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AZULENOIDS

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Abstract. Azulenoids are polygonal systems with one pentagon each and otherwise only heptagons (simply connected mono–5–polyheptagons). Topological properties (invariants, circumscribing, extremal systems, chemical formulas) of azulenoids are treated. Enumerations and classifications from computer programming are reported.

INTRODUCTION

A polygonal system consists of connected polygons, where any two polygons either share exactly one edge or are disjoint. As chemical graphs [1], the polygonal systems represent polycyclic conjugated hydrocarbons, a current source of investigations in organic chemistry, as well as physical, theoretical and mathematical chemistry. Any vertex in a polygonal system has degree two or three, corresponding to a secondary or tertiary carbon atom, respectively. In the present work, only simply connected polygonal systems, say P, are considered. They have no holes (in contrast to coronoids [2]) and correspond to completely condensed polycyclic conjugated hydrocarbons. The number of polygons (or rings) in P is identified by the symbol r. The C_nH_s isomers of the systems of this category with different ring sizes have been treated [3–5]. In particular, the isomer enumeration problem of P systems [4–11] has been solved completely for $r \leq 5$ [9], and an extension to larger r values seems to be very complicated. Instead, several subclasses of P have been considered, such as:

benzenoids [12,13]/polyhexes [13] (exclusively hexagons);
polypentagons [14] (exclusively pentagons);
fluoranthenoids/fluorenoids [15–19] (one pentagon, otherwise hexagons);
indacenoids [20] (two pentagons, otherwise hexagons);

biphenylenoids [21] (one tetragon, otherwise hexagons);

terphenylenoids [22] (two tetragons, otherwise hexagons).

The fluor(anth)enoids and biphenylenoids belong to mono–q–polyhexes [21–30] for $q = 5$ and 4, respectively. A mono–q–polyhex contains exactly one q–gon and otherwise hexagons (if any). In an analogous way, the mono–q–polyheptagons are defined as polygonal systems with exactly one q–gon and otherwise only heptagons. The simply connected mono–5–polyheptagons, which include the azulenoids as a subclass, are the subject of the present work.

AZULENE

The prototype of azulenoids (for a precise definition, see below) is $C_{10}H_8$ azulene; see Fig. 1. Here is not the place for a comprehensive survey of the literature on this well known molecule in organic chemistry; we only wish to give a few selected references to some chemical properties of azulene [31,32] and to some works in structural chemistry [33,34] and molecular vibrations [34–38].

Azulene is isomeric with $C_{10}H_8$ naphthalene. In total, there are four $C_{10}H_8$ bicyclic isomers of conjugated hydrocarbons [5,7–9]. The azulene and naphthalene systems have several topological properties in common: as bicyclic polygonal systems they are catacondensed; they possess the same number of vertices, edges and vertices of degree two, the same perimeter length in terms of the number of external edges or vertices, and the same number of edges in the 1–factor [39]. This last feature manifests itself in the fact that each Kekulé structure of azulene or naphthalene possesses five double bonds. However, azulene has only two Kekulé structures in total, while naphthalene has three.

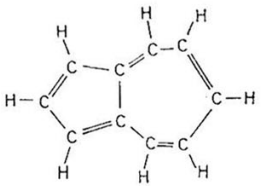


Fig. 1. Azulene, $C_{10}H_8$.

DEFINITION AND TOPOLOGICAL PROPERTIES

Definitions. Denote by M a simply connected mono–*5*–polyheptagon. Then M is a polygonal system with exactly one pentagon and otherwise only heptagons (if any). A system M may be geometrically planar (nonhelicenic) or geometrically nonplanar (helicenic), defined in the same way as the analogous concepts in polyhexes [13,40]. An azulenoid is a geometrically planar, simply connected mono–*5*–polyheptagon. In precise terms, an azulenoid is completely defined by a closed path on the mono–*5*–polyheptagonal lattice as shown in Fig. 2. This path constitutes the perimeter of the given azulenoid.

