

# Strain-Free Sextet-Resonant Benzenoids and Their Antisextet Dualists

Alexandru T. Balaban\* and Thomas G. Schmalz

Texas A&M University at Galveston, 5007 Avenue U, Galveston, Texas 77551

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By introducing *antisextet dualists* of sextet-resonant benzenoids that have only “full” and “empty” rings as defined by Clar, it was possible to devise a simple algorithm for an exhaustive enumeration of such sextet-resonant benzenoids (SRBs). Several relationships between invariants of such SRBs are described. All possible SRBs with up to 10 sextet rings are enumerated. A unique coding of SRBs is presented, based on the peripheral “sextet-polyphenyl-necklace” formed by the benzenoid rings circumscribing the SRB.

## INTRODUCTION

The term “aromatic sextet” and the large circle symbolizing it were introduced by Armit and Robinson,<sup>1</sup> but Crocker had published in *J. Am. Chem. Soc.* a few years earlier a paper discussing the connection between aromaticity and six  $\pi$ -electrons in cyclic conjugated systems.<sup>2</sup> The history of the large circle symbolizing  $\pi$ -electron sextets is presented in a recent article in *Chem. Rev.*<sup>3</sup> Polycyclic benzenoids have received much attention due to their aromaticity and applications<sup>4–13</sup> and to the fact that some of them are carcinogenic.<sup>14</sup>

Benzenoids have been variously defined either as polycyclic aromatic hydrocarbons (PAHs) that are portions of the graphene lattice (thus excluding helicenes) or as PAHs formed by benzenoid rings that share CC bonds (thus including helicenes). Although noncapped single-wall carbon nanotubes are also composed only of hexagonal conjugated carbon rings, they have not traditionally been considered as benzenoids.

Benzenoids are classified as peri-condensed or cata-condensed according to whether they do or not contain carbon atoms common to three rings. A simpler and yet a more comprehensive classification relies on their dualists formed by vertices corresponding to centers of benzenoid rings and edges connecting vertices corresponding to condensed rings, i.e., rings sharing one CC bond:<sup>15,16</sup> cata-/peri-/corona-condensed benzenoids are then those having in their dualists no ring/three-membered ring(s)/larger rings, respectively.

Eric Clar prepared hundreds of new PAHs, published two influential monographs on PAHs in 1964<sup>4</sup> and 1972,<sup>5</sup> and made an important contribution to the theory of PAHs by showing that sextet circles (called “Clar sextets”, placed according to a set of simple rules) explain well the chemical reactivity and the electronic absorption spectra of PAHs. Thus, phenanthrene has the marginal rings as sextet rings and the middle ring with a double bond, which easily adds halogens or hydrogen.

## SEXTET RESONANT BENZENOIDS

Recently chemists have preferred to use shorter names and acronyms. Thus, *benzenoid hydrocarbons* or *polycyclic*

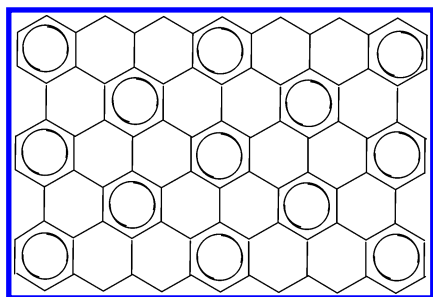
*aromatic hydrocarbons* (PAHs) are increasingly named *benzenoids*. One should note that now *benzenoid* is a noun and not an adjective. When benzenoids contain only two types of rings, namely either with (“sextet rings”) or without Clar sextets (“empty rings”), but no rings with one or two double bonds, we will call them *sextet resonant benzenoids* (abbreviated henceforth as SRBs). An example is triphenylene with an empty central ring and three sextet rings. Such SRBs have been also called in the past fully-/all-/total-benzenoid/resonant PAHs. We believe that expressions such as “fully-/all-/total-benzenoid benzenoids”, where the same word (benzenoid) is both adjective and noun, are clumsy, and therefore we propose the new name, *sextet resonant benzenoids*.

Starting with Polansky<sup>17–19</sup> and Clar,<sup>4,5,20</sup> and continuing with Rouvray,<sup>18</sup> Gutman,<sup>9,10,19,21</sup> Cyvin,<sup>9,10,21–27</sup> Randić,<sup>13,28</sup> Dias,<sup>8,29–35</sup> and Trinajstić with co-workers,<sup>36</sup> considerable theoretical effort has been dedicated to SRBs. A pair of discordant papers on C<sub>60</sub> benzenoids<sup>37,38</sup> that ended in concert may be mentioned in this context.<sup>39</sup>

Recent experimental contributions of Klaus Müllen’s research group<sup>40–46</sup> have brought sextet resonant benzenoids into the limelight because giant polycyclic aromatic hydrocarbons have become accessible via intramolecular Scholl reactions:<sup>47</sup> for instance C<sub>222</sub>H<sub>42</sub> with hexagonal symmetry was thus synthesized; its number of Kekulé structures is higher than 10<sup>15</sup>.

A two-volume influential monograph on PAHs was published in 1987 by Jerry R. Dias,<sup>8</sup> who had introduced the periodic chart of PAHs. In this monograph, sextet resonant benzenoids are called total resonant sextet benzenoids. Figure 3.6 (pp 86–96) of this *Handbook of Polycyclic Hydrocarbons (Part A)*<sup>8</sup> as well as Figure 1 of ref 35 contains 60 Kekuléan strain-free (i.e. devoid of steric crowding) sextet-resonant benzenoids with C<sub>24</sub> to C<sub>54</sub>.<sup>8</sup> Four structures (we will call them “addenda”) have been added on p 367 in *Part B* of the above monograph and on p 72 of ref 38.<sup>38</sup> Steric strain due to crowding means that unlike *meta*- or *para*-terphenyl (which are included in Clar’s book *The Aromatic Sextet*),<sup>5</sup> *ortho*-terphenyl and its benzoannulated derivatives (which are not included in that book) have steric crowding due to two hydrogen atoms and must therefore adopt a nonplanar structure. Such sterically strained

\* Corresponding author e-mail: balabana@tamug.edu.



**Figure 1.** A portion of the graphene lattice, with inscribed Clar circles.

SRBs are not included in the present paper (this topic will again be discussed in connection with Figures 7 and 8).

By eliminating the two overcrowded hydrogens in *ortho*-terphenyl, one obtains triphenylene, which is a normal strain-free SRB. Hexabenzo[*bc,ef,hi,kl,no,qr*]coronene, also a highly symmetric strain-free SRB, is so thermally stable that its melting point is higher than the temperature at which a glass capillary melts. It appears that among all isomeric benzenoids, such SRBs devoid of steric crowding possess the highest stability and the highest numbers of Kekulé structures. Interestingly, unlike their non-SRB isomers, strain-free SRBs are insoluble in concentrated sulfuric acid.

One can observe certain regularities within the set of SRBs. Since a benzenoid ring in such a system can be either “empty” or can have a sextet of  $\pi$ -electrons denoted by a large circle, and since its number  $C$  of carbon atoms is equal to the number of its  $\pi$ -electrons, SRBs have  $S = C/6$  sextets, and  $C$  must be a multiple of 6. In the present discussion we will consider  $S \geq 3$ , i.e., here benzene is not considered to be an SRB.

#### ANTISEXTET DUALISTS OF SEXTET-RESONANT BENZENOIDS

We adopt the convention of drawing hexagons such that one pair of bonds is vertical. A portion of the graphene sheet with inscribed sextet circles is shown in Figure 1.

It is well-known that the dualist graph of the hexagonal (honeycomb) lattice is a triangular lattice and vice versa. By drawing lines between centers of the large circles symbolizing sextets for hexagons in biphenyl-like positions, one obtains a benzenoid with a larger triangular dualist, which will be called the *sextet dualist* (Figure 2, middle structures). Such sextet dualists have been described by Polansky and Rouvray.<sup>18</sup> If one inscribes in the center of each triangle a point and if one connects the points of triangles sharing an edge, the result is an *antisextet dualist* of the SRB, consisting of  $G$  gaps between a pair of points and/or lines;  $P$  points;  $L$  lines (a line or edge of the antisextet dualist covers just the distance between the centers of two condensed hexagons); and  $R$  rings. As in any hexagonal lattice, two lines having a common vertex must meet at an angle of  $120^\circ$ ; here, however, they may also have one gap between them (a gap, corresponding to one Clar-sextet ring, may also exist between two points and/or lines). Evidently, as seen from Figure 2, the antisextet dualist is formed by points that are the centers of all the “empty” hexagons and by lines connecting points belonging to condensed hexagons. The importance of the “empty rings” was underlined by Polansky and Gutman’s method of obtaining the number  $K$

of Kekulé structures for SRBs, wherein the “starring of empty sextets” played a central part.<sup>19</sup>

It is clear that the reverse construction of the initial SRB from its antisextet dualist is simple. The number of sextet rings in the SRB is denoted by  $S$ . To follow more closely the four benzenoids from Figure 2, their values for  $S$ ,  $G$ ,  $P$ ,  $R$ , and  $L$  are as follows: for **15A**, 8, 2, 4, 0, and 1; for **32A** and **34A**, 9, 2, 5, 0, and 2; and for **52A**, 9, 0, 7, 0, and 6. These are the four “addenda” structures.

The present paper discusses only cata-condensed or pericondensed SRBs but not corona-condensed SRBs such as hexabenzokekulene or its higher homologues. Such corona-condensed systems arise when one or more “holes” with internal hydrogen atoms are created instead of a benzenoid, and in such cases the enumeration formulas depend on the genus  $\neq 0$  corresponding to the topology of the antisextet dualist. These systems will be discussed in a future paper.

The following general relationships can be observed to hold, where the number of hexagons is denoted by  $h$ , the number of Clar sextets is denoted by  $S$ , the number of CC aromatic bonds (edges of the benzenoid graph) is denoted by  $E$ , and the numbers of carbon and hydrogen atoms are denoted by  $C$  and  $H$ , respectively.

$$h = S + P \quad (1)$$

$$C = 6S \quad (2)$$

$$H = 2S + 2G - 2R + 6 = 2P + 4G - 4R + 10 = 4S - 2P + 2 \quad (3)$$

$$E = 3/2C - 1/2H = C + h - 1 = 7S + P - 1 \quad (4)$$

$$L = P - G + R - 1 = 2P - S + 1 \quad (5)$$

It may be observed that in eqs 1–5 all parameters on the left-hand side can be expressed in terms of only two independent parameters, namely  $S$  and  $P$ . Additionally, the difference  $G - R$  can be expressed as

$$G - R = S - P - 2 \quad (6)$$

but a third independent parameter (either  $R$  or  $G$ ) is needed to completely determine all the introduced SRB invariants of the antisextet dualist. Variation of  $R$  (or  $G$ ) for given values of  $S$  and  $P$  will be discussed later in this paper for strain-free SRBs with  $S = 10$ .

