

Strain-Free Total Resonant Sextet Benzenoids and Their Antisextet Dualists and Retro-Leapfrogs

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The relationships between inner dual, dualist, sextet dualist, and antisextet dualist graphs and excised internal structures are fully delineated. It is proven that the antisextet dualist graph uniquely characterizes all strain-free benzenoids. At the same time, it is shown that the excised internal structure and dualist graph of the retro-leapfrog of all strain-free total resonant sextet benzenoids correspond to their antisextet dualist and sextet dualist graphs, respectively.

INTRODUCTION

Strain-free total resonant sextet (TRS) benzenoids constitute a subclass of benzenoids that comply with Clar's sextet principle.¹ TRS benzenoids contain only two types of rings, either with (circles) or without (no circles) Clar sextets. A circle inscribed within a hexagon represents three mutually permuting double bonds; no ring is allowed to have a single or pair of double bonds. The Clar sextets represented by hexagons containing inscribed circles must be disjoint, that is, surrounded by empty rings. Among other things, TRS benzenoids have a number of carbons (N_c) divisible by six, are devoid of coves and fissures, and have a maximum number of bay regions given by $\eta_o(\text{TRS}) = \frac{1}{2}N_H - 3$ (N_H = number of hydrogens). An astounding isomorphism exists between the whole class of benzenoids and TRS benzenoids if one includes the nonfused polyphenylenes with the TRSs.²

An adaptation of Fowler's leapfrog algorithm³ for fullerenes to benzenoids provided a second proof to the isomorphism that exists between ordinary benzenoids and TRS benzenoids.⁴

Recently, Balaban and Schmalz introduced the use of the antisextet dualist in devising a simple algorithm for the exhaustive enumeration of TRS benzenoids.⁵ The purpose of this paper is to review our alternate algorithm for the exhaustive enumeration of TRS benzenoids and at the same time provide a proof to their observation, "It is remarkable that under the restriction of this paper dealing only with SRBs that are portions of the graphene lattice and have no steric crowding, the antisextet dualist characterizes uniquely all systems **1–60** from Figures 3–6." This proof also shows that this must be true in general for all strain-free TRS benzenoids.

SOME DEFINITIONS

A molecular graph of a benzenoid hydrocarbon (used interchangeably with the term "benzenoid") is its σ -bond skeleton with all the carbons, hydrogens, and π bonds omitted; in discrete mathematics, it is called a polyhex. The molecular graph for a TRS benzenoid will frequently be

augmented with disjoint circles representing aromatic sextets. The benzenoid notation for the total number of carbons (N_c), hydrogens (N_H), and σ bonds is equivalent to the polyhex (molecular graph) notation for total number of vertices (n), degree-2 vertices (s), and lines or edges (q), respectively. There are three distinct kinds of benzenoid carbons, the number of which are denoted by N_{pc} , N_{ic} , and N_H ($N_c = N_{ic} + N_{pc} + N_H$) where N_{pc} and N_{ic} correspond to the peripheral and internal degree-3 molecular graph vertices and N_H to the degree-2 vertices.

Drawing lines between the centers of adjacent hexagons of any benzenoid molecular graph, one obtains a dualist graph.⁶ In general, the dualist graph of the graphite polyhex graph is a triangular lattice. From any given dualist graph, a unique molecular graph can be constructed by placing a regular hexagon around every vertex such that the hexagons are connected only by sharing edges. The dualist graph differs from the inner dual in that any two lines having a common vertex must meet at angles of 60, 120, or 180°; the inner dual has no angle implication. In other words, two or more nonisomorphic polyhexes cannot possess the same dualist but may have the same inner dual.⁶ The dualist graph has also been called a characteristic graph⁷ and bual.⁸

Drawing lines between the centers of the circles symbolizing sextets in hexagons in biphenyl-like positions of a TRS benzenoid, one obtains a triangular dualist called the sextet dualist after discarding the polyhex graph.^{5,9} If one inscribes a point in the center of each triangle within a sextet dualist and connects the points of triangles sharing an edge with a line, the result is an antisextet dualist after discarding the sextet dualist graph.⁵ Alternatively, the antisextet dualist can be generated from a TRS benzenoid by inserting a dot within every empty hexagon, connecting those dots in adjacent empty rings, and peeling away the precursor TRS benzenoid.