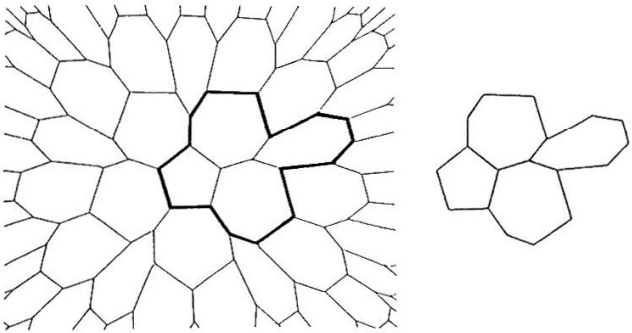


Fig. 2. An azulenoid ($C_{18}H_{12}$) defined by its perimeter on the mono–*5*–heptagonal lattice.

Invariants. In Table 1 a number of invariants are defined for the M systems (which include azulenoids), and relations between them are specified in terms of the selected independent pairs (r, n_i) and (n, s). The chemical formula of M reads C_nH_s. Relations analogous to those of Table 1 are readily available for simply connected polyhexes (including benzenoids and helicenes) [40] and simply connected mono–*5*–polyhexes (including fluoranthenoids/fluorenoids) [17]. In both of these latter cases, the two invariants s and t are not independent. However, as an interesting fact, the pair (s, t) does provide independent invariants for M, by which all the other given invariants can be expressed as linear combinations.

Table 1. Invariants of simply connected mono–5–polyheptagons (M), including azulenoids.

Invariant*	Function of (r, n_i)	Function of (n, s)
r	r	$\frac{1}{2}(n-s)+1$
n	$5r-n_i$	n
m	$6r-n_i-1$	$\frac{1}{2}(3n-s)$
n_i	n_i	$\frac{1}{2}(3n-5s)+5$
n_e	$5r-2n_i$	$\frac{1}{2}(5s-n)-5$
s	$3r-n_i+2$	s
t	$2r-n_i-2$	$\frac{1}{2}(3s-n)-5$

* r = # polygons
n = # vertices
m = # edges
n_i = # internal vertices
n_e = # external vertices (on the perimeter,
= # edges on the perimeter = perimeter length)
s = # vertices of degree two (on the perimeter)
t = # vertices of degree three on the perimeter

Circumscribing. The circumscribing of a polygonal system by heptagons [41–43] leads to an algebra quite different from the algebra of circumscribing by hexagons [18,44,45]. Assume that a system M with the invariants r_0, $(n_i)_0$, n_0, s_0 can be circumscribed by heptagons. Then the following was deduced (starting from $r_1 = r_0 + s_0$) for the new invariants r_1, etc. pertaining to circum–M:

$$r_1 = 4r_0 - (n_i)_0 + 2 \ , \quad (n_i)_1 = 5r_0 - (n_i)_0 \tag{1}$$

$$n_1 = \tfrac{1}{2}(3n_0 + 5s_0) + 5 \ , \quad s_1 = \tfrac{1}{2}(n_0 + 3s_0) + 5 \tag{2}$$

Assume now that M can be circumscribed k times. It is not a quite trivial task to find the invariants r_k, etc. for the k–fold circumscribed M, viz. k–circum–M. The following explicit expressions were found in terms of the Fibonacci numbers ($F_0 = F_1 = 1$, $F_{N+1} = F_N + F_{N-1}$ for $N > 0$):

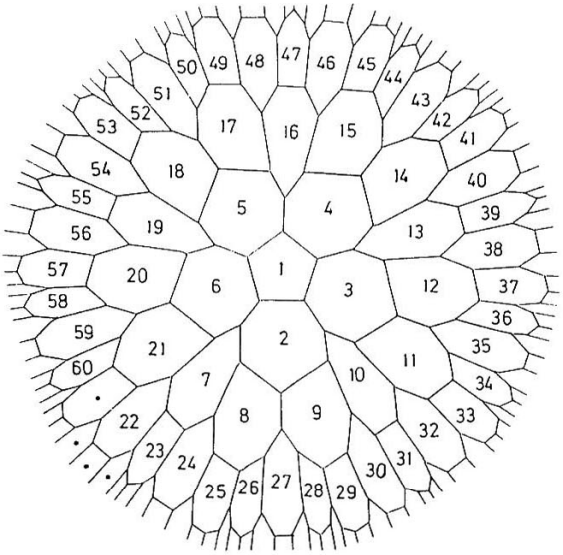
$$\begin{aligned} r_k &= [6 - r_0 + (n_i)_0]F_{2k} + [2r_0 - (n_i)_0 - 2]F_{2k+1} - 4 \ , \\ (n_i)_k &= [20 - 5r_0 + 4(n_i)_0]F_{2k} + [5r_0 - 3(n_i)_0 - 10]F_{2k+1} - 10 \end{aligned} \tag{3}$$

