

Indacenoid Isomers of Semibuckminsterfullerene (Buckybowl) and Their Topological Characteristics

Jerry Ray Dias

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

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Further details on the prior enumeration of the 45 $C_{30}H_{12}$ indacenoid isomers of semibuckminsterfullerene (circofulvalene) are reported. The smallest even-carbon diradical indacenoids are identified. Topological/molecular orbital characteristics of circofulvalene and its related indacenoid isomers are compared.

INTRODUCTION

An indacenoid is a conjugated $p\pi$ system of fused rings of which two are pentagonal and all others are hexagonal. In our determination of the 51 constant-isomer indacenoids of the formula $C_{58}H_{16}$, the 45 predecessor $C_{30}H_{12}$ indacenoid isomers were enumerated but not explicitly reported.¹ In this work, our observed topological paradigm for fused benzenoids² and fluorenoids/fluoranthenoids³ was extended to indacenoids. In brief, the observed topological paradigm consists of the following elements: (1) A corresponding formula periodic table contains edge formulas that belong to constant-isomer series generated by successive circumscribing. (2) As the formula of the first generation members to each successive constant-isomer series increases so does the corresponding number of isomers. (3) The number of isomers increases according to a regular pattern where some of the isomer numbers repeat. (4) In those constant-isomer series having the same number of isomers, there is a one-to-one matching between the structures. (5) The topological invariants in this one-to-one matching of structures are symmetry, number of bay regions and selective lineations, and the adjacency/nonadjacency of pentagonal rings.

The recent synthesis of the $C_{30}H_{12}$ indacenoid referred to as semibuckminsterfullerene or buckybowl⁴ has renewed our interest in indacenoid polycyclic hydrocarbons composed of two pentagonal rings among otherwise hexagonal ones. In analogy to Clar's use of circobiphenyl for the most stable $C_{38}H_{16}$ benzenoid, we will refer to Rabideau's buckybowl⁴ as circofulvalene. Herein, all depictions will be given in terms of (planar) molecular graphs which are C–C σ -bond skeletons. While reviewing our method for indacenoid enumeration with $C_{30}H_{12}$, we will extend these results. Specifically, it will be argued that circofulvalene is among the more stable $C_{30}H_{12}$ indacenoid isomers, if not the most stable. The smallest radical even-carbon indacenoids will be depicted. There are two kinds of even-carbon radical excised internal structures which have distinctly opposite properties in regard to circumscribing. For indacenoids with isolated pentagonal rings (IPRs) another topological invariant for indacenoids is the presence/absence of the fulvalene substructure which can participate in the Stone–Wales transformation.⁵ The eigenvector topological invariants associated with the eigenvalues of ± 1 , $\pm\sqrt{2}$, and ± 2 will be discussed.⁶ The subspectrality of the two more stable D_{2h} $C_{30}H_{12}$ isomers will be detailed.

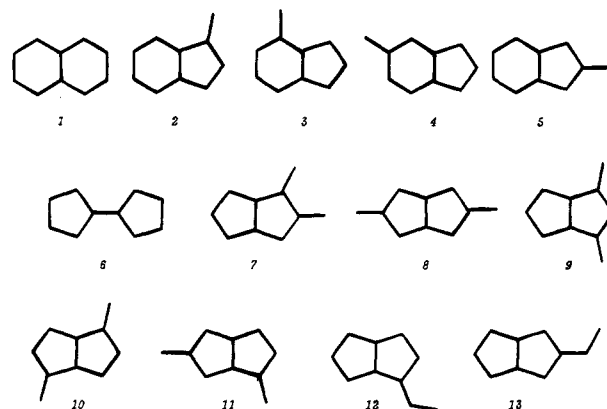


Figure 1. The ultimate excised internal structures of the 45 $C_{30}H_{12}$ indacenoid isomers.