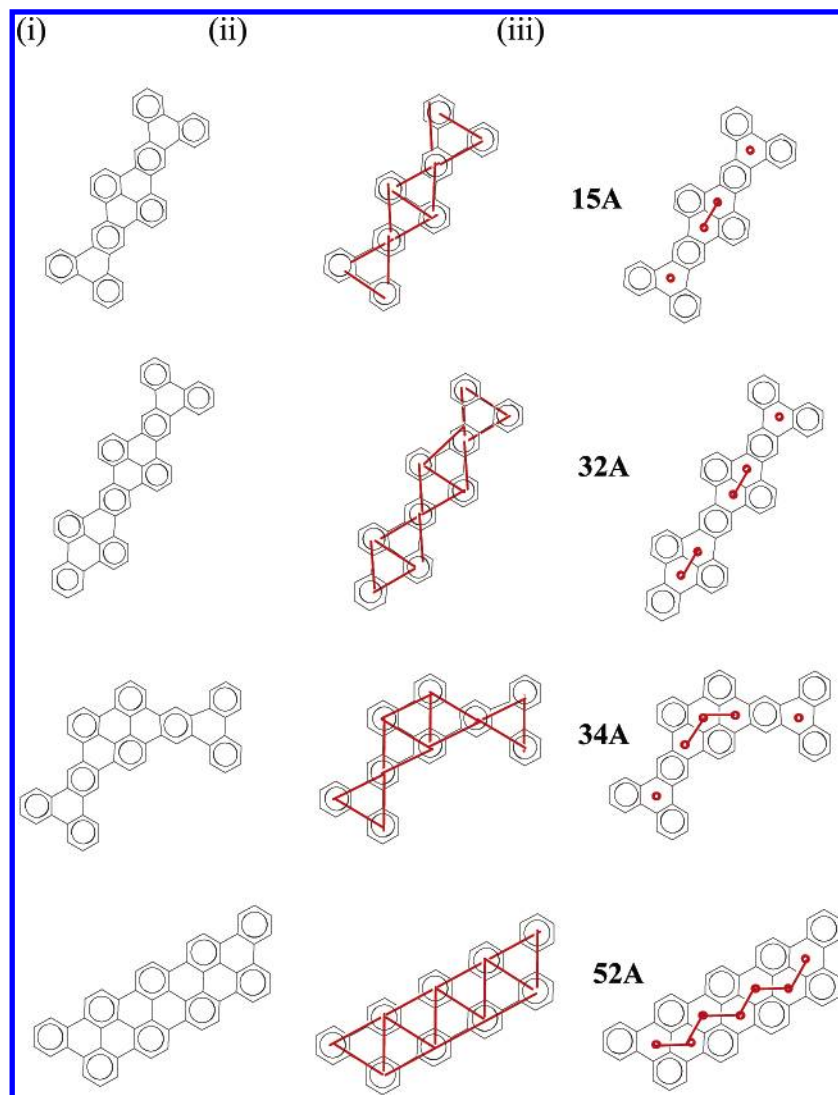
It is common to designate the carbon atoms in a benzenoid by  $v_2$  (for CH groups at the periphery of the benzenoid connected to 2 other carbon atoms),  $v_3$  (for carbon atoms at the periphery of the benzenoid connected to 3 other carbon atoms), and  $v_{\text{int}}$  (for carbon atoms inside the benzenoid connected to 3 other carbon atoms). Then the following relationships hold:

$$v_2 = H \quad (7)$$

$$v_{\text{int}} = 2L \quad (8)$$

$$v_3 = C - v_2 - v_{\text{int}} \quad (9)$$

It may be seen from Table 1 that the energy of the highest occupied Hückel molecular orbital  $E_{\text{HOMO}}$  (in  $\beta$  units) characterizes uniquely each benzenoid from that table. The HOMO–LUMO gap for all such bipartite graphs is  $2E_{\text{HOMO}}$ . On the other hand, the number  $K$  of Kekulé structures



**Figure 2.** From left to right: (i) converting an SRB (from top to bottom, benzenoids denoted as **15A**, **32A**, **34A**, and **52A**) into (ii) a “triangulated” SRB with the *sextet dualist* drawn in red, and then (iii) inscribing its *antisextet dualist* containing  $P$  points (red),  $L$  lines (red),  $G$  gaps, and in these cases  $R = 0$  rings. Numerical values are to be found in the text and in Table 1.

presents degeneracies, some of which are accidental, but some are predictable, being due to the structure of the benzenoid, uniquely associated with its antisextet dualist. In Table 1 such systems are indicated by boldface characters (however, accidental degeneracy is also included in most cases). The distinction between accidental and structural degeneracy of  $K$  values and the rules for such structural degeneracy will be discussed in a future paper.

One can observe that adjacent lines in the antisextet dualists never have between them angles of  $180^\circ$  but only  $120^\circ$  and  $240^\circ$  (coded by digits 1 and 2). Cata-fused benzenoids with such nonbranched dualists have  $K$  values that are Fibonacci numbers.<sup>48</sup>

In the graphene lattice (Figure 1), empty rings are adjacent to each other, whereas sextet rings are isolated. By contrast, in the sextet dualists the vertices corresponding to Clar sextet rings form a connected graph, whereas in the antisextet dualists the vertices (now corresponding to empty rings) may be connected or disconnected.

Table 1 contains data corresponding to all SRBs listed in Figure 3.6 of the Dias Handbook,<sup>8</sup> with the same numbering as in this book, plus triphenylene and four “addenda” SRBs

have been added. Three of these four “addenda” SRBs that are represented in Figures 2 and 4–6 (denoted by **15A**, **32A**, **34A**, and **52A**) have the same  $K$  values as SRB **15** (for **15A**), **32** (for **32A**), and SRBs **51** and **52** (for **52A**). In subsequent papers, Dias published the correct count of SRBs classified according to their symmetry. Sven Cyvin and co-workers have published several papers counting SRBs and discussed their symmetries and topological properties.<sup>19</sup> Cyvin coauthored several books with Ivan Gutman and included therein considerable information on SRBs.<sup>9,10</sup> Cyvin et al.’s enumeration of SRBs extended as far as systems with up to  $h = 18$  benzenoid rings (including also strained systems), but the structures that are displayed, ordered according to increasing  $h$  values, reach only as far as  $h = 13$  hexagons.

The construction of SRBs with the help of the above antisextet dualist allows an easy algorithm for finding all possible strain-free SRBs with numbers  $S$  of sextets that are not too large. The SRBs in Dias’s book<sup>8</sup> and paper<sup>35</sup> (plus triphenylene and the four “addenda” with numbers followed by letter A) are presented in Figures 3–6 with their antisextet dualists.

