumscribing followed by an edge capping (Figure 4) is equivalent to a one-step capping with indenyl. Figure 5 shows that circumscribing pentalenehexyl once and capping with  $C_6$  benzenehexyl also gives  $C_{26}$  ( $D_{3h}$ ). The reverse starts with  $C_6$  as the EIS and caps with pentalenehexyl. Again, it should be obvious that a  $C_8$  circumscribing followed by edge capping (Figure 5) is equivalent to a one-step capping with pentalenehexyl. Figures 6 and 7 present the generation of the two  $C_{28}$  structures, one which corresponds to an enantiomeric pair which is also the first fullerene cage to have adjacent hexagonal rings. Circumscribing acepentylenehexyl twice gives  $C_{28}$  ( $T_d$ ), shown in Figure 7. Going in the reverse direction, starting with  $C_6$  as the base EIS, circumscribing with pentagonal rings, and capping with acepentylenehexyl also gives  $C_{28}$  ( $T_d$ ). Here, one should note that a  $C_9$  circumscribing followed by a carbon capping (Figure 7) is equivalent to a one-step capping with acepentylenehexyl.  $C_{28}$  was the subject of a model ab initio study of the energetics of the Stone–Wales pyracylene rearrangement and appears to be the smallest fullerene to form in significant amounts.<sup>7</sup>

#### GENERATION OF $C_{70}$ (IPRS) FALMERENE BY CIRCUMSCRIBING WITH A COMBINATION OF PENTAGONAL AND HEXAGONAL RINGS

Achiba and co-workers have proposed a ring-stacking kinetic model for the assembly of fullerenes with even carbon rings<sup>8</sup> which is really akin to circumscribing.<sup>1-5</sup> Figure 8 presents a Schlegel of falmerene, where the ultimate (base) EIS is

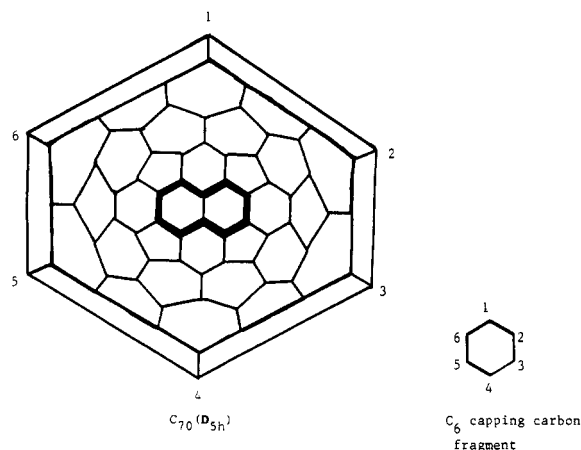


**Figure 6.** Generation of the chiral  $C_{28}$  fullerene by circumscribing and capping.

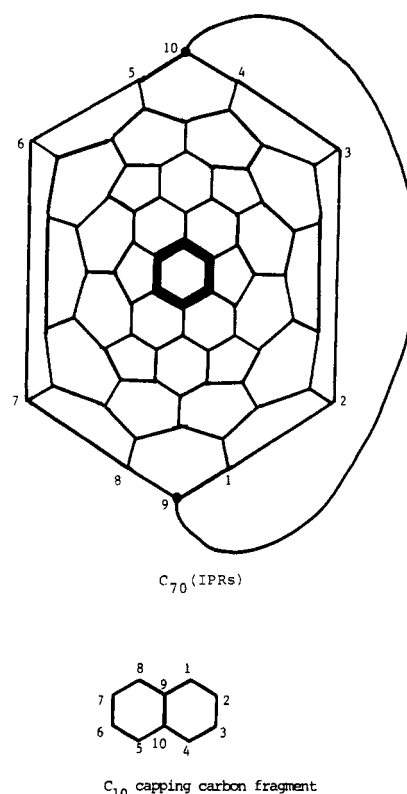


**Figure 7.** Generation of the achiral  $C_{28}$  fullerene by circumscribing and capping.

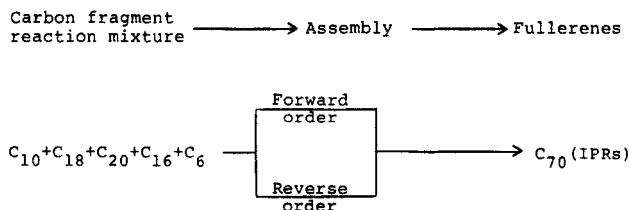
shown in bold. Successive circumscribing of naphthalenoctyl gives falmerene where the last circumscribing is equivalent to capping with the benzenehexyl carbon fragment (Figure 8). Reversing this process by interchanging the base EIS of naphthalenoctyl and capping carbon fragment of benzenehexyl and reversing the order of circumscribing carbon rings gives the Schlegel shown in Figure 9. This is summarized in Figure 10. Again, notice that the circumference of falmerene is 20 carbon atoms.



**Figure 8.** Circumscribing naphthalenoctyl ( $C_{10}$ ) four successive times with a combination of pentagonal and hexagonal rings, generating the Schlegel of falmerene. The ultimate excised internal structure (EIS) is shown in bold.



**Figure 9.** Generation of falmerene by successively circumscribing benzenehexyl four times and capping with an edge in the final step.



**Figure 10.**  $C_{70}$  (IPRs) fullerene assembly by the ring-stacking model of Achiba and co-workers.

## CONCLUSION

The excised internal structure/circumscribing concept has been employed to further our understanding of the topological relationships of fullerenes. It is believed that this algorithm incorporates elements that can be linked to the way that fullerenes are actually formed. For this algorithm to achieve

its maximum convenience, a rapid method which does require one to compute the characteristic polynomials for distinguishing between two isomeric Schlegels would be desirable.

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