ENUMERATION OF $C_{30}H_{12}$ INDACENOID ISOMERS

The following recursion equations give the formula of an indacenoid derived by circumscribing where N_C is the number of carbons and N_H is the number of hydrogens before circumscribing, and N'_C and N'_H are these numbers after circumscribing

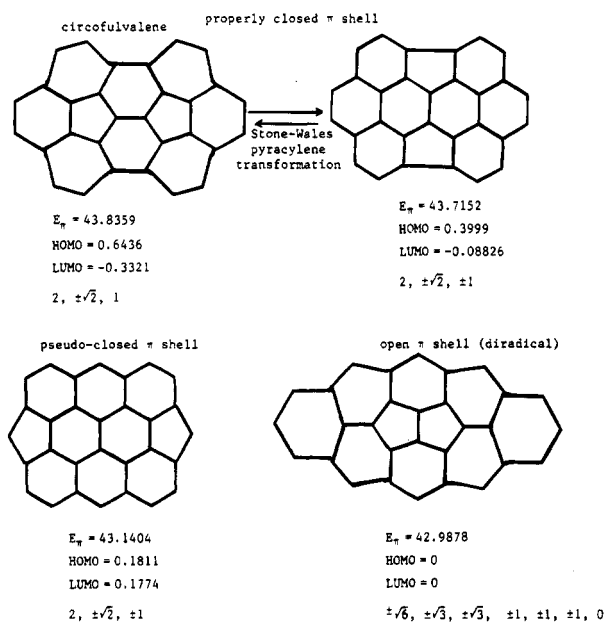
$$N'_C = N_C + 2N_H + 4 \quad \text{and} \quad N'_H = N_H + 4$$

Decircumscribing an indacenoid of formula C_nH_s ($n = N_C$ and $s = N_H$) gives an excised internal structure of the formula $C_{n-2s+4}H_{s-4}$. Decircumscribing the $C_{30}H_{12}$ indacenoids give excised internal structures of the formula $C_{10}H_8$. Figure 1 gives all the circumscribable $C_{10}H_8$ structures having two hexagonal (1, naphthalene), one pentagonal and one hexagonal (2–5, methylenylindenes), and two pentagonal (6–13, fulvalene, dimethylenylpentalenenes, and vinylpentalenenes) rings. Circumscribing naphthalene (1) with all possible arrangements of two pentagonal and six hexagonal rings gives 10 distinct $C_{30}H_{12}$ indacenoid isomers. Circumscribing of the methylenylindenes 2–5 with all possible arrangements of one pentagonal and seven hexagonal rings gives seven, seven, eight, and five $C_{30}H_{12}$ indacenoid isomers, respectively. Circumscribing each of the excised internal structures 6–13 with eight hexagonal rings gives eight more $C_{30}H_{12}$ indacenoid isomers. This gives a total of 45 $C_{30}H_{12}$ indacenoid isomers (Table 1). No other $C_{30}H_{12}$ indacenoid isomers are possible. Of these, 15 C_s , 1 C_{2h} , 4 C_{2v} , and 3 D_{2h} isomers have IPRs. Note that circumscribing excised internal structures with exclusively hexagonal rings results in uniquely defined successor structures where symmetry is preserved

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Table 1. Antecedent Indacenoid Isomers to Constant-Isomer Series

formula	no. of isomers pseudosymmetry classification			
	C_s	C_{2h}	C_{2v}	D_{2h}
$C_{15}H_9$	4	1		
$C_{20}H_{10}$	11	3	5	
$C_{25}H_{11}$	21	4		
$C_{30}H_{12}$	34	2	5	4