The excised internal structure of any benzenoid molecular (polyhex) graph is the graph formed by the internal degree-3 vertices (vertices at the juncture of three hexagons) after stripping away the perimeter carbon vertices.¹⁰ In general, stripping off the perimeter of a C_nH_s benzenoid gives a $C_{n-2s+6}H_{s-6}$ excised internal structure. For example, stripping off the perimeter of 14 carbons ($2s - 6 = 2 \times 10 - 6$)

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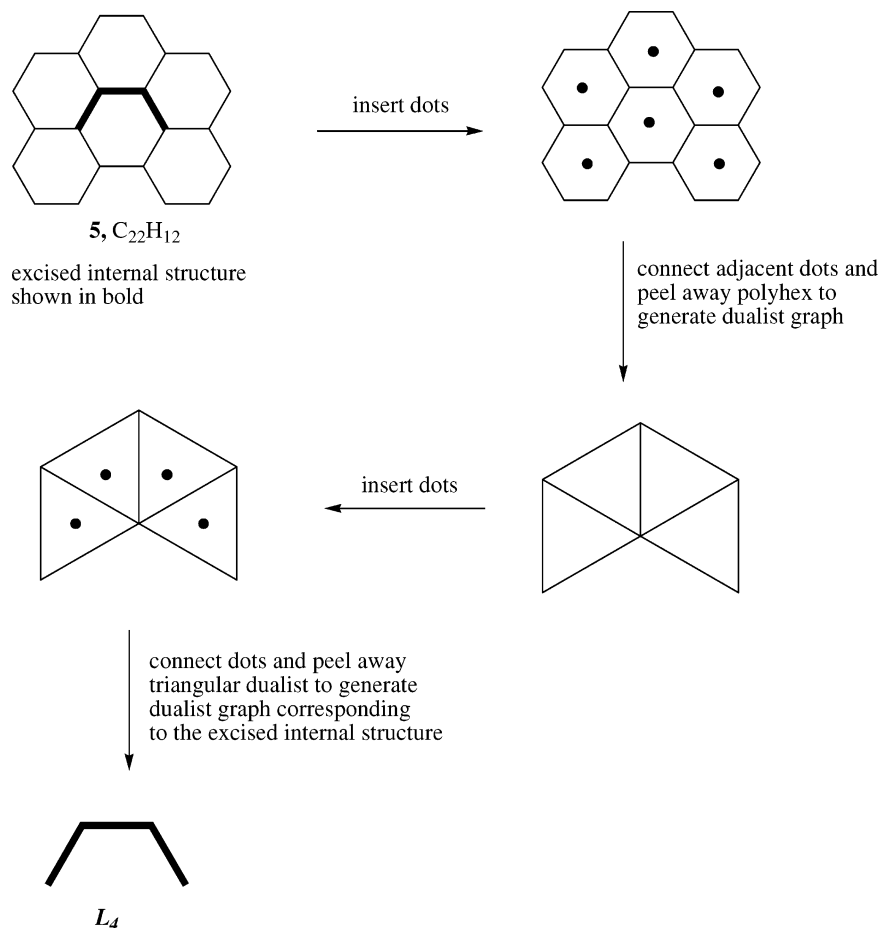


Figure 1. Illustration of the graph theoretical operation to generate the dualist graph and excised internal structure of a polyhex corresponding to benzo[ghi]perylene. The inner dual of the inner dual of a benzenoid gives the excised internal structure of the benzenoid.

from pyrene (C₁₆H₁₀) gives ethene (C₂H₄) upon the transfer of four hydrogens ($s - 6 = 10 - 6$). One needs to distinguish between *peri*-condensed and *strictly peri*-condensed. Strictly *peri*-condensed benzenoids have no cata-condensed appendages or disconnected excised internal structures. Thus, benzo[*a*]pyrene and perylene are *peri*-condensed but are not “strictly *peri*-condensed” because the former has a benzo group which is the smallest cata-condensed appendage and the latter has a disconnected excised internal structure comprised of two methyl radicals. It was shown by Hall⁸ that the inner dual of the inner dual of a strictly *peri*-condensed benzenoid is its excised internal structure (Figure 1); note here that the inner dual and dualist graphs are identical for strictly *peri*-condensed benzenoids. In an initial paper by Cyvin and co-workers, inner dual and excised internal structure was incorrectly interchanged.¹¹