$$\begin{aligned} n_k &= \tfrac{1}{2}(3n_0 - 5s_0 + 30)F_{2k} + \tfrac{1}{2}(5s_0 - n_0 - 10)F_{2k+1} - 10 \ , \\ s_k &= \tfrac{1}{2}(3s_0 - n_0 - 10)F_{2k} + \tfrac{1}{2}(n_0 - s_0 + 10)F_{2k+1} \end{aligned} \tag{4}$$

The relations (3), from which (4) follow, have been proved by complete induction; see Appendix A.

Extremal Systems. An extremal M is defined in the same way as an extremal benzenoid [12,44–46]. All extremal M systems are azulenoids. One representative of the extremal azulenoids for each r value is generated by the spiral walk [17,46,47], as is illustrated in Fig. 3. When r increases, $(n_i)_{\max}$ is constant only in the very first step; otherwise it acquires an increment of one or two units. It has not proved possible to deduce $(n_i)_{\max}$ as an explicit function of r in analogy with the known functions for benzenoids [12,46–48], simply connected mono–q–polyhexes [17,21,26] and some di–q–polyhexes [22]. A formula of $(n_i)_{\max}$ for azulenoids is an open problem as well as for polyheptagons [42]. However, some significant results have been achieved for a class of extremal azulenoids, viz. the k–fold circumscribed cyclopentadienyls.

Polycircum–Cyclopentadienyls. Cyclopentadienyl, C_5H_5, is represented by a single pentagon. Here the k–circum–C_5H_5 systems are considered. In Fig. 3, the k–circum–C_5H_5 systems up to $k = 3$ are found. For $k > 0$, a heptagon at the perimeter of a k–circum–C_5H_5 system has either two or three vertices of second degree; they can appropriately be referred to as *2*H– or *3*H–heptagons, respectively. Furthermore, these heptagons occur always in the combinations *2*H*3*H*2*H or *2*H*3*H*3*H*2*H and so that two *2*H



r	$(n_i)_{\max}$	r	$(n_i)_{\max}$	r	$(n_i)_{\max}$
1	0	11	11	21	25
2	0	12	12	22	26
3	1	13	14	23	27
4	2	14	15	24	29
5	3	15	16	25	30
6	5	16	18	26	31
7	6	17	19	27	33
8	7	18	20	28	34
9	8	19	22	29	35
10	10	20	23	30	37

Fig. 3. Extremal azulenoids generated by the spiral walk. Increments by two units in $(n_i)_{\max}$ (when r increases) are indicated by arrows in the list of $(n_i)_{\max}(r)$.

Table 3. Chemical formulas of simply connected mono–5–polyheptagons (M), including azulenoids.

	n_i										
r	0	1	2	3	4	5	6	7	8	9	10
1	C_5H_5										
2	$C_{10}H_8$										
3	$C_{15}H_{11}$	$C_{14}H_{10}$									
4	$C_{20}H_{14}$	$C_{19}H_{13}$	$C_{18}H_{12}$								
5	$C_{25}H_{17}$	$C_{24}H_{16}$	$C_{23}H_{15}$	$C_{22}H_{14}$							
6	$C_{30}H_{20}$	$C_{29}H_{19}$	$C_{28}H_{18}$	$C_{27}H_{17}$	$C_{26}H_{16}$	$C_{25}H_{15}$					
7	$C_{35}H_{23}$	$C_{34}H_{22}$	$C_{33}H_{21}$	$C_{32}H_{20}$	$C_{31}H_{19}$	$C_{30}H_{18}$	$C_{29}H_{17}$				
8	$C_{40}H_{26}$	$C_{39}H_{25}$	$C_{38}H_{24}$	$C_{37}H_{23}$	$C_{36}H_{22}$	$C_{35}H_{21}$	$C_{34}H_{20}$	$C_{33}H_{19}$			
9	$C_{45}H_{29}$	$C_{44}H_{28}$	$C_{43}H_{27}$	$C_{42}H_{26}$	$C_{41}H_{25}$	$C_{40}H_{24}$	$C_{39}H_{23}$	$C_{38}H_{22}$	$C_{37}H_{21}$		
10	$C_{50}H_{32}$	$C_{49}H_{31}$	$C_{48}H_{30}$	$C_{47}H_{29}$	$C_{46}H_{28}$	$C_{45}H_{27}$	$C_{44}H_{26}$	$C_{43}H_{25}$	$C_{42}H_{24}$	$C_{41}H_{23}$	$C_{40}H_{22}$