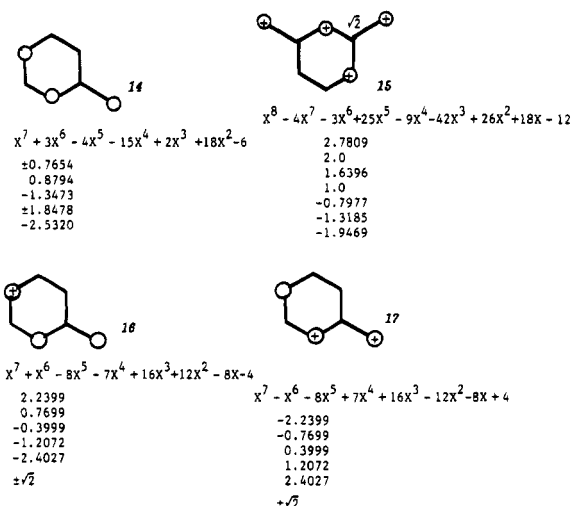
**Figure 2.** The four D_{2h} molecular graphs of the $C_{30}H_{12}$ indacenoid isomers and their HMO parameters.

as illustrated by the circumscribing of 6–13 versus 1–5 (Figure 1). The 51 first generation structures belonging to the $C_{58}H_{16}$ constant-isomer indacenoid series are obtained by circumscribing these 45 $C_{30}H_{12}$ indacenoid isomers along with the six methylenyl derivatives of the $C_{29}H_{11}$ first generation structure of the C_{2v} one-isomer indacenoid series shown in Figure 1 of ref 1. Note that the point group symmetry used here disregards the fact that pentagonal rings induce curvature in the molecular system.

Table 1 also summarizes the pseudosymmetry classification for the 19 indacenoid isomers of corannulene $C_{20}H_{10}$. Of these, $4C_s$, $2C_{2h}$, and $4C_{2v}$ isomers have IPRs.

TOPOLOGICAL/MOLECULAR ORBITAL CHARACTERISTICS

Molecular Orbital Results. In the following molecular orbital discussion, it will be assumed that the effects of curvature induced by the pentagonal rings can be partitioned out as an additive component which will be treated in terms of adjacency/nonadjacency of the pentagonal rings. Figure 2 summarizes the HMO results for the (planar) molecular graphs of the four D_{2h} $C_{30}H_{12}$ indacenoid isomers. The MO comparison of these four isomers turns out to be the most fascinating example that the author has ever encountered. The molecular graph of circofulvalene has the largest HMO E_π energy and HOMO–LUMO difference and is the only $C_{30}H_{12}$ D_{2h} isomer to have been synthesized.⁴ The second structure in Figure 2 is related to circofulvalene, the first structure, via the Stone–Wales pyracylene transformation.⁵ Mirror-plane fragmentation, twice in perpendicular directions, of circofulvalene and its Stone–Wales isomer leads to four edge/vertex weighted graphs of each.⁷ Circofulvalene and

**Figure 3.** Mirror-plane fragments of circofulvalene and its Stone–Wales isomer.

its Stone–Wales isomer are subspectral since fragments 14 and 15 in Figure 3 occur in both. In addition, the complementary fragments 16 and 17 having complementary eigenvalues also occur in circofulvalene and its Stone–Wales isomer, respectively. In all, circofulvalene and its Stone–Wales isomer have 17 common eigenvalues out of 30. Based on the principle that reactions involving minimal electronic reorganization will have lower activation energies, one should expect that the Stone–Wales transformation between these first two structures should be reasonably favorable. Phenalenyl is a mirror-plane fragment of the fourth structure in Figure 2 establishing that it has eigenvalues of $\pm\sqrt{6}$, $\pm\sqrt{3}$, $\pm\sqrt{3}$, ± 1 , ± 1 , ± 1 , and 0; this last structure has the smallest E_π value, a zero HOMO–LUMO difference, and adjacent pentagonal rings. By all measures, the order of stability of the four D_{2h} $C_{30}H_{12}$ molecular graphs in Figure 2 progressively decreases from the first to the last molecular graph.