LEAPFROG AND RETRO-LEAPFROG ALGORITHMS

One way of converting any C_nH_s benzenoid to its corresponding TRS benzenoid involves drawing slightly smaller hexagons turned by 30° within each hexagon of the parent benzenoid, connecting the adjacent hexagons so generated, and peeling away the parent graph.¹² In the transformation of a parent (*P*) to its successor leapfrog (*L*), the following correlations are applicable:⁴



The second relationship states that the internal degree-3

$$N_{lc} \rightarrow r(\text{empty})$$

$$r \rightarrow r(\text{sextet})$$

$$N_{pc} \rightarrow \eta_o'$$

$$\eta_i \rightarrow \eta_{i+1}'$$

carbon vertices in the precursor benzenoid become the empty rings in the successor TRS benzenoid. The crucial point that evolves from this correlation is that the excised internal structure of the retro-leapfrog is equal to the antisextet dualist of the leapfrog. The third relationship states that the number of rings in the precursor benzenoid become sextet rings in the successor TRS benzenoid. Thus, the sextet dualist graph obtained by drawing lines between centers of the large circles (i.e., sextet rings) in the TRS benzenoid (leapfrog) is equal to the dualist graph obtained by drawing lines between the centers of the hexagons belonging to the precursor benzenoid (retro-leapfrog). The sextet dualist graph of a TRS benzenoid is identical to the dualist graph of its retro-leapfrog. This is illustrated by comparing the sextet dualist of TRS benzenoid **5** with its retro-leapfrog in Figure 2. To obtain the retro-leapfrog, simply reverse the leapfrog operation.¹² The dualist operation on the triangular graph in Figure 2 gives the **L₄**

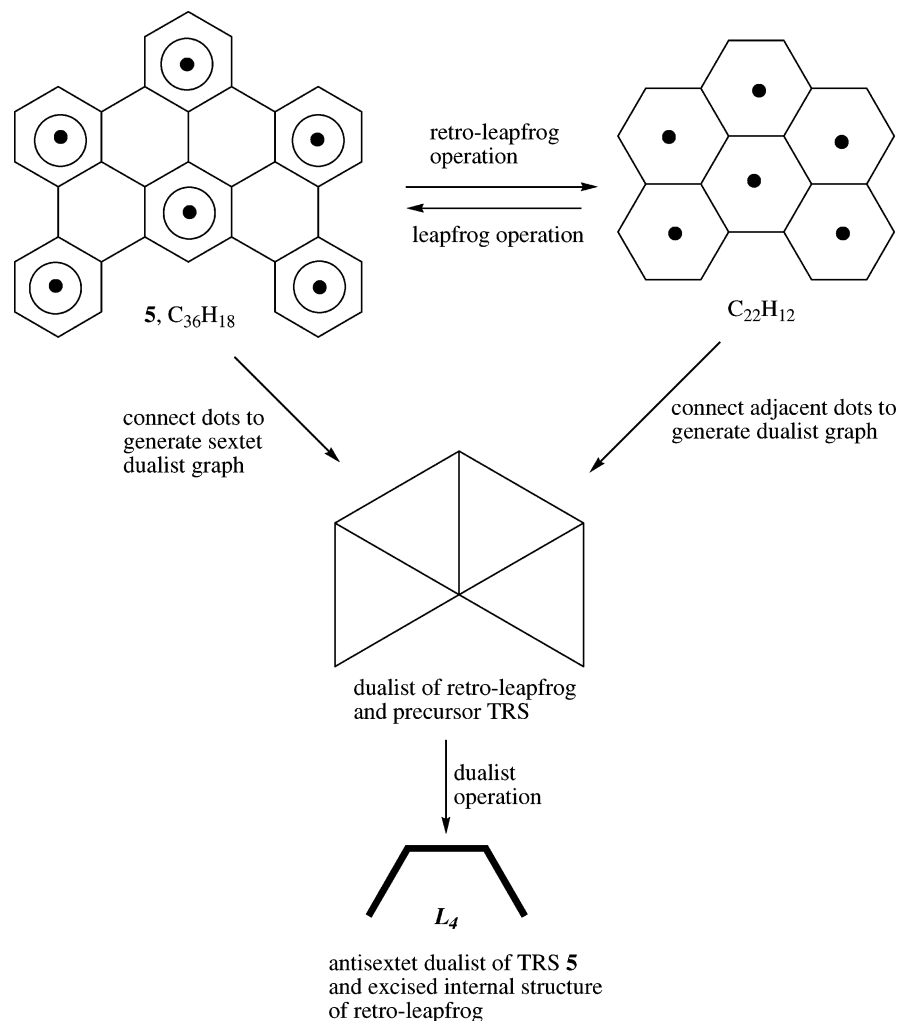


Figure 2. Illustration of the retro-leapfrog of a TRS benzenoid and their corresponding dualist graphs. Compare the latter L_4 graph with that in Figure 1.

graph, which is both the sextet dualist graph belonging to the TRS benzenoid **5** and the excised internal structure belonging to its retro-leapfrog, benzo[ghi]perylene ($C_{22}H_{12}$).