**Table 1.** Strain-Free Sextet-Resonant Benzenoids with 8–54 Carbon Atoms<sup>a</sup>

| compd<br>no. | $E_{\text{HOMO}}$<br>( $\beta$ ) | Clar<br>sextets $S$ | formula |    | hexagons<br>$h$ | Kekulé<br>structures $K$ | CC bonds<br>$E$ | antisextet dualist |     |     |     | code         |
|--------------|----------------------------------|---------------------|---------|----|-----------------|--------------------------|-----------------|--------------------|-----|-----|-----|--------------|
|              |                                  |                     | C       | H  |                 |                          |                 | $G$                | $P$ | $R$ | $L$ |              |
| 0            | 0.68404                          | 3                   | 18      | 12 | 4               | 9                        | 21              | 0                  | 1   | 0   | 0   | 222          |
| 1            | 0.55496                          | 4                   | 24      | 14 | 6               | 20                       | 29              | 0                  | 2   | 0   | 1   | 2121         |
| 2            | 0.57740                          | 5                   | 30      | 18 | 7               | 40                       | 36              | 1                  | 2   | 0   | 0   | 221221       |
| 3            | 0.50294                          | 5                   | 30      | 16 | 8               | 45                       | 37              | 0                  | 3   | 0   | 2   | 21120        |
| 4            | 0.53024                          | 6                   | 36      | 20 | 9               | 89                       | 44              | 1                  | 3   | 0   | 1   | 2211211      |
| 5            | 0.50710                          | 6                   | 36      | 18 | 10              | 100                      | 45              | 0                  | 4   | 0   | 3   | 211121       |
| 6            | 0.51763                          | 6                   | 36      | 18 | 10              | 104                      | 45              | 0                  | 4   | 0   | 3   | 202020       |
| 7            | 0.45191                          | 6                   | 36      | 18 | 10              | 101                      | 45              | 0                  | 4   | 0   | 3   | 210210       |
| 8            | 0.54997                          | 7                   | 42      | 24 | 10              | 178                      | 51              | 2                  | 3   | 0   | 0   | 221212211    |
| 9            | 0.49697                          | 7                   | 42      | 22 | 11              | 198                      | 52              | 1                  | 4   | 0   | 2   | 21112111     |
| 10           | 0.48471                          | 7                   | 42      | 22 | 11              | 200                      | 52              | 1                  | 4   | 0   | 2   | 22111201     |
| 11           | 0.45638                          | 7                   | 42      | 20 | 12              | 225                      | 53              | 0                  | 5   | 0   | 4   | 2110211      |
| 12           | 0.45340                          | 7                   | 42      | 20 | 12              | 230                      | 53              | 0                  | 5   | 0   | 4   | 2020121      |
| 13           | 0.41820                          | 7                   | 42      | 20 | 12              | 227                      | 53              | 0                  | 5   | 0   | 4   | 2101200      |
| 14           | 0.46476                          | 7                   | 42      | 18 | 13              | 250                      | 54              | 0                  | 6   | 1   | 6   | 111111       |
| 15           | 0.50831                          | 8                   | 48      | 26 | 12              | <b>396</b>               | 59              | 2                  | 4   | 0   | 1   | 2112122111   |
| 15A          | 0.51394                          | 8                   | 48      | 26 | 12              | <b>396</b>               | 59              | 2                  | 4   | 0   | 1   | 2211122111   |
| 16           | 0.47032                          | 8                   | 48      | 24 | 13              | 445                      | 60              | 1                  | 5   | 0   | 3   | 211112110    |
| 17           | 0.48432                          | 8                   | 48      | 24 | 13              | 461                      | 60              | 1                  | 5   | 0   | 3   | 221020201    |
| 18           | 0.44259                          | 8                   | 48      | 24 | 13              | 449                      | 60              | 1                  | 5   | 0   | 3   | 221102101    |
| 19           | 0.48964                          | 8                   | 48      | 24 | 13              | 445                      | 60              | 1                  | 5   | 0   | 3   | 221111211    |
| 20           | 0.42442                          | 8                   | 48      | 22 | 14              | 505                      | 61              | 0                  | 6   | 0   | 5   | 210111210    |
| 21           | 0.45295                          | 8                   | 48      | 22 | 14              | 500                      | 61              | 0                  | 6   | 0   | 5   | 21112111     |
| 22           | 0.43608                          | 8                   | 48      | 22 | 14              | <b>510</b>               | 61              | 0                  | 6   | 0   | 5   | 21021211     |
| 23           | 0.42945                          | 8                   | 48      | 22 | 14              | 519                      | 61              | 0                  | 6   | 0   | 5   | 21120200     |
| 24           | 0.42601                          | 8                   | 48      | 22 | 14              | 509                      | 61              | 0                  | 6   | 0   | 5   | 21112010     |
| 25           | 0.42915                          | 8                   | 48      | 22 | 14              | <b>510</b>               | 61              | 0                  | 6   | 0   | 5   | 21002121     |
| 26           | 0.42507                          | 8                   | 48      | 22 | 14              | 520                      | 61              | 0                  | 6   | 0   | 5   | 20212021     |
| 27           | 0.39141                          | 8                   | 48      | 22 | 14              | <b>510</b>               | 61              | 0                  | 6   | 0   | 5   | 21002100     |
| 28           | 0.41683                          | 8                   | 48      | 20 | 15              | 575                      | 62              | 0                  | 7   | 1   | 7   | 2011110      |
| 29           | 0.52434                          | 9                   | 54      | 30 | 13              | 793                      | 66              | 3                  | 4   | 0   | 0   | 221122112211 |
| 30           | 0.52272                          | 9                   | 54      | 30 | 13              | <b>792</b>               | 66              | 3                  | 4   | 0   | 0   | 221111221211 |
| 31           | 0.52243                          | 9                   | 54      | 30 | 13              | <b>792</b>               | 66              | 3                  | 4   | 0   | 0   | 221212122111 |
| 32           | 0.50091                          | 9                   | 54      | 28 | 14              | <b>881</b>               | 67              | 2                  | 5   | 0   | 2   | 211212121111 |
| 32A          | 0.48923                          | 9                   | 54      | 28 | 14              | <b>881</b>               | 67              | 2                  | 5   | 0   | 2   | 221111212111 |
| 33           | 0.47590                          | 9                   | 54      | 28 | 14              | <b>890</b>               | 67              | 2                  | 5   | 0   | 2   | 221212112011 |
| 34           | 0.47348                          | 9                   | 54      | 28 | 14              | <b>890</b>               | 67              | 2                  | 5   | 0   | 2   | 221210211111 |
| 34A          | 0.46978                          | 9                   | 54      | 28 | 14              | 889                      | 67              | 2                  | 5   | 0   | 2   | 221111221101 |
| 35           | 0.46309                          | 9                   | 54      | 26 | 15              | <b>1000</b>              | 68              | 1                  | 6   | 0   | 4   | 2111112010   |
| 36           | 0.42296                          | 9                   | 54      | 26 | 15              | <b>1000</b>              | 68              | 1                  | 6   | 0   | 4   | 2111021110   |
| 37           | 0.48139                          | 9                   | 54      | 26 | 15              | 1026                     | 68              | 1                  | 6   | 0   | 4   | 2110202011   |
| 38           | 0.47489                          | 9                   | 54      | 26 | 15              | 990                      | 68              | 1                  | 6   | 0   | 4   | 2111112111   |
| 39           | 0.43497                          | 9                   | 54      | 26 | 15              | 999                      | 68              | 1                  | 6   | 0   | 4   | 2101121110   |
| 40           | 0.43198                          | 9                   | 54      | 26 | 15              | 1021                     | 68              | 1                  | 6   | 0   | 4   | 2210201211   |
| 41           | 0.44707                          | 9                   | 54      | 26 | 15              | 1020                     | 68              | 1                  | 6   | 0   | 4   | 2210212101   |
| 42           | 0.44774                          | 9                   | 54      | 26 | 15              | <b>1000</b>              | 68              | 1                  | 6   | 0   | 4   | 2211121101   |
| 43           | 0.41132                          | 9                   | 54      | 26 | 15              | 1009                     | 68              | 1                  | 6   | 0   | 4   | 2211012001   |
| 44           | 0.44610                          | 9                   | 54      | 26 | 15              | 1024                     | 68              | 1                  | 6   | 0   | 4   | 2211020211   |
| 45           | 0.44618                          | 9                   | 54      | 26 | 15              | 1001                     | 68              | 1                  | 6   | 0   | 4   | 2211102111   |
| 46           | 0.39914                          | 9                   | 54      | 24 | 16              | 1164                     | 69              | 0                  | 7   | 0   | 6   | 210020210    |
| 47           | 0.40821                          | 9                   | 54      | 24 | 16              | 1136                     | 69              | 0                  | 7   | 0   | 6   | 210102110    |
| 48           | 0.43281                          | 9                   | 54      | 24 | 16              | 1149                     | 69              | 0                  | 7   | 0   | 6   | 210211201    |
| 49           | 0.43195                          | 9                   | 54      | 24 | 16              | <b>1150</b>              | 69              | 0                  | 7   | 0   | 6   | 211120201    |
| 50           | 0.39703                          | 9                   | 54      | 24 | 16              | 1135                     | 69              | 0                  | 7   | 0   | 6   | 211002101    |
| 51           | 0.43056                          | 9                   | 54      | 24 | 16              | <b>1125</b>              | 69              | 0                  | 7   | 0   | 6   | 211011211    |
| 52           | 0.42299                          | 9                   | 54      | 24 | 16              | <b>1125</b>              | 69              | 0                  | 7   | 0   | 6   | 211112011    |
| 52A          | 0.37105                          | 9                   | 54      | 24 | 16              | 1146                     | 69              | 0                  | 7   | 0   | 6   | 210012000    |
| 53           | 0.44277                          | 9                   | 54      | 24 | 16              | 1134                     | 69              | 0                  | 7   | 0   | 6   | 211211211    |
| 54           | 0.40838                          | 9                   | 54      | 24 | 16              | <b>1150</b>              | 69              | 0                  | 7   | 0   | 6   | 211120021    |
| 55           | 0.43004                          | 9                   | 54      | 24 | 16              | 1158                     | 69              | 0                  | 7   | 0   | 6   | 211202121    |
| 56           | 0.40305                          | 9                   | 54      | 24 | 16              | <b>1150</b>              | 69              | 0                  | 7   | 0   | 6   | 210021121    |
| 57           | 0.40433                          | 9                   | 54      | 22 | 17              | 1275                     | 70              | 0                  | 8   | 1   | 8   | 21011111     |
| 58           | 0.39433                          | 9                   | 54      | 22 | 17              | 1300                     | 70              | 0                  | 8   | 1   | 8   | 20111021     |
| 59           | 0.40123                          | 9                   | 54      | 22 | 17              | 1330                     | 70              | 0                  | 8   | 1   | 8   | 20110200     |
| 60           | 0.38197                          | 9                   | 54      | 22 | 17              | 1320                     | 70              | 0                  | 8   | 1   | 8   | 20102010     |

<sup>a</sup> In the seventh column degenerate  $K$  values are boldface; see text for explanation of notation.

## GENERATION OF SRBS

The generation procedure for SRBs takes into account that  $S$  and  $L$  have opposite parities. This can be proved as follows. Equations 5 and 6 indicate that

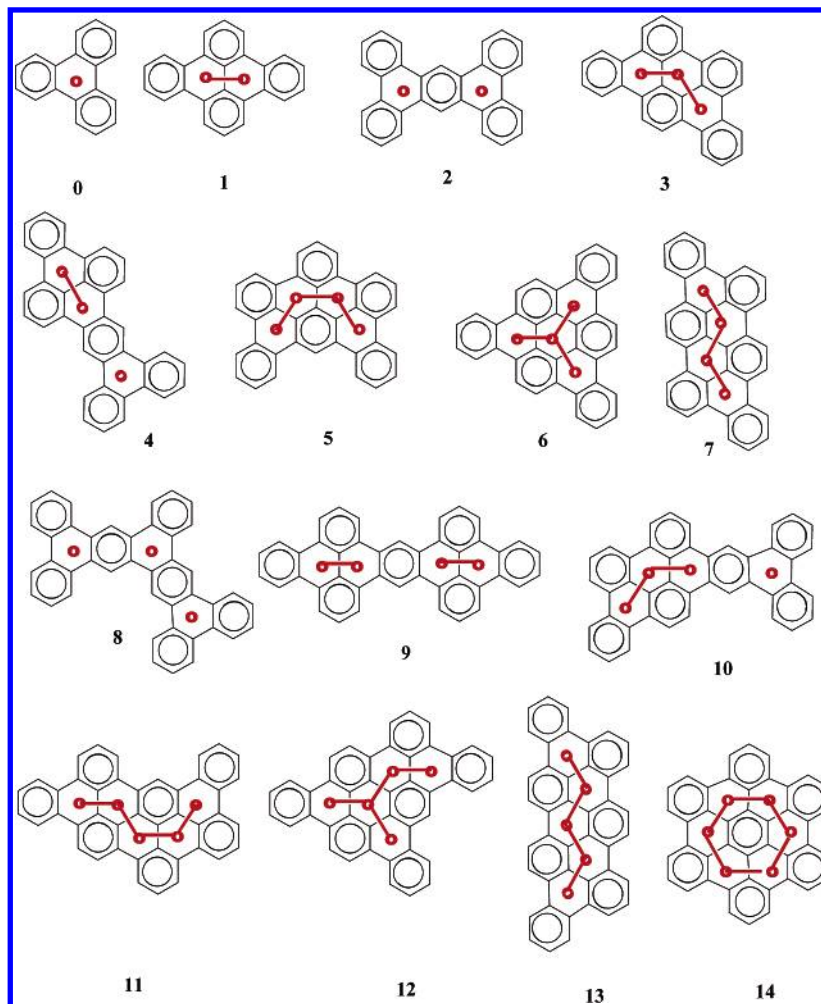
$$P = L + G - R + 1 = S - G + R - 2, \text{ hence:} \\ G = R + (S - L - 3)/2 \quad (10)$$

therefore  $S$  and  $L$  must have different parities because all parameters are integers.

For even values of  $S = 2k$ , the number of gaps in the benzenoid  $C_{12k}H_{6k+2}$  with maximal number of hydrogen atoms is  $G = k - 2$  (antisextet dualist without rings and one line), and the number of points is  $P = k$ .

Accordingly, for a given odd value  $S = 2k + 1$ , the number  $L$  of lines in the antisextet dualists must be even. The  $6S$  carbon atoms can form a cata-condensed system (catafusene) when  $R = L = 0$  (namely when the antisextet dualist has no ring and is a sequence of  $P = k = (S - 1)/2$  isolated points);





**Figure 3.** Strain-free sextet-resonant benzenoids having 18–42 carbon atoms with their numbers from the Dias book (except for triphenylene denoted here by **0**) and their antisextet dualists.

in this case the SRB has  $3k + 1$  hexagons, its antisextet dualist has  $k - 1$  gaps, the number of hydrogen atoms is maximal, and the formula is  $C_{12k+6}H_{6k+6}$ . For such catafusenes,  $E = 6S + 3P$ . When there are four internal carbon atoms,  $L = 2$  lines,  $P = k + 1$  points,  $G = k - 2$  gaps, and the formula is  $C_{12k+6}H_{6k+4}$ . For two more pairs of internal carbon atoms (i.e. 8 such atoms) one obtains  $L = 4$  lines,  $P = k + 2$  points,  $G = k - 3$  gaps, with molecular formula  $C_{12k+6}H_{6k+2}$ , and so on till the number of lines becomes  $L = 2k = P - 1$ . For any  $S > 6$ , one can have rings in the antisextet dualist. For each added ring, as for each added line in the antisextet dualist, one reduces the number of hydrogens by two.