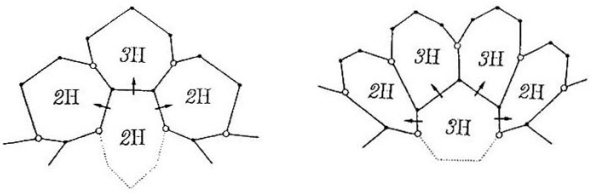


Fig. 4. Two schemes for the generation of heptagons at the perimeter of a k–circum–C_5H_5 system.

Table 2.Invariants and chemical formulas for k–circum–C_5H_5 systems.

k	r_k	$(n_i)_k$	C_nH_s
0	1	0	C_5H_5
1	6	5	$C_{25}H_{15}$
2	21	25	$C_{80}H_{40}$
3	61	80	$C_{225}H_{105}$
4	166	225	$C_{605}H_{275}$
5	441	605	$C_{1600}H_{720}$

heptagons are never neighbours (e.g. ... 3H2H3H3H2H3H2H3H ...); cf. Fig. 4. In Table 2, the (r, n_i) invariants and C_nH_s chemical formulas for some of the systems under consideration are summarized. On inserting $r_0 = 1$, $(n_i)_0 = 0$, $n_0 = 5$, $s_0 = 5$ in eqns. (3) and (4), the following expressions for k–circum–C_5H_5 systems emerge.

$$r_k = 5F_{2k} - 4 \ , \quad (n_i)_k = 15F_{2k} - 5F_{2k+1} - 10 \tag{5}$$

$$n_k = 10F_{2k} + 5F_{2k+1} - 10 \ , \quad s_k = 5F_{2k+1} \tag{6}$$

These equations are very similar to the corresponding ones for circumscribed heptagon [43]. In Appendix B, the recurrence relations for the above quantities are given, and an alternative form of the explicit relation for r_k is included.

Chemical Formulas. For a given r, the C_nH_s formulas of the M systems or azulenoids span from $C_{5r}H_{3r+2}$ to the formula for the pertinent extremal M system(s). These latter formulas are readily obtained from $(n_i)_{max}$, of which the tabulation in Fig. 3 is supposed to be sufficient for all practical purposes, although a general formulation is not available. All azulenoid C_nH_s formulas for $r \leq 10$ are listed in Table 3.

A spectrum of hydrocarbon formulas has been defined [49]: benzenoid formulas from catabenzenoid to extremalbenzenoid; infrabenzenoid formulas are found on the hydrogen–rich side (beyond catabenzenoid); ultrabenzenoid formulas are on the hydrogen–poor side (beyond extremalbenzenoid). In Table 3, the benzenoid formulas are separated from the rest by a heavy line. Catabenzenoid formulas are found right above the staircase boundary. All the catabenzenoid formulas for $r > 1$ (i.e. all but C_6H_6) are also azulenoid formulas, but $C_{10}H_8$ is the only extremalbenzenoid formula among them. The formulas below the staircase boundary in Table 3 are infrabenzenoid. There is one single ultrabenzenoid formula, viz. C_5H_5, among the azulenoids.

GENERATION AND ENUMERATION

A computer program for generation and enumeration of benzenoids [50,51] was adapted to azulenoids. Numerical results for the C_nH_s isomers up to $r = 7$ are collected in Table 4. The distributions into symmetry groups are included. There is no entry for the C_{5h} symmetry in Table 4, although this symmetry group does occur; the smallest C_{5h} azulenoid is a unique system at $r = 11$.