To see this more explicitly, all the retro-leapfrogs of the TRS structures **0–14** in Figure 3 of the Balaban and Schmalz paper⁵ are given in Figure 3 of this paper with their excised internal structures shown in bold. A comparison of the Figure 3 excised internal structures with the antisextet dualists of the TRS structures **0–14** in Figure 3 of the Balaban and Schmalz paper⁵ clearly shows this equality.

LEAPFROG ALGORITHM FOR GENERATING TRS BENZENOID FROM STANDARD BENZENOID

To identify the precursor parent (**P**) formulas corresponding to structures from leapfrogging results in TRS benzenoid structures (**L**), the following equations are applicable:

$$N_c = \frac{1}{3}N_c(\text{TRS}) + \frac{1}{2}N_H(\text{TRS}) + 1$$

For this purpose, the listing of benzenoid structures up to

$$N_H = \frac{1}{2}N_H(\text{TRS}) + 3$$

nine hexagons compiled by Knop and co-workers is useful.¹³ All TRS structures listed in our books¹⁴ can be generated

from this source.¹³ For example, consider the TRS benzenoids **32**, **32A**, **33**, **34**, and **34A** having $r(\text{sextet}) = 54/6 = 9$, $r(\text{empty}) = N_{lc} = 5$, $N_c(\text{TRS}) = 54$, and $N_H(\text{TRS}) = 28$. Using these equations gives $N_c = 33$ and $N_H = 17$. There are 154 numbered structures (9.5.1–9.5.154) listed in the Knop et al. reference,¹³ and eliminating all phenyl and TRS aryl-substituted TRS benzenoid structures from the leapfrogs of these depictions gives **32** from **3**, **32A** from **5**, **33** from **9**, **34** from **17**, and **34A** from **14** from this listing (Figure 4).

CONCLUSION

While delineating the relationships between various dualist graphs and the excised internal structure, it has been demonstrated that the sextet and antisextet dualist graphs of strain-free TRS benzenoids are identical to the dualist graph and excised internal structure of the corresponding retro-leapfrogs of the TRS benzenoids, respectively. The leapfrog and retro-leapfrog require prior knowledge of the respective benzenoid structures for isomeric enumeration, whereas the enumeration of TRS benzenoids via the algorithm based on the antisextet dualist does not require such prior knowledge. Here, we see that the convergence of identical results by two different methods is mutually reinforcing.