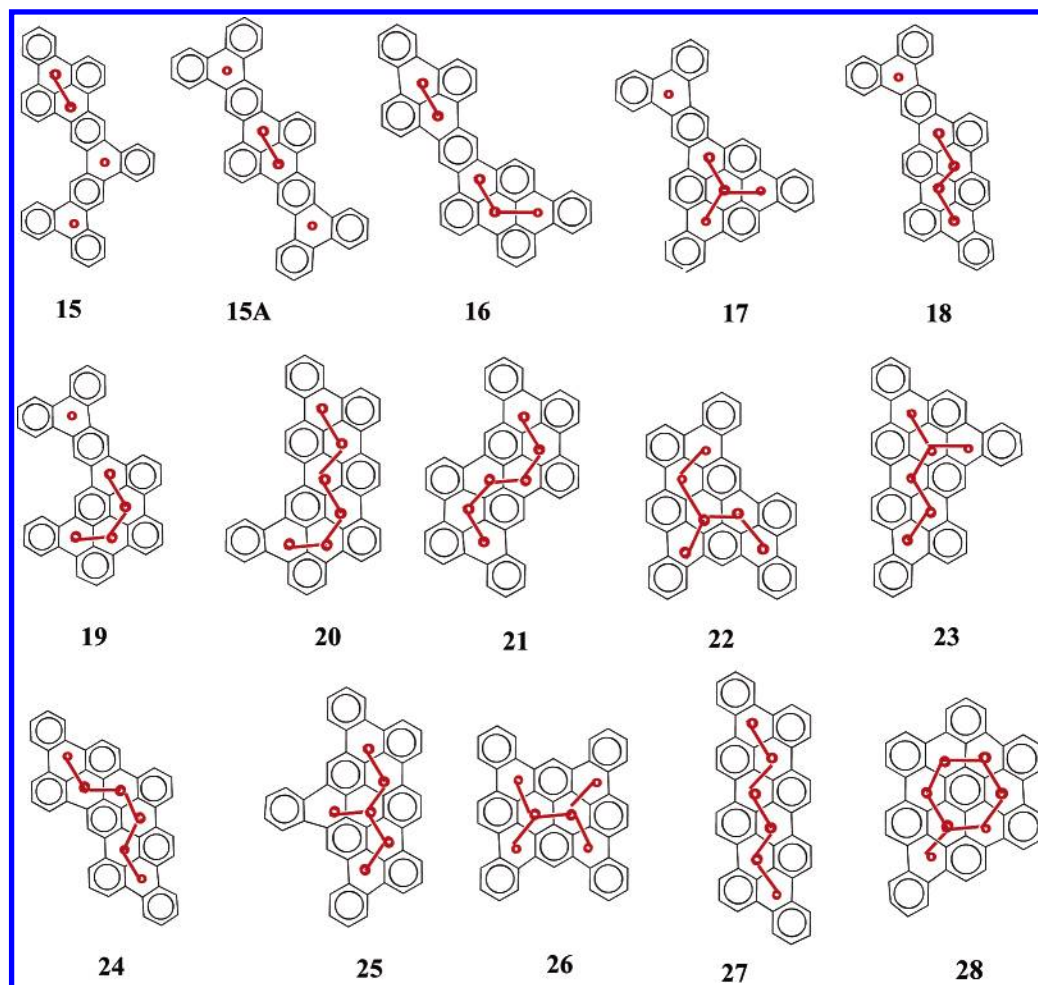
The enumeration of SRBs is based on *ordered partitions* of the sum of points and gaps ( $P + G = S + R - 2$ ) in the antisextet dualists with restrictions caused by the odd/even number of lines and on the geometry of the fibonacenic sequences of adjacent lines.<sup>48</sup> Inspection of the graphene lattice with sextet circles shows that there are no three linearly condensed (anthracenic) empty rings. For example, a few SRBs from Figure 3 will be commented upon in more detail.

(i) When  $S = 5$ , one obtains two SRBs with the following descriptors of antisextet dualists derived from the partitions of 3:  $P = 2$  isolated points and 1 gap (benzenoid **2** with  $L = 0$  lines), or  $P = 3$  adjacent points connected by  $L = 2$  lines (benzenoid **3**).

(ii) For  $S = 6$ , the partitions of 4 are as follows: 3 points + 1 gap (**4**, with 1 line joining 2 points, plus 1 isolated point) or 0 gaps + 4 adjacent points connected by 3 lines (a branched, **6**, or a linear chain; in the latter case, there are two geometries, *s-cisoid* **5** and *s-transoid* **7**); partitions such as 4 points + 0 gaps, 2 points + 2 gaps, or 1 point + 3 gaps are not possible.

(iii) For  $S = 7$ , the partitions of 5 are as follows: first when  $R = 0$  rings, **8** with 3 isolated points and 2 gaps; 2+2 (**9**) and 3+1 points (**10**) with 1 gap and 2 lines; and 0 gaps + 5 adjacent points connected by 4 lines (a branched chain, **12**, or a linear chain, and in the latter case there are two geometries, **11** and **13**); second, when  $R = 1$  ring, the antisextet dualist is a cyclic ring of 6 adjacent points and 6 lines (**14**).

It is known that benzenoid catafusenes differing in their dualist notation by interconversion of 1 and 2 digits [see coding system below, under (i)] are isoarithmic<sup>48,49</sup> and even isoresonant.<sup>50,51</sup> Thus, there is no surprise that the sextet-resonant cata-condensed benzenoids **30** and **31** from Figure 5 share the same  $K = 792$  value. The ordering of SRBs according to  $S$ , as in the enumeration by Dias, is better than the ordering according to  $h$  as in Cyvin's enumeration, because  $K$  values are mainly determined by the number  $S$  of sextet rings, and to a lesser extent by  $h$ ,  $H$ ,  $P$ ,  $G$ , or  $L$ , which are all mutually intercorrelated.



**Figure 4.** Strain-free sextet-resonant benzenoids 15–28 having 48 carbon atoms with their numbers from the Dias book (except for 15A) and their antisextet dualists.

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. If steric crowding would be allowed, this would no longer be true, as shown in Figure 7. Another such sterically hindered SRB is presented in Figure 8; in this case the structure is no longer a derivative of *ortho*-terphenyl, as for all examples in Figure 7.

#### PERIPHERAL “SEXTET-POLYPHENYL-NECKLACE CODING” OF SEXTET-RESONANT BENZENOIDS

Several types of coding systems have been proposed for benzenoids, among which we mention the following:

(i) for catafusenes, a system based on digits 0 for straight annelation, and 1 or 2 for kinked annelation, which may be nonbranched<sup>15</sup> or branched (brackets are to be used for each separate branch);<sup>16</sup>

(ii) the boundary code based on the directions of bonds at the periphery of the benzenoid;<sup>36,52,53</sup>

(iii) Cioslowski and Turek’s compact coding;<sup>54</sup>

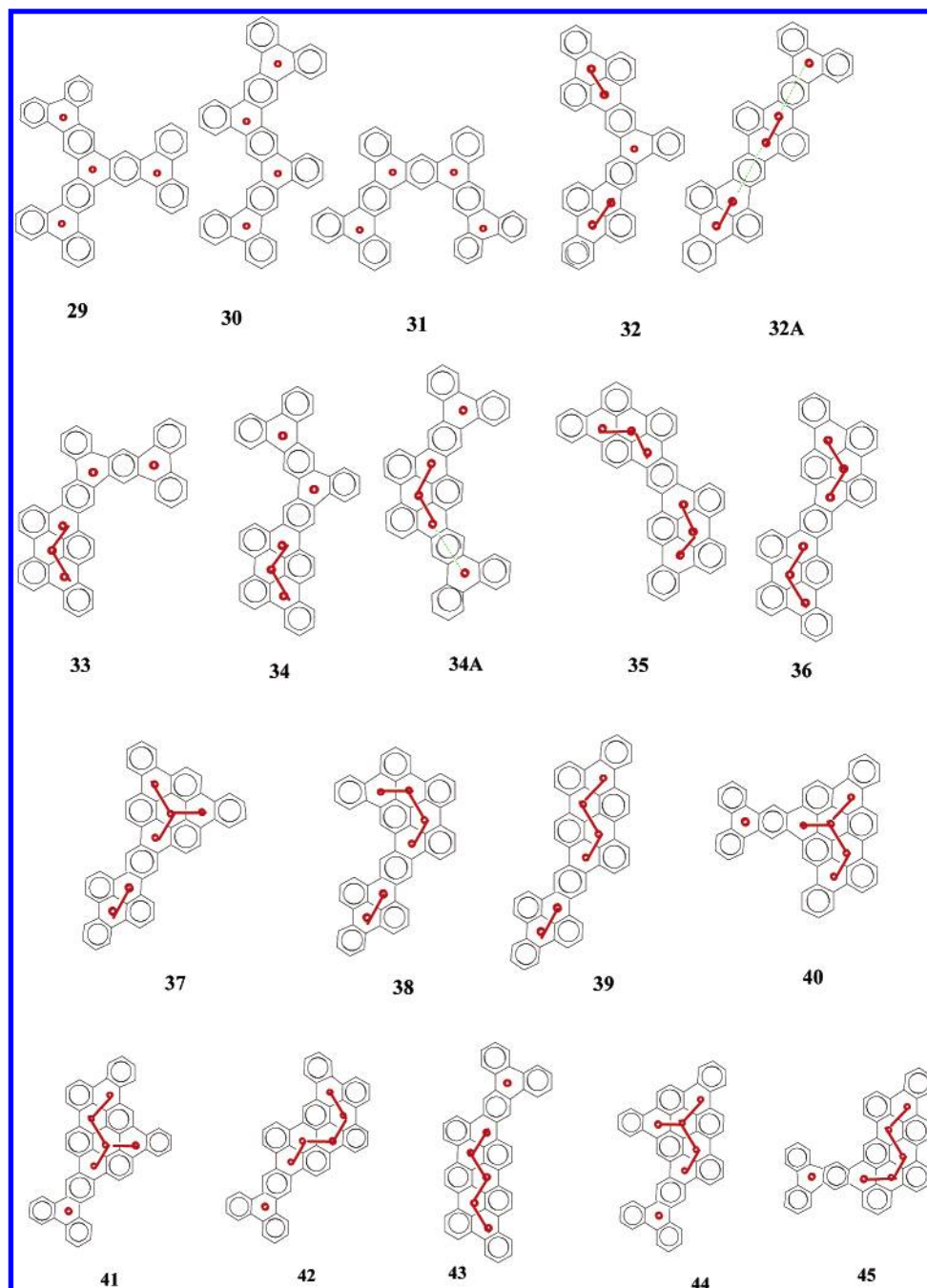
(iv) The Knop–Müller–Szymanski–Trinajstić name consisting of three numbers separated by two dots:  $h.v_{int}.#$ . However, unlike the three preceding ones, this is not a structural system but needs the “code book” to look for the last number # that discriminates among benzenoids sharing the first two numbers.<sup>55</sup>

(v) Kirby’s “compacted maximal adjacency code”<sup>56</sup> is derived from the maximized adjacency matrix of Hendrickson et al.<sup>57</sup> and consists of a sequence of numbers indicating the successive strings of digits 1 and 0 obtained on sequential reading the rows of this matrix.<sup>56,57</sup> This code may be applied to any chemical graph.

(vi) By contrast, the “coiled-hexagon code” developed by Bonchev and Balaban,<sup>58</sup> and developed by Kirby,<sup>59</sup> was designed for benzenoids.

Here a different system will be introduced; it was specifically designed for SRBs, taking into account that for the SRBs discussed in the present paper (devoid of steric hindrance and of internal holes) the boundary is a continuous “polyphenyl-necklace or -string” of sextet benzenoid rings. At each one of these rings the string makes a certain angle around the periphery. To devise a code it is sufficient to adopt conventions on (i) how to code for the four types of angles and (ii) to have a starting point and a direction around this periphery. Codes are then enclosed in square brackets.