In Table 5 the catacondensed ($n_i = 0$) azulenoids up to $r = 7$ are classified into unbranched and branched systems. Here the single pentagon ($r = 1$; cyclopentadienyl) is the only catacondensed azulenoid belonging to D_{5h}, while C_{5h} is not at all possible.

The 4 and 22 azulenoids with $r = 3$ and 4, respectively, are depicted in Fig. 5.

OPEN PROBLEM

Constant–isomer series are certain sequences of C_nH_s formulas where, for a given class of chemical graphs, the number of isomers is the same. Such sequences have been detected for benzenoids [52–54], fluoranthenoids/fluorenoids [15,16,18], indacenoids [20], biphenylenoids [21] and terphenylenoids [22]. It is not known whether constant–isomer series exist for azulenoids.

Table 4. Numbers of azulenoid isomers.

r	n_i	Formula	D_{5h}	C_{2v}	C_s	Total
1	0	C_5H_5	1	0	0	1
2	0	$C_{10}H_8$	0	1	0	1
3	0	$C_{15}H_{11}$	0	1	2	3
	1	$C_{14}H_{10}$	0	1	0	1
4	0	$C_{20}H_{14}$	0	1	13	14
	1	$C_{19}H_{13}$	0	2	4	6
	2	$C_{18}H_{12}$	0	2	0	2
5	0	$C_{25}H_{17}$	0	4	75	79
	1	$C_{24}H_{16}$	0	3	40	43
	2	$C_{23}H_{15}$	0	3	11	14
	3	$C_{22}H_{14}$	0	1	2	3
6	0	$C_{30}H_{20}$	0	4	455	459
	1	$C_{29}H_{19}$	0	7	319	326
	2	$C_{28}H_{18}$	0	9	122	131
	3	$C_{27}H_{17}$	0	2	35	37
	4	$C_{26}H_{16}$	0	3	5	8
	5	$C_{25}H_{15}$	1	0	0	1
7	0	$C_{35}H_{23}$	0	18	2782	2800
	1	$C_{34}H_{22}$	0	14	2428	2442
	2	$C_{33}H_{21}$	0	13	1159	1172
	3	$C_{32}H_{20}$	0	10	408	418
	4	$C_{31}H_{19}$	0	7	101	108
	5	$C_{30}H_{18}$	0	1	19	20
	6	$C_{29}H_{17}$	0	1	0	1

APPENDIX A

From eqn. (1), one has the following.

$$r_{k+1} = 4r_k - (n_i)_k + 2 \ , \quad (n_i)_{k+1} = 5r_k - (n_i)_k \tag{A1}$$

Suppose that the relations (3) are valid for a certain k value. Then:

$$r_{k+1} = 4\{[6 - r_0 + (n_i)_0]F_{2k} + [2r_0 - (n_i)_0 - 2]F_{2k+1} - 4\}$$

Table 5. Numbers of catacondensed azulenoids.

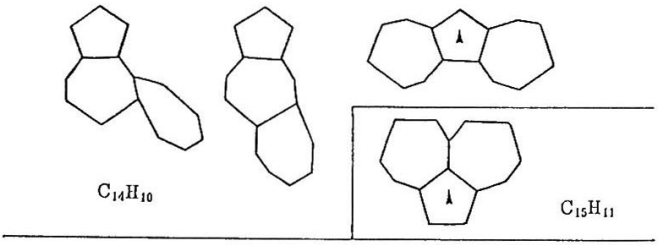
r	Form	D_{5h}	C_{2v}	C_s	Total
1	unbranched	1	0	0	1
2	unbranched	0	1	0	1
3	unbranched	0	1	2	3
4	unbranched	0	0	12	12
	branched	0	1	1	2
5	unbranched	0	4	54	58
	branched	0	0	21	21
6	unbranched	0	0	256	256
	branched	0	4	199	203
7	unbranched	0	15	1141	1156
	branched	0	3	1641	1644

$$
\begin{aligned}
&-\{[20-5r_0+4(n_i)_0]F_{2k}+[5r_0-3(n_i)_0-10]F_{2k+1}-10\}+2\\
&=(4+r_0)F_{2k}+[2+3r_0-(n_i)_0]F_{2k+1}-4\\
&=(4+r_0)(F_{2k}+F_{2k+1})+[2r_0-(n_i)_0-2]F_{2k+1}-4\\
&=(4+r_0)F_{2k+2}+[2r_0-(n_i)_0-2](F_{2k+3}-F_{2k+2})-4\\
&=[6-r_0+(n_i)_0]F_{2k+2}+[2r_0-(n_i)_0-2]F_{2k+3}-4 \qquad \text{(A2)}
\end{aligned}
$$