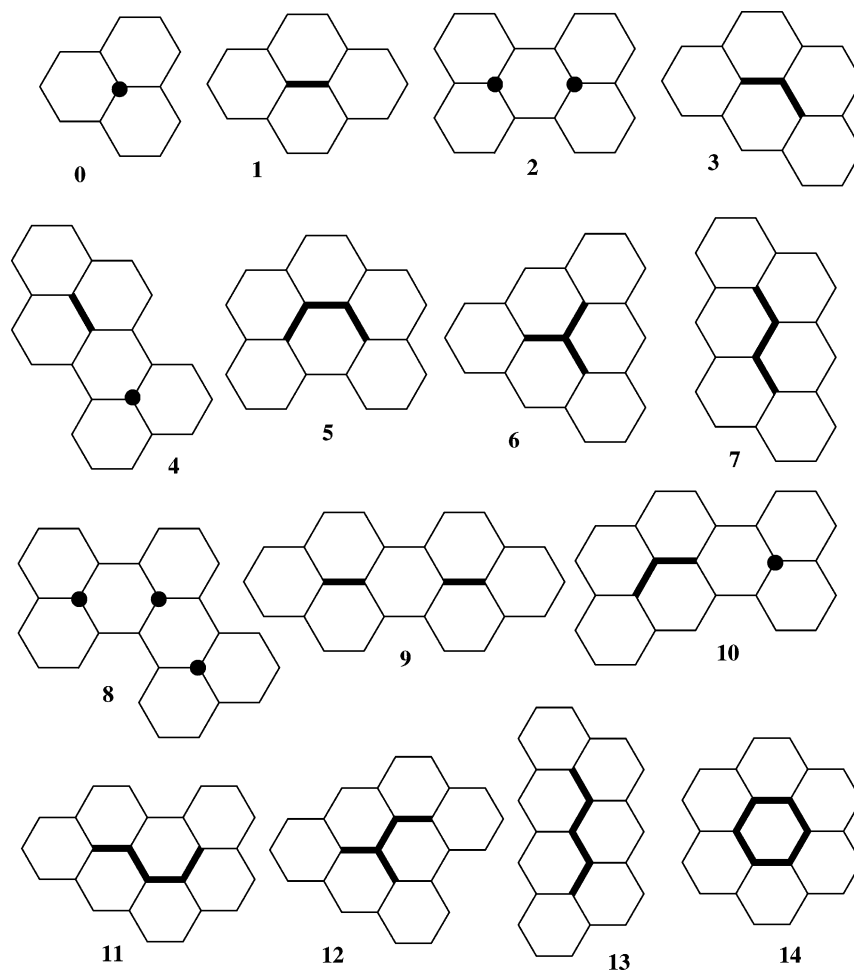


Figure 3. Retro-leapfrog benzenoids corresponding to the TRS benzenoids in Figure 3 of the Balaban and Schmalz paper. The excised internal structures shown in bold are identical to the antisextet dualist of the TRS benzenoids.

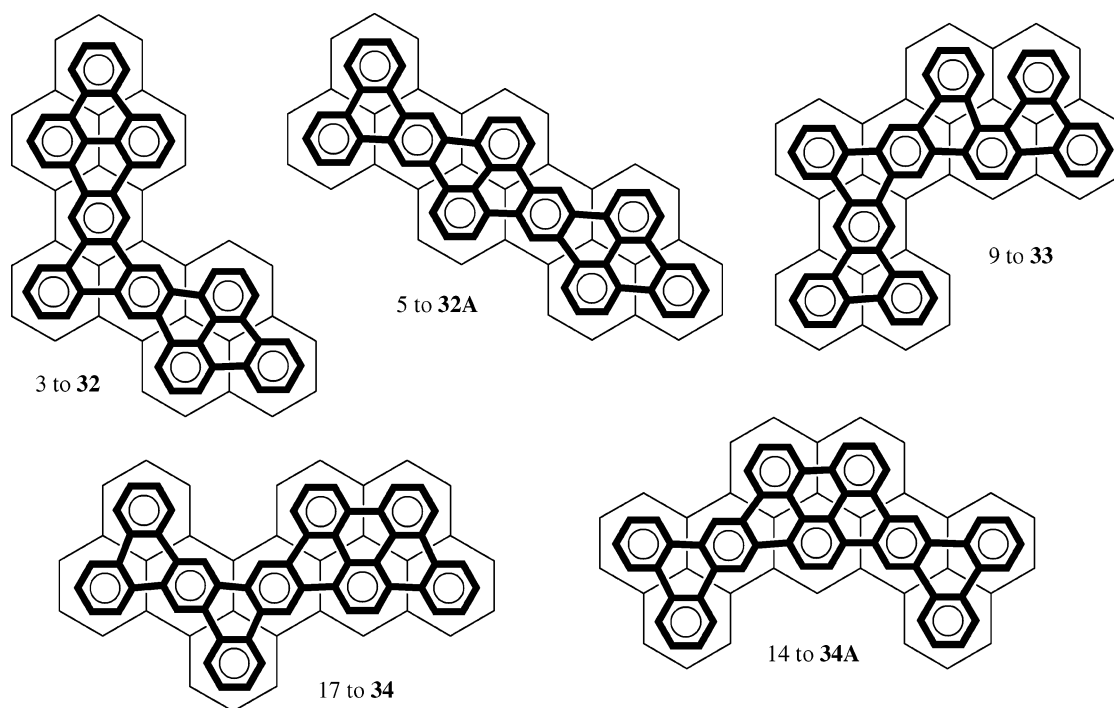


Figure 4. Leapfrog generation of the $C_{54}H_{28}$ TRS benzenoids (in bold) from the $C_{33}H_{17}$ benzenoids.

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