(i) In going around the perimeter of the SRB we ascribe weight +1 for a 60° change of direction, say clockwise, and necessarily –1 for the opposite direction; a full turn around the periphery then needs 6 such steps. For “convex angles” 60° and 120° at a benzenoid ring, one has digits 2 and 1, respectively, as the numbers of 60° units resulting from the difference between 180° and these angles. For an unchanged (straight) direction of 180° one has digit 0, and for a concave



**Figure 5.** Strain-free sextet-resonant benzenoids **29–45** having 54 carbon atoms with their numbers from the Dias book (except for **32A** and **34A**) and their antisextet dualists.

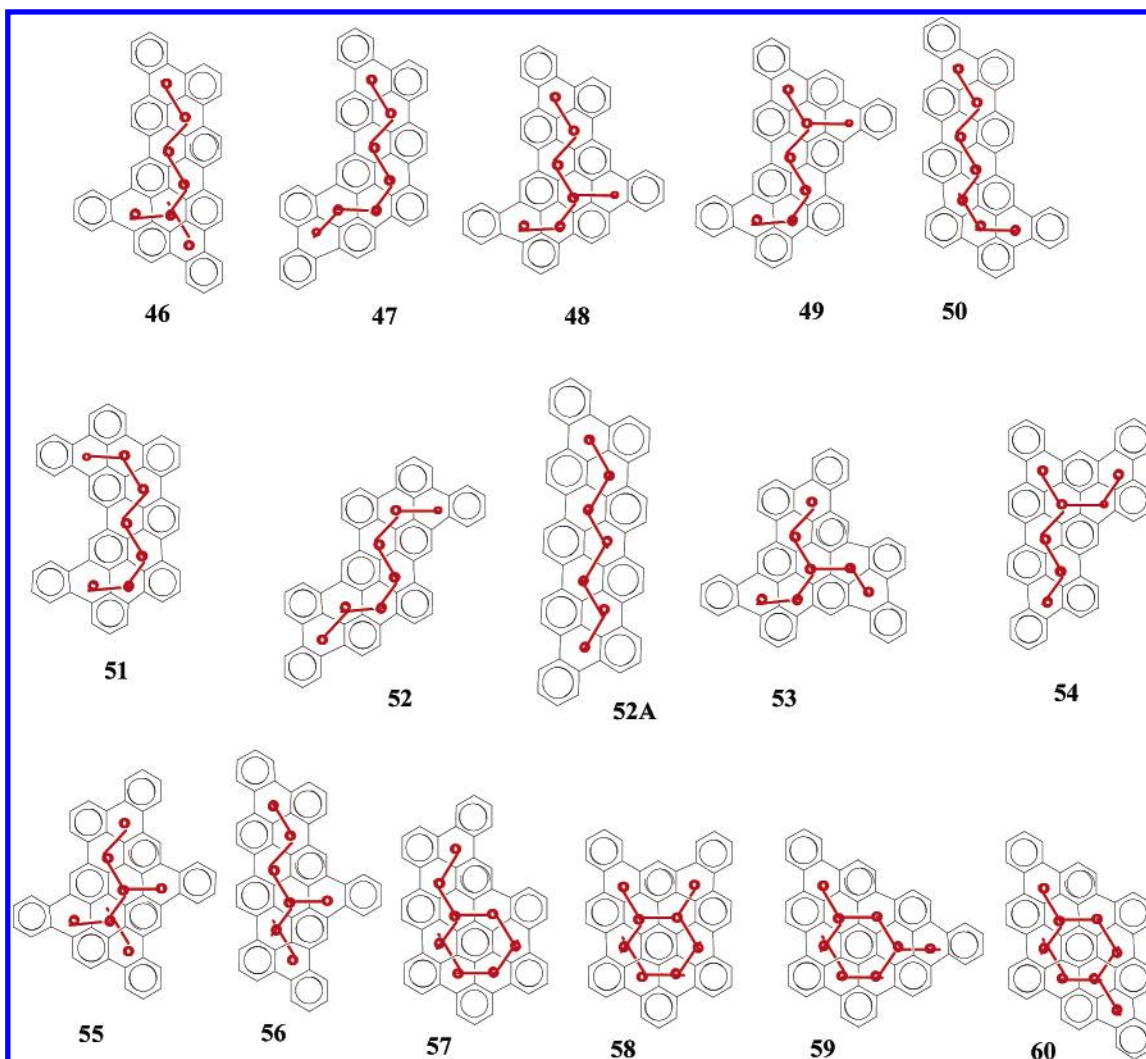
angle of  $120^\circ$  one has a value of  $-1$  which for convenience will be denoted here by **1**. The sum of all these digits around the SRB is 6; the central ring in tetrabenzo[*a,c,h,j*]anthracenic moieties (as in **2**) is counted twice, each time with the value  $-1$  on going around the benzenoid.

(ii) The starting point and the direction of recording the digit associated with each benzenoid are dictated by the convention to arrive at the largest number on reading the digits sequentially and counting an underlined or boldface digit **1** as  $-1$  (therefore lower than 0), in evaluating the application of rule (i). More explicitly, the following hierarchical order holds for the first three digits:  $221 > 220 > 22\mathbf{1} > 212 > 21\mathbf{1} > 210 > 2\mathbf{11} > 202 > 20\mathbf{1} > 200 > 20\mathbf{1}$ . When the first three digits are not enough, the next digit(s) are taken into account.

Figure 9 illustrates with a few examples this coding, which is displayed for all SRBs in Table 1. One may observe that the number of digits in the code is equal to the number of benzenoid rings on the periphery, except for (i) systems having one or several “concave” tetrabenzo[*a,c,h,j*]anthracenic groupings, each of which increases by one the number of digits because values **1** associated with them go in pairs, as exemplified by **4** (otherwise such **1** values can be single, as exemplified by **5**); and (ii) systems with  $R > 0$ , when the number of digits is reduced by  $R$ . For sterically crowded SRBs, one would need to include into the code either  $-2$  (i.e. **2**) as for systems from Figure 7 or a sequence of **1111** as for the SRB from Figure 8.

One could also characterize uniquely SRBs by yet another code, namely the “012-code” of the branched or nonbranched





**Figure 6.** Strain-free sextet-resonant benzenoids **46–60** having 54 carbon atoms with their numbers from the Dias book (except for **52A**) and their antisextet dualists.

antisextet dualist sequence of benzenoid rings formed by “empty-rings” and, in addition, by the gaps between them (which are sextet rings). As an example, for the branched cata-condensed benzenoids **30** and **31** from Figure 4 the notations are 1(2)01(2)02(1)01(2) and 1(2)01(2)01(2)01(2), respectively (the zeroes correspond to “straight walks” that include the gaps). However, because round brackets are needed for branched systems, this latter coding seems less easy to implement and to decode than the previous one (“sextet-polyphenyl-necklace coding”) that is included in Table 1. Both this sextet dualist graph code and the sextet-polyphenyl-necklace coding are uniquely associated with the corresponding strain-free SRBs.

#### ENUMERATION OF $C_{60}$ BENZENOIDS

The enumeration of  $C_{60}$  benzenoids was reported previously by Dias and then commented on by Dias, Cyvin, and Brunvoll. Here we present in Table 2 and in Figures 10A–D a complete survey of all possible strain-free SRBs with 60 carbon atoms, denoted by the sextet number 10 followed by a digit from 1 to 78.

It will be observed that for  $S = 10$  and  $P = 8$  there exist 26 isomeric  $C_{60}H_{26}$  benzenoids: 25 of these (**10-43–10-67**) have  $R = G = 0$ , and one (**10-68**) has  $R = G = 1$ . This

proves that there are three independent parameters ( $S$ ,  $P$ , and either  $R$  or  $G$ ) determining all other parameters discussed in the present paper for isomeric classes of SRBs. Similar cases of isomeric strain-free SRBs with the same  $S$  and  $P$  values, but differing in  $R = G$  values, can be found for  $S = 11$ ,  $P = 9$ , and  $G = R = 0$  or 1; also for  $S = 12$ ,  $P = 10$ , and  $G = R = 0$  or 1, and numerous larger SRBs. The lowest bound for such cases is compound **10-68** because this system corresponds to the smallest possible antisextet dualist with one ring (of course, acyclic antisextet dualists, i.e., SRBs with  $R = 0$ , are always possible).

#### HETEROCYCLIC CONGENERS OF SEXTET RESONANT BENZENOIDS

In an SRB there are six kinds of sextet benzenoid rings, according to the way they are adjacent to “empty” rings: (i) internal sextet rings with no CH groups; (ii) sextet rings with one CH group, flanked by four empty rings; (iii) with two adjacent CH groups, flanked by three condensed empty rings; (iv) with two *meso*-CH groups, in cata-condensed SRBs, flanked by two nonadjacent empty rings; (v) with three CH groups, flanked by two condensed empty rings; and (vi) with four adjacent CH groups, adjacent to one empty ring. As a consequence, there are five types of CH groups



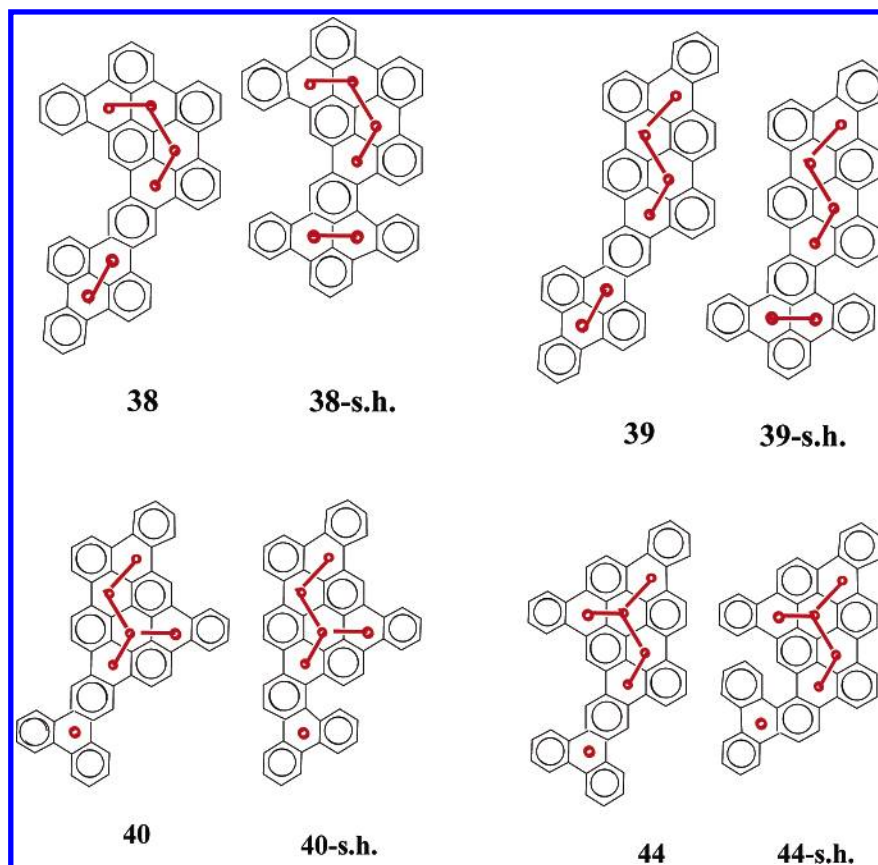


Figure 7. Examples of pairs of SRBs without and with steric hindrance (s.h.) sharing the same antisextet dualist.