Hence the first one of relations (3) is valid on substituting k by $k+1$. In the same way, it is found for the last one of relations (3) that:

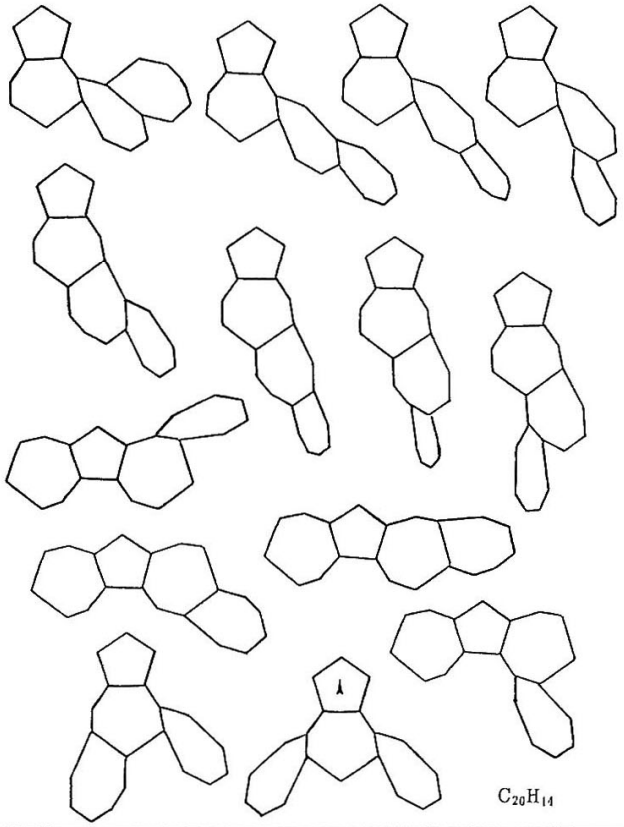
$$(n_i)_{k+1}=[20-5r_0+4(n_i)_0]F_{2k+2}+[5r_0-3(n_i)_0-10]F_{2k+3}-10 \qquad \text{(A3)}$$

The relations (3) are readily found to be valid for $k=0$; hence they are proved by complete induction to be valid in general.



$C_{14}H_{10}$

$C_{15}H_{11}$



$C_{20}H_{14}$

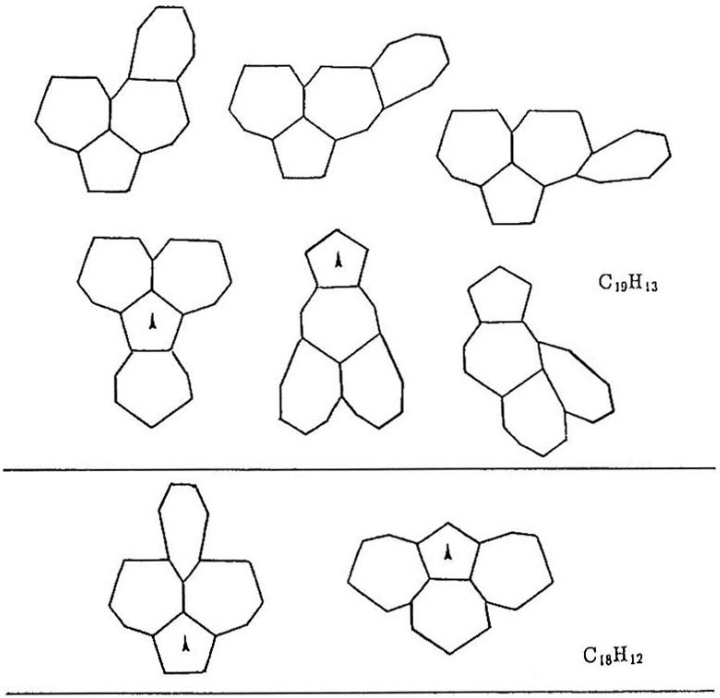


Fig. 5. The azulenoids with $r = 3$ and $r = 4$. Arrowheads indicate C_{2v} symmetry; the remaining system belong to C_s.