Using Fowler's terminology,⁸ both circofulvalene and its Stone–Wales isomer (Figure 2) are properly closed π shell, the third D_{2h} isomer is pseudoclosed π shell, and the fourth D_{2h} isomer is open π shell. A $p\pi$ -electronic molecular system is properly closed shell if its HOMO is a bonding and its LUMO is an antibonding MO, pseudoclosed shell if its LUMO is a bonding MO, and open shell if its HOMO and LUMO are degenerate. Most fullerenes have been shown to be pseudoclosed shell.⁸ Placing sulfur at the solo position of each pentagonal ring in the third isomer in Figure 2 should lead to interesting conducting properties similar to those exhibited by tetrathiafulvalene.⁹

EVEN-CARBON RADICAL SYSTEMS

Our prior work with benzenoids demonstrated that there were two types of diradicals which have opposite results in regard to preservation of radical character upon circumscribing. Circumscribing bisallyl diradical gave the nonradical benzenoid, bisanthene ($C_{28}H_{14}$), whereas circumscribing trimethylenemethane diradical gave triangulene diradical ($C_{22}H_{12}$).¹⁰ Borden classifies bisallyl as a disjoint radical and trimethylenemethane as a nondisjoint diradical.¹¹ In Figure 1, 8 and 9 are diradicals. While circumscribing 9 gives a nonradical successor $C_{30}H_{12}$ indacenoid, circumscribing 8 gives the fourth D_{2h} $C_{30}H_{12}$ structure in Figure 2, which is a diradical, and circumscribing it again gives the diradical

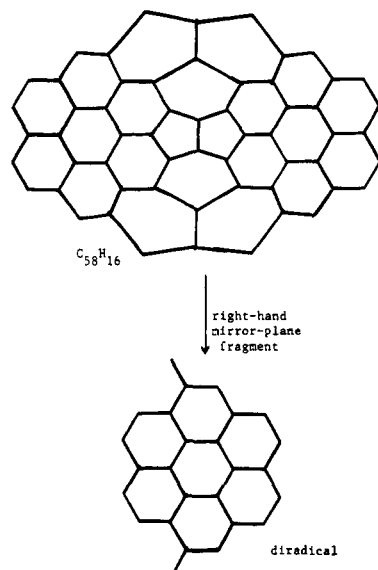


Figure 4. Mirror-plane fragmentation of the above $C_{58}H_{16}$ member of a constant-isomer indacenoid series proves that it is a diradical.

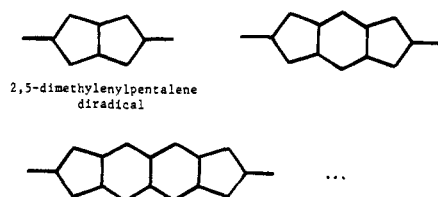


Figure 5. Family of ultimate excised internal structures that generate indacenoid diradicals upon successive circumscribing with hexagonal rings.

$C_{58}H_{16}$ structure shown in Figure 4; mirror-plane fragmentation¹² of the $C_{58}H_{16}$ structure in Figure 4 gives 2,7-dimethylenylcoronene diradical proving that the predecessor $C_{58}H_{16}$ structure must also be at least a diradical. Thus, circumscribing **9** and **8** with hexagonal rings is analogous to circumscribing bisallyl and trimethylenemethyl diradical with hexagonal rings, respectively. The $C_{58}H_{16}$ structure in Figure 4 represents the smallest even-carbon diradical constant-isomer indacenoid. A family of ultimate excised internal structures that give diradical even-carbon indacenoids upon successive circumscribing with hexagonal rings is given in Figure 5.

The above examples involved an ultimate excised internal structure that was connected. Appropriate circumscribing of two (disconnected) methyl radicals with hexagonal rings give the nonradical benzenoid, perylene. Appropriate circumscribing of two trimethylenemethyl diradicals gives a $C_{38}H_{18}$ benzenoid referred to as Clar's goblet.¹³ Since Clar's goblet has the same number of peaks as valleys but is still a diradical, it is called a concealed non-Kekulean (diradical) benzenoid. Clar's goblet is a concealed diradical because it contains two less Davison–Gordon paths than peaks (or valleys).¹⁴ This difference becomes zero upon circumscribing Clar's goblet with hexagonal rings resulting in a $C_{80}H_{24}$ nonradical benzenoid. Peak/valley differences are preserved during circumscribing, and, therefore, only concealed non-Kekulean benzenoids can become Kekulean when circumscribed a sufficient number of times. This property was essential for the results and conclusions that we obtained for the polyradical subsets of constant-isomer benzenoid series.¹⁵