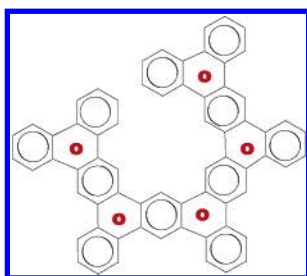


Figure 8. Another example of an SRB that is sterically crowded.

corresponding to cases (ii)–(vi) above. Except for case (iv), the sextet benzenoid ring with CH groups is a “marginal” or “peripheral” one.

A peripheral sextet ring of types (iii), (v), and (vi) forming a convex angle of  $120^\circ$  or  $60^\circ$  in the necklace (a ring coded by digit 1 or 2, respectively) may have external CH=CH fragments replaced by heteroatoms such as O, NR, or S. In this case, five-membered rings as oxa-, aza-, or thiaheterocyclic congeners of SRBs will result, and many examples are known. We illustrate this section with triphenylene congeners (Figure 11). Thus there are two possible monohetero derivatives ( $X = \text{O}$ ,  $\text{N}-\text{R}$ , or  $\text{S}$ , where the group  $\text{R}$  can be hydrogen, alkyl, or aryl) denoted by structures **A** and **B**.<sup>60–73</sup> There are six possible dihetero derivatives (**C–H**) with the same type of heteroatom,<sup>69–74</sup> and nine if the two heteroatoms are different, because **D**, **F**, and **H** give rise to two compounds each in such cases. With  $X = \text{S}$  or  $\text{NR}$ , **E** forms coordination compounds with transition metals. Among the numerous trihetero derivatives **I–O**, we highlight only one structure, namely **I**;<sup>72–75</sup> the compound with  $X = \text{S}$  is a [6]radialenic tris-thiophene.<sup>76</sup> Case (iv) stands apart: if one examines less symmetrical SRBs in Figure 3 than tri-

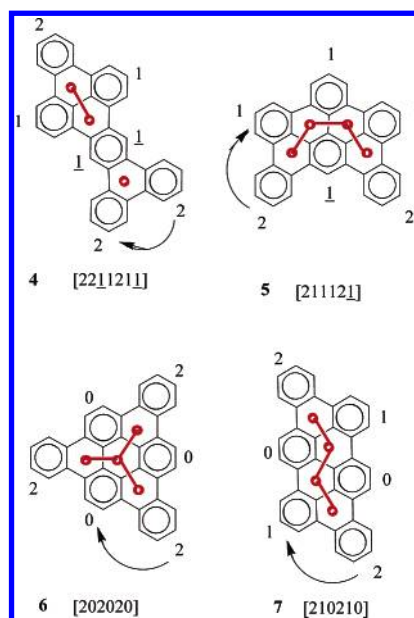


Figure 9. Illustration of how to apply coding rules for SRBs 4–7. The curved arrow indicates the start and direction of the walk along the polyphenyl-string periphery of the SRB. Underlined 1 should be read as boldface **1**.

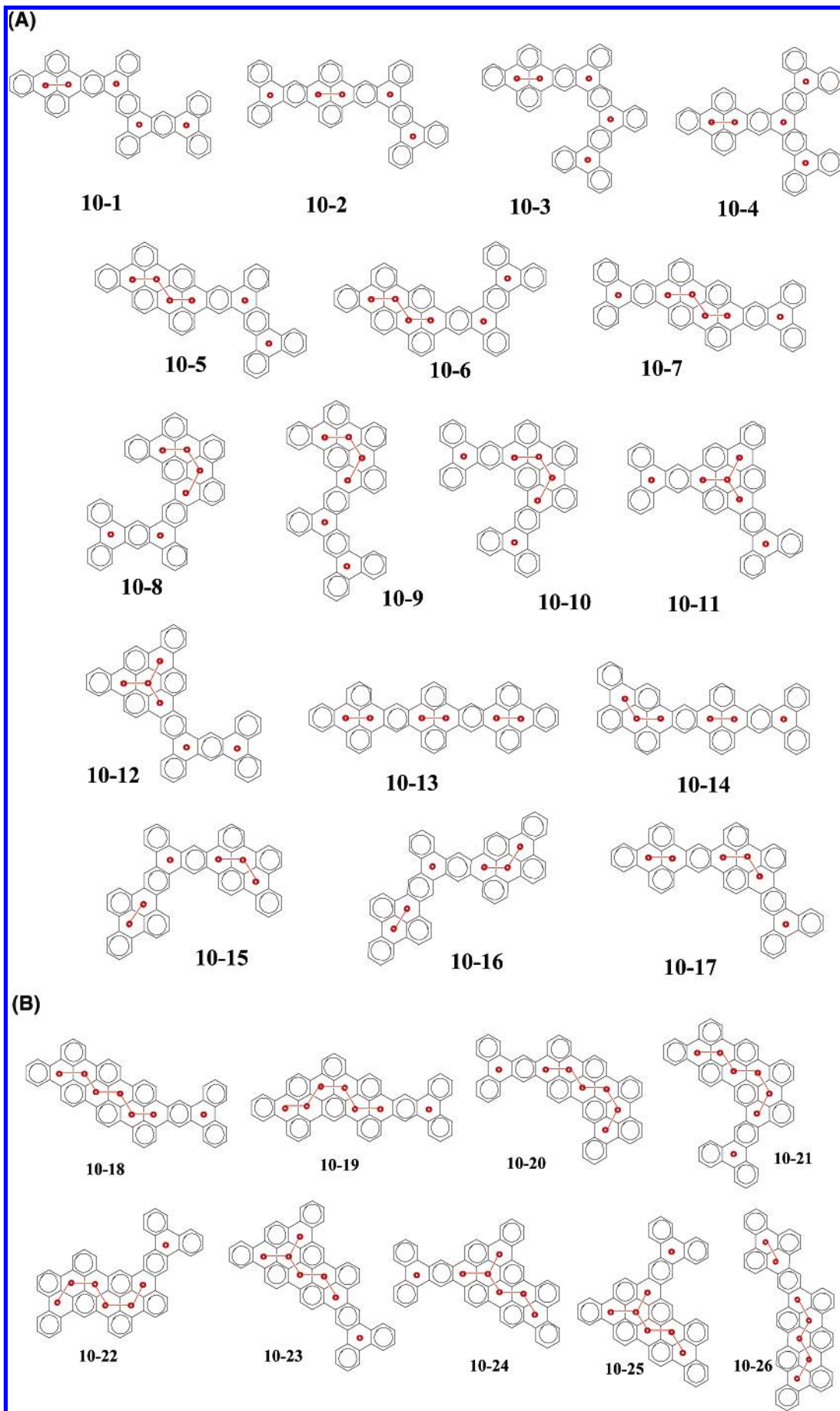
phenylene **0** (such as system **2**) for substitution by heteroatoms, O/NR/S-heteroderivatives can result by replacing either a CC bond in one of the four peripheral rings or the pair of *meso*-CH groups in the central benzenoid ring, which becomes a five-membered heterocyclic ring.<sup>77–81</sup>

On the other hand, azaheterocyclic congeners of SRBs can result whenever a *meso* or peripheral CH group is replaced by a “pyridinic nitrogen” heteroatom. Part B of the Dias

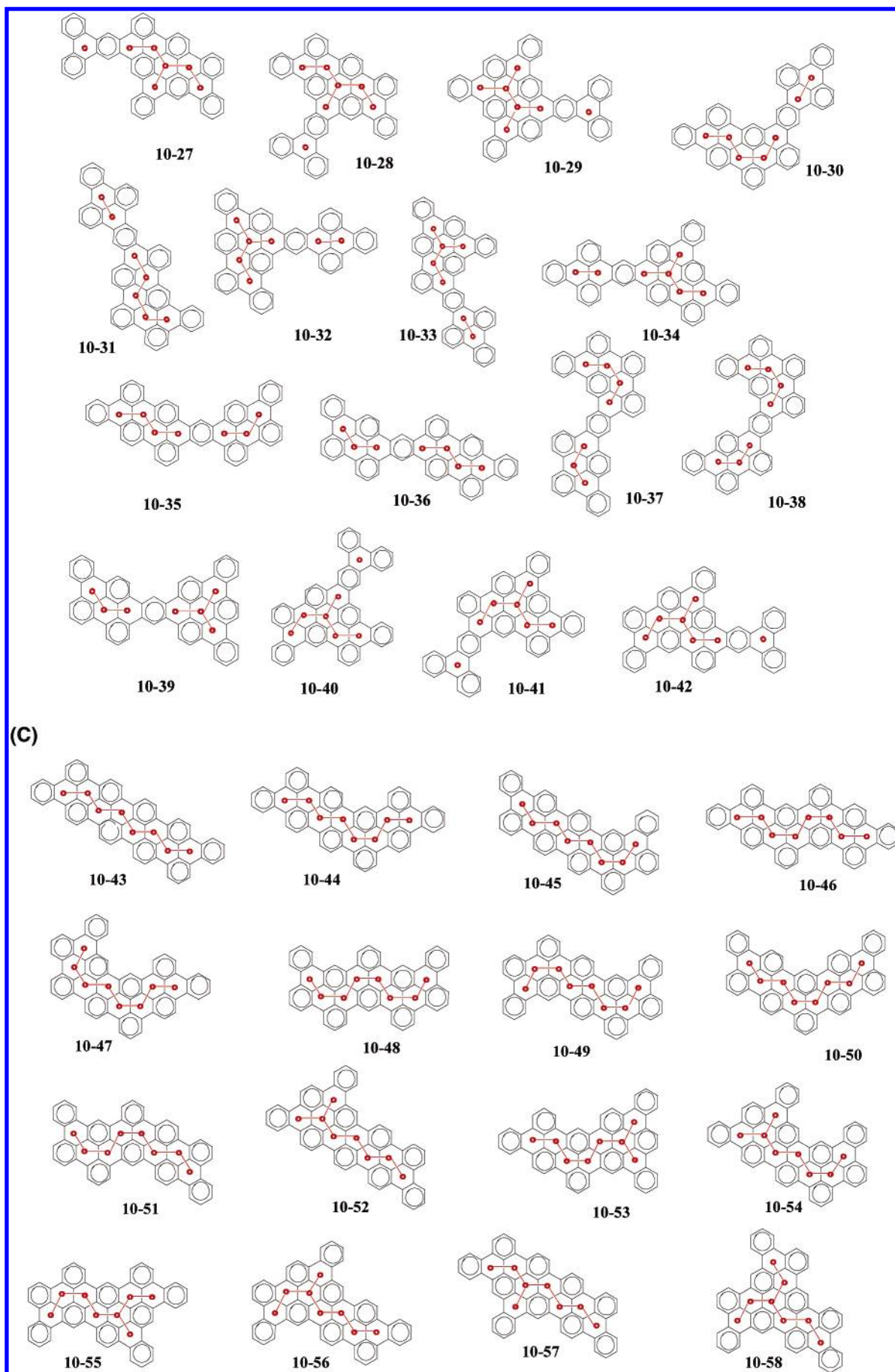
**Table 2.** Strain-Free Sextet-Resonant Benzenoids with 60 Carbon Atoms and  $S = 10$  Sextets<sup>a</sup>

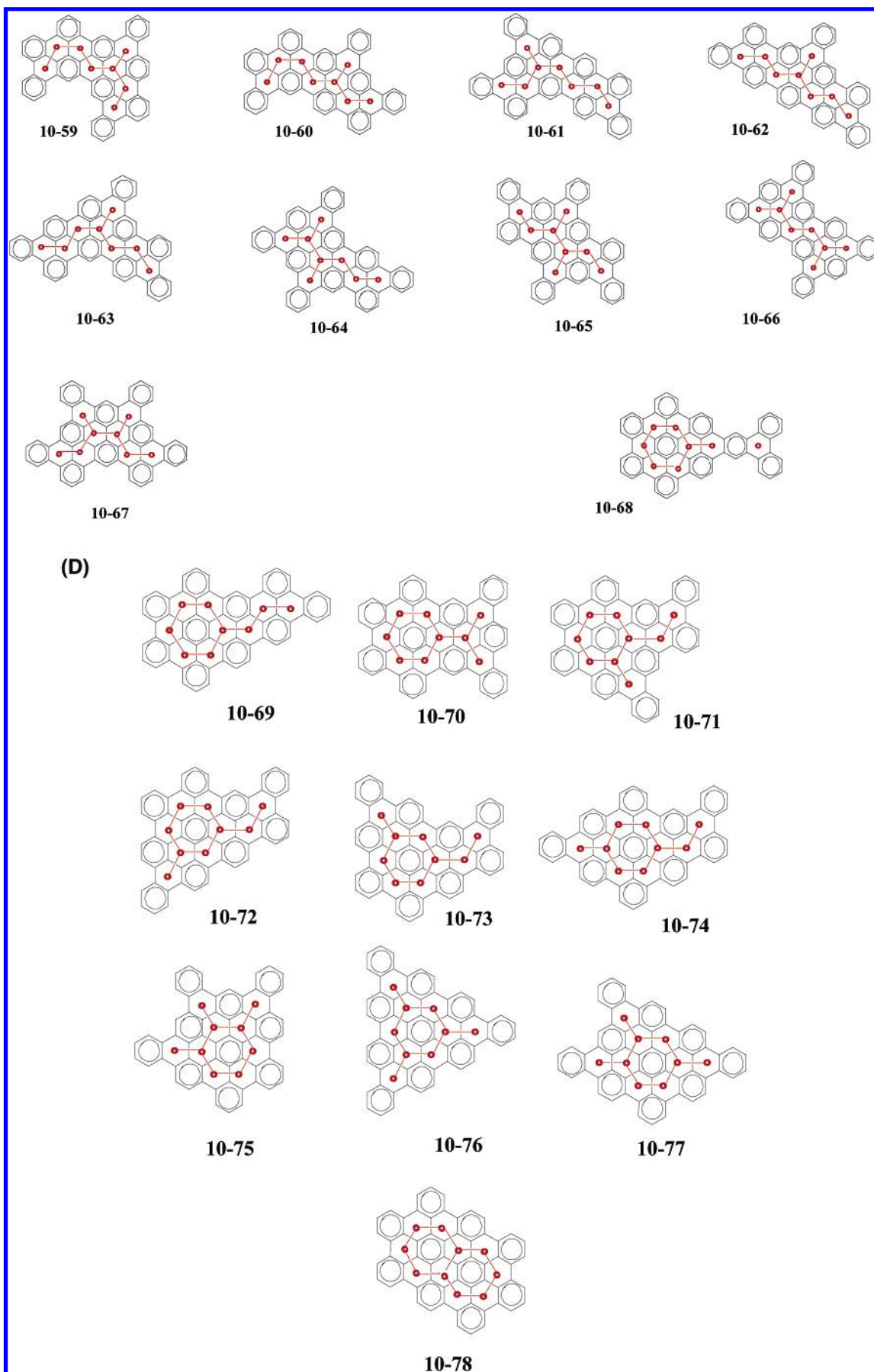
| compd<br>no. | formula |    | hexagons<br><i>h</i> | Kekulé<br>structures <i>K</i> | CC bonds<br><i>E</i> | antisextet |          | dualist  |          | code          |
|--------------|---------|----|----------------------|-------------------------------|----------------------|------------|----------|----------|----------|---------------|
|              | C       | H  |                      |                               |                      | <i>G</i>   | <i>P</i> | <i>R</i> | <i>L</i> |               |
| 10-1         | 60      | 32 | 15                   | <b>1762</b>                   | 74                   | 3          | 5        | 0        | 1        | 2212111211211 |
| 10-2         | 60      | 32 | 15                   | <b>1762</b>                   | 74                   | 3          | 5        | 0        | 1        | 2212111221211 |
| 10-3         | 60      | 32 | 15                   | <b>1762</b>                   | 74                   | 3          | 5        | 0        | 1        | 2212121121111 |
| 10-4         | 60      | 32 | 15                   | 1764                          | 74                   | 3          | 5        | 0        | 1        | 2211221112111 |
| 10-5         | 60      | 30 | 16                   | <b>1998</b>                   | 75                   | 2          | 6        | 0        | 3        | 2212101120111 |
| 10-6         | 60      | 30 | 16                   | <b>1998</b>                   | 75                   | 2          | 6        | 0        | 3        | 2212110210111 |
| 10-7         | 60      | 30 | 16                   | 1996                          | 75                   | 2          | 6        | 0        | 3        | 2211012211011 |
| 10-8         | 60      | 30 | 16                   | <b>1980</b>                   | 75                   | 2          | 6        | 0        | 3        | 2212111121111 |
| 10-9         | 60      | 30 | 16                   | <b>1980</b>                   | 75                   | 2          | 6        | 0        | 3        | 2212112111111 |
| 10-10        | 60      | 30 | 16                   | <b>1980</b>                   | 75                   | 2          | 6        | 0        | 3        | 2211111221111 |
| 10-11        | 60      | 30 | 16                   | 2044                          | 75                   | 2          | 6        | 0        | 3        | 2210201221011 |
| 10-12        | 60      | 30 | 16                   | 2052                          | 75                   | 2          | 6        | 0        | 3        | 2212102020111 |
| 10-13        | 60      | 30 | 16                   | 1960                          | 75                   | 2          | 6        | 0        | 3        | 2111111211111 |
| 10-14        | 60      | 30 | 16                   | <b>1980</b>                   | 75                   | 2          | 6        | 0        | 3        | 2211111201111 |
| 10-15        | 60      | 30 | 16                   | <b>1980</b>                   | 75                   | 2          | 6        | 0        | 3        | 2111211211110 |
| 10-16        | 60      | 30 | 16                   | <b>1980</b>                   | 75                   | 2          | 6        | 0        | 3        | 2111112112110 |
| 10-17        | 60      | 30 | 16                   | 1978                          | 75                   | 2          | 6        | 0        | 3        | 2211111211101 |
| 10-18        | 60      | 28 | 17                   | <b>2267</b>                   | 76                   | 1          | 7        | 0        | 5        | 22110011001   |
| 10-19        | 60      | 28 | 17                   | 2249                          | 76                   | 1          | 7        | 0        | 5        | 22111120101   |
| 10-20        | 60      | 28 | 17                   | <b>2245</b>                   | 76                   | 1          | 7        | 0        | 5        | 22110112101   |
| 10-21        | 60      | 28 | 17                   | 2247                          | 76                   | 1          | 7        | 0        | 5        | 22111012011   |
| 10-22        | 60      | 28 | 17                   | <b>2225</b>                   | 76                   | 1          | 7        | 0        | 5        | 22111121111   |
| 10-23        | 60      | 28 | 17                   | 2306                          | 76                   | 1          | 7        | 0        | 5        | 22111202001   |
| 10-24        | 60      | 28 | 17                   | 2301                          | 76                   | 1          | 7        | 0        | 5        | 22101112001   |
| 10-25        | 60      | 28 | 17                   | 2303                          | 76                   | 1          | 7        | 0        | 5        | 22102002111   |
| 10-26        | 60      | 28 | 17                   | <b>2245</b>                   | 76                   | 1          | 7        | 0        | 5        | 21011121100   |
| 10-27        | 60      | 28 | 17                   | <b>2270</b>                   | 76                   | 1          | 7        | 0        | 5        | 22110121211   |
| 10-28        | 60      | 28 | 17                   | <b>2267</b>                   | 76                   | 1          | 7        | 0        | 5        | 22112101211   |
| 10-29        | 60      | 28 | 17                   | 2310                          | 76                   | 1          | 7        | 0        | 5        | 22102120211   |
| 10-30        | 60      | 28 | 17                   | 2227                          | 76                   | 1          | 7        | 0        | 5        | 21111021111   |
| 10-31        | 60      | 28 | 17                   | <b>2225</b>                   | 76                   | 1          | 7        | 0        | 5        | 21101121111   |
| 10-32        | 60      | 28 | 17                   | 2272                          | 76                   | 1          | 7        | 0        | 5        | 21020112111   |
| 10-33        | 60      | 28 | 17                   | 2278                          | 76                   | 1          | 7        | 0        | 5        | 21110202111   |
| 10-34        | 60      | 28 | 17                   | <b>2270</b>                   | 76                   | 1          | 7        | 0        | 5        | 21011211021   |
| 10-35        | 60      | 28 | 17                   | <b>2245</b>                   | 76                   | 1          | 7        | 0        | 5        | 21111021010   |
| 10-36        | 60      | 28 | 17                   | <b>2245</b>                   | 76                   | 1          | 7        | 0        | 5        | 21110120110   |
| 10-37        | 60      | 28 | 17                   | <b>2225</b>                   | 76                   | 1          | 7        | 0        | 5        | 21111021111   |
| 10-38        | 60      | 28 | 17                   | <b>2225</b>                   | 76                   | 1          | 7        | 0        | 5        | 21111112011   |
| 10-39        | 60      | 28 | 17                   | 2305                          | 76                   | 1          | 7        | 0        | 5        | 21110202010   |
| 10-40        | 60      | 28 | 17                   | 2265                          | 76                   | 1          | 7        | 0        | 5        | 22101211211   |
| 10-41        | 60      | 28 | 17                   | <b>2270</b>                   | 76                   | 1          | 7        | 0        | 5        | 22110212111   |
| 10-42        | 60      | 28 | 17                   | <b>2270</b>                   | 76                   | 1          | 7        | 0        | 5        | 22111210211   |
| 10-43        | 60      | 26 | 18                   | 2575                          | 77                   | 0          | 8        | 0        | 7        | 2100021000    |
| 10-44        | 60      | 26 | 18                   | <b>2553</b>                   | 77                   | 0          | 8        | 0        | 7        | 2101120100    |
| 10-45        | 60      | 26 | 18                   | <b>2550</b>                   | 77                   | 0          | 8        | 0        | 7        | 2110012001    |
| 10-46        | 60      | 26 | 18                   | 2531                          | 77                   | 0          | 8        | 0        | 7        | 2111021110    |
| 10-47        | 60      | 26 | 18                   | 2530                          | 77                   | 0          | 8        | 0        | 7        | 2110102111    |
| 10-48        | 60      | 26 | 18                   | 2500                          | 77                   | 0          | 8        | 0        | 7        | 2111112111    |
| 10-49        | 60      | 26 | 18                   | <b>2525</b>                   | 77                   | 0          | 8        | 0        | 7        | 2110121101    |
| 10-50        | 60      | 26 | 18                   | <b>2550</b>                   | 77                   | 0          | 8        | 0        | 7        | 2101012010    |
| 10-51        | 60      | 26 | 18                   | <b>2525</b>                   | 77                   | 0          | 8        | 0        | 7        | 21110210111   |
| 10-52        | 60      | 26 | 18                   | 2617                          | 77                   | 0          | 8        | 0        | 7        | 2101202000    |
| 10-53        | 60      | 26 | 18                   | 2589                          | 77                   | 0          | 8        | 0        | 7        | 2110202110    |
| 10-54        | 60      | 26 | 18                   | 2595                          | 77                   | 0          | 8        | 0        | 7        | 2110020211    |
| 10-55        | 60      | 26 | 18                   | <b>2550</b>                   | 77                   | 0          | 8        | 0        | 7        | 2111121201    |
| 10-56        | 60      | 26 | 18                   | 2578                          | 77                   | 0          | 8        | 0        | 7        | 2102102101    |
| 10-57        | 60      | 26 | 18                   | <b>2580</b>                   | 77                   | 0          | 8        | 0        | 7        | 2100121121    |
| 10-58        | 60      | 26 | 18                   | <b>2553</b>                   | 77                   | 0          | 8        | 0        | 7        | 2111201211    |
| 10-59        | 60      | 26 | 18                   | <b>2550</b>                   | 77                   | 0          | 8        | 0        | 7        | 2111201211    |
| 10-60        | 60      | 26 | 18                   | <b>2550</b>                   | 77                   | 0          | 8        | 0        | 7        | 2111212101    |
| 10-61        | 60      | 26 | 18                   | <b>2580</b>                   | 77                   | 0          | 8        | 0        | 7        | 2100212110    |
| 10-62        | 60      | 26 | 18                   | 2594                          | 77                   | 0          | 8        | 0        | 7        | 2112112000    |
| 10-63        | 60      | 26 | 18                   | 2592                          | 77                   | 0          | 8        | 0        | 7        | 21120021110   |
| 10-64        | 60      | 26 | 18                   | 2606                          | 77                   | 0          | 8        | 0        | 7        | 2112120210    |
| 10-65        | 60      | 26 | 18                   | <b>2576</b>                   | 77                   | 0          | 8        | 0        | 7        | 2112121121    |
| 10-66        | 60      | 26 | 18                   | 2641                          | 77                   | 0          | 8        | 0        | 7        | 2020120201    |
| 10-67        | 60      | 26 | 18                   | <b>2576</b>                   | 77                   | 0          | 8        | 0        | 7        | 2111212121    |
| 10-68        | 60      | 26 | 18                   | <b>2550</b>                   | 77                   | 1          | 8        | 1        | 7        | 2210111101    |
| 10-69        | 60      | 24 | 19                   | 2875                          | 78                   | 0          | 9        | 1        | 9        | 2111111100    |
| 10-70        | 60      | 24 | 19                   | <b>2895</b>                   | 78                   | 0          | 9        | 1        | 9        | 2021111111    |
| 10-71        | 60      | 24 | 19                   | <b>2895</b>                   | 78                   | 0          | 9        | 1        | 9        | 2112011111    |
| 10-72        | 60      | 24 | 19                   | 2945                          | 78                   | 0          | 9        | 1        | 9        | 2100201111    |
| 10-73        | 60      | 24 | 19                   | 2940                          | 78                   | 0          | 9        | 1        | 9        | 2101102011    |
| 10-74        | 60      | 24 | 19                   | 2930                          | 78                   | 0          | 9        | 1        | 9        | 2101020111    |
| 10-75        | 60      | 24 | 19                   | 2960                          | 78                   | 0          | 9        | 1        | 9        | 2011021211    |
| 10-76        | 60      | 24 | 19                   | 3100                          | 78                   | 0          | 9        | 1        | 9        | 200200200     |
| 10-77        | 60      | 24 | 19                   | 3000                          | 78                   | 0          | 9        | 1        | 9        | 2010200211    |
| 10-78        | 60      | 22 | 20                   | 3250                          | 79                   | 0          | 10       | 2        | 11       | 11101110      |