From the above it should be evident that facile methods for recognition radical versus nonradical benzenoids are

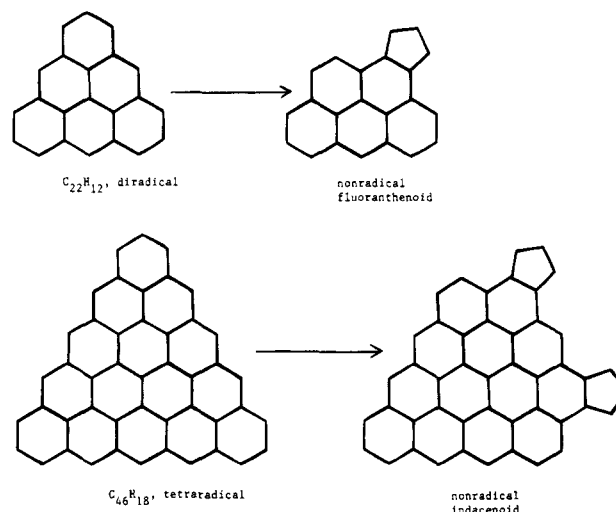


Figure 6. Transforming polyradical benzenoids to nonradical isomeric $p\pi$ -systems.

much better developed than they are for other polycyclic conjugated hydrocarbons.^{14,16} Further insights toward recognition of diradical fluoranthene and even-carbon indacenoids are provided by the possible transformations given in Figure 6. Triangulene diradical ($C_{22}H_{12}$, $\delta = 2$) can be transformed to a nonradical fluoranthene and pentaangulene tetraradical ($C_{46}H_{18}$, $\delta = 4$) can be transformed to a nonradical indacenoid as shown. From these results one can surmise that although a given even-carbon benzenoid formula can correspond to many more fluoranthene or indacenoid isomers, there must be far fewer diradical species.

EIGENVECTORS FOR THE EIGENVALUES OF 2, $\sqrt{2}$, AND 1

Our previous paper⁶ detailed an algorithm which implemented the following equation in determining the unnormalized eigenvector coefficients for a given eigenvalue X_i

$$-X_i C_{iu} + C_{ir} + C_{is} + C_{it} = 0$$

where C_{iu} is the eigenvector coefficient for some central (carbon) vertex u with adjacent vertices of r , s , and t . Figure 7 presents the unnormalized eigenvector coefficients appended to the ovalene-related structures for the eigenvalue of 2 which were determined by this method.⁶ The first three structures in Figure 7 are the three nonradical D_{2h} $C_{30}H_{12}$ indacenoids from Figure 2, the fourth structure is ovalene, and the last structure is a fluorene discussed on p 96 of ref 7. A general pattern is evident. Note these eigenvectors are symmetric in regard to the vertical and horizontal molecular symmetry axes. The eigenvector for the -2 eigenvalue of ovalene can be obtained via the pairing-theorem by simply changing the signs of the coefficients at the nonstarred positions.

The second and third molecular graphs shown in Figure 2 are embeddable by ethene and consequently possess the ± 1 eigenvalues of ethene. The corresponding eigenvectors can easily be from those embedding patterns. Circofulvalene is semiembeddable by ethene.⁷ The third molecular graph of Figure 2 is also embeddable by allyl and has eigenvalues of $\pm\sqrt{2}$. The eigenvectors for the eigenvalues of $\pm\sqrt{2}$ belonging to circofulvalene and its Stone–Wales isomer can be determined using our algorithm.⁶