<sup>a</sup> In the fifth column degenerate *K* values are indicated in boldface; see text for explanation of notation.

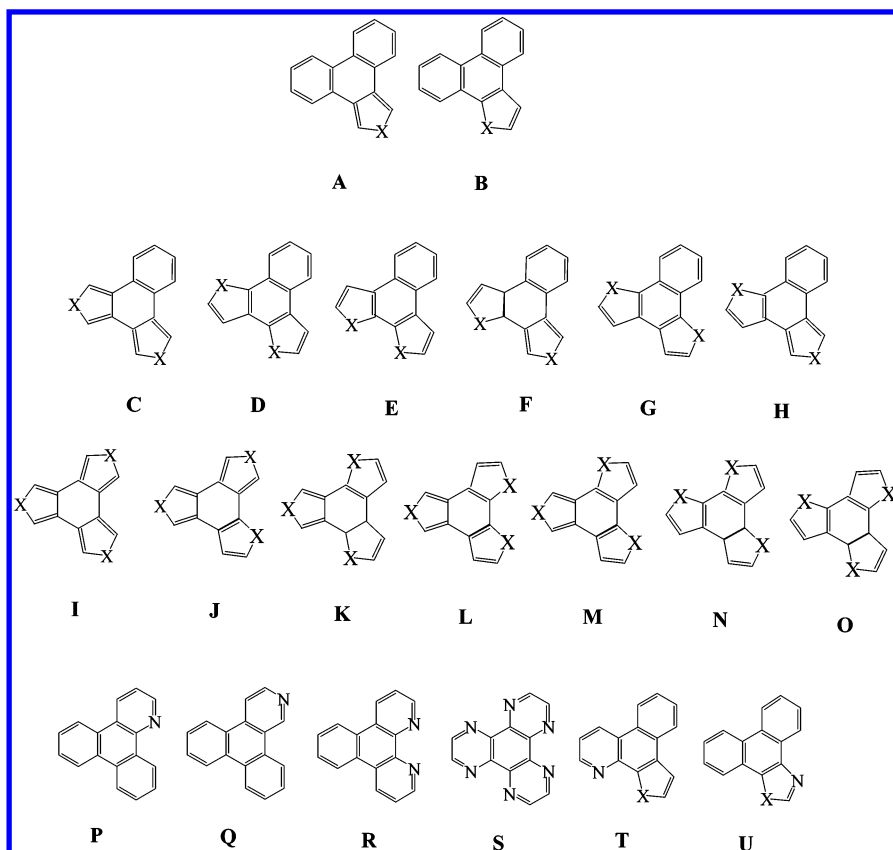








**Figure 10.** A. The four strain-free SRBs with  $S = 10$  and  $P = 5$  (10-1–10-4) and the 13 strain-free SRBs with  $S = 10$  and  $P = 6$  (10-5–10-17). B. The 25 strain-free SRBs with  $S = 10$  and  $P = 7$  (10-18–10-42). C. The 26 strain-free SRBs with  $S = 10$ ,  $P = 8$ , and  $R = G = 0$  (10-43–10-67) or  $R = G = 1$  (10-68). D. The nine strain-free SRBs with  $S = 10$  and  $P = 9$  (10-69–10-77) and the unique strain-free SRB with  $S = 10$  and  $P = 10$  (10-78).



**Figure 11.** Structures of heterocyclic analogues of SRBs.

*Handbook* contains nine aza and polyaza analogues of triphenylene and two derivatives of **2** (Figure 3), in which one or both CH groups of the central ring are substituted by nitrogen.<sup>8</sup> There are two possible monoazatriphenylenes, **P** and **Q**.<sup>82,83</sup> From the many di- and polyazatriphenylenes we cite only one diaza-derivative (benzophenanthroline, **R**)<sup>84,85</sup> and the hexa-aza derivative **S**.<sup>86–91</sup> Like phenanthroline, compounds **R** and **S** afford metallic complexes that are interesting for biological studies. Metallic complexes of **S** (hexaazatriphenylene, HAT) have also obtained prominence for their applications as coordination polymers and for hydrogen storage.

Finally, one may combine both types of substitution of CH groups: aza-substitution may occur in different peripheral rings (e.g. **T**), in the same peripheral ring which becomes an (iso)thiazole or (is)oxazole ring (e.g. **U**), or in both types of rings for polyaza-derivatives.

It was mentioned earlier that SRBs are the most stable among all isomeric benzenoids. They are among the most abundant benzenoids formed in pyrolytic reactions, and they are present in the interstellar medium surrounding carbon-rich stars.<sup>92,93</sup> It is expected that their heteroanalogues will also benefit from high stability due to  $\pi$ -electron delocalization.

## CONCLUSIONS

Clar formulas of benzenoids carry a substantial amount of information if drawn correctly.<sup>94</sup> The partition of  $\pi$ -electrons among rings of benzenoids can be assigned either according to all Kekulé structures<sup>95</sup> or only to those, fewer, corresponding to Clar structures.<sup>96,97</sup>

Theoretical explorations on the connections between Clar structures for graphene, fullerenes, nanotubes, nanotubes, and nanotubes<sup>98,99</sup> as well as the impressive recent achievements of Müllen and co-workers in the synthesis of large benzenoids<sup>40,41</sup> have opened fascinating research avenues in this area. The steric constraints cause one member of an isomeric hexabenzocoronene pair with hexagonal symmetry to be planar (namely the SRB hexabenzob[bc,ef,hi,kl,no,qr]coronene),<sup>44</sup> while the other, a sterically strained hexabenzob[a,d,g,j,m,p]coronene, is nonplanar.<sup>100</sup>

Unlike acenes which are extremely reactive when they have 7 or more linearly condensed benzenoid rings, SRBs that do include such strings with 7 or more linearly condensed benzenoid rings are perfectly stable because they have no *meso*-CH groups and a sextet-resonant distribution of their  $\pi$ -electrons, as proved experimentally by Clar and co-workers who synthesized tetrabenzooheptacene (**9** in Figure 3).<sup>20</sup>

For any strain-free sextet-resonant benzenoid (SRB), its antisextet dualist is formed by vertices that are centers of “empty rings” and by edges that connect such vertices when the corresponding “empty rings” are adjacent. The main parameters of SRBs are the number *S* of sextets (one-sixth of the number of carbon atoms in the SRB) and the number *P* of vertices in the antisextet dualist. For a given number *H* of hydrogen atoms in the SRB, the relationship  $P = H/2 - S - 1$  holds. Groups of SRBs sharing a pair of *S* and *P* values (but differing in the geometry of annelation) share also other parameters such as the total number of benzenoid rings and have numbers of Kekulé structures within close ranges. Some of these relationships have been previously



published by Cyvin et al.,<sup>101</sup> Dias,<sup>102</sup> and Gutman and Babić.<sup>103</sup>

All 65 possible strain-free SRBs with 3–9 Clar sextets have been displayed in Table 1 and Figures 3–6 (four more than the structures initially published by Dias, plus triphenylene). The HOMO energies characterize them uniquely. Also all 78 possible strain-free SRBs with 10 Clar sextets have been presented in Table 2 and Figures 10A–D. In addition, a unique structural coding system using four digits (–1, 0, 1, and 2 associated with the angle deviation from 180° at each benzenoid ring), based on the geometry of the sextet benzenoid rings at the periphery of the SRB, has been devised and presented in Tables 1 and 2.

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