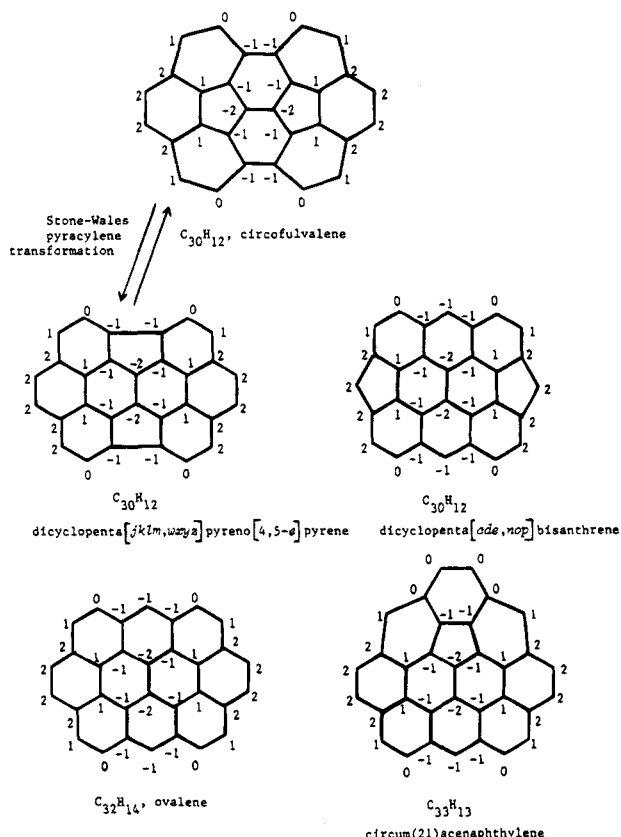


Figure 7. The unnormalized eigenvector coefficients are shown on the above ovalene-related structures for the eigenvalue of 2.

THE FULVALENE SUBSTRUCTURE AS AN INVARIANT

Correspondent constant-isomer indacenoid series have the same isomer number and symmetry distribution among their membership. Two nonisomeric indacenoids, each belonging to the same generation of a correspondent series, having the same pseudosymmetry, number of bay regions, adjacency/nonadjacency of pentagonal rings, and subset relative stability ranking are called correspondents. In this one-to-one matching of two correspondents, we now give a finer classification of nonadjacency of pentagonal rings. Nonadjacent pentagonal rings will either be close enough to form a fulvalene substructure or more remote and unable to do so. This criterion is related to Taylor's meta relationship that permits minimization of bond orders in pentagonal rings¹⁷ and is a necessary structural prerequisite for the Stone-Wales rearrangement⁵ to take place. Preliminary evaluation of a limited number of constant-isomer indacenoid series suggests that the formation of a fulvalene substructure in indacenoids also has a one-to-one matching between correspondents. This can be seen by comparing the two ($C_{17}H_9$ versus $C_{27}H_{11}$) six-isomer indacenoid constant-isomer series in Figure 5 of ref 18. This represents another matching topological invariant between two correspondent constant-isomer indacenoid pairs.

CONCLUSION

In this work we have brought to light a number of important new findings in regard to indacenoids that may lend themselves to model studies of fullerenes. Different measures of stability suggest that circocofulvalene is one of the more stable $C_{30}H_{12}$ indacenoids, if not the most stable. Rabideau's research group has also synthesized cyclopent-

tacorannulene which is probably the the most stable member of the $C_{22}H_{10}$ seven-isomer indacenoid constant-isomer series.¹⁹ The topological origin of the eigenvalue 2 in the indacenoid of this study is revealed. It has been argued that introduction of pentagonal rings reduces the probably of formation of even-carbon radical polycyclics. Using the excised internal structure concept, 2,5-dimethylenylpentalene and related molecular systems have been identified as leading to even-carbon diradical indacenoids upon successive circumscribing. The fulvalene substructure has been shown to be an important topological unit in the study of indacenoids and fullerenes. The recent synthesis of $C_{26}H_{12}$ and $C_{30}H_{14}$ indacenoids²⁰ further attests to the timeliness of this work.

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