APPENDIX B

From relations (1) and (2), the following is obtained straightforwardly.

$$r_{k+1} = 4r_k - (n_i)_k + 2 \ , \quad (n_i)_{k+1} = 5r_k - (n_i)_k \tag{B1}$$

$$n_{k+1} = \frac{1}{2}(3n_k + 5s_k) + 5 \ , \quad s_{k+1} = \frac{1}{2}(n_k + 3s_k) + 5 \tag{B2}$$

These coupled recurrence relations yield:

$$r_{k+2} = 3r_{k+1} - r_k + 4 \tag{B3}$$

$$(n_i)_{k+2} = 3(n_i)_{k+1} - (n_i)_k + 10 \tag{B4}$$

$$n_{k+2} = 3n_{k+1} - n_k + 10 \tag{B5}$$

$$s_{k+2} = 3s_{k+1} - s_k \tag{B6}$$

Herefrom the explicit expressions for the different invariants in terms of k are available by the standard method of difference equations, which was exploited extensively for the enumerations of benzenoid Kekulé structures in particular [39].

Consider r_k as a representative example. Rewrite the recurrence relation (B3) as

$$r'_{k+2} = 3r'_{k+1} - r'_k \tag{B7}$$

where

$$r'_k = r_k + 4 \tag{B8}$$

for arbitrary k values. The characteristic equation, viz.

$$x^2 = 3x - 1 \tag{B9}$$

yields

$$x = \frac{3 \pm \sqrt{5}}{2} \tag{B10}$$

Consequently,

$$r'_k = A\left[\frac{3 + \sqrt{5}}{2}\right]^k + B\left[\frac{3 - \sqrt{5}}{2}\right]^k \tag{B11}$$

As well as for r'_k, the form (B11) is also valid for $(n'_i)_k = (n_i)_k + 10$, $n'_k = n_k + 10$ and s_k; only the constants A and B have to be adjusted individually from initial conditions of the different invariants. Turn back to r'_k, and for the sake of simplicity consider the special case of k–circum–C_5H_5 (cf. Table 2). Then, in consistency with eqn. (B8), the initial conditions for $k = 0$ and 1 are $r'_k = 5$ and 10, respectively. Consequently,

$$A + B = 5 \ , \quad \frac{3 + \sqrt{5}}{2} A + \frac{3 - \sqrt{5}}{2} B = 10 \tag{B12}$$

which yields:

$$A = \frac{\sqrt{5}}{2}(1 + \sqrt{5}) \ , \quad B = -\frac{\sqrt{5}}{2}(1 - \sqrt{5}) \tag{B13}$$

The result for r_k is:

$$r_k = \frac{\sqrt{5}}{2}\left[(1 + \sqrt{5})\left[\frac{3 + \sqrt{5}}{2}\right]^k - (1 - \sqrt{5})\left[\frac{3 - \sqrt{5}}{2}\right]^k\right] - 4 \tag{B14}$$

In order to establish the equivalence of (B14) with the first one of relations (5), notice that

$$3 + \sqrt{5} = \frac{(1 + \sqrt{5})^2}{2} \ , \quad 3 - \sqrt{5} = \frac{(1 - \sqrt{5})^2}{2} \tag{B15}$$

Hence eqn. (B14) can be modified in the following way.

$$r_k = \frac{\sqrt{5}}{2}\left[(1+\sqrt{5})\left[\frac{1+\sqrt{5}}{2}\right]^{2k} - (1-\sqrt{5})\left[\frac{1-\sqrt{5}}{2}\right]^{2k}\right] - 4$$

$$= \sqrt{5}\left[\left[\frac{1+\sqrt{5}}{2}\right]^{2k+1} - \left[\frac{1-\sqrt{5}}{2}\right]^{2k+1}\right] - 4 = 5F_{2k} - 4 \qquad \text{(B16)}$$

Here the identification with Fibonacci numbers emerges through Binet's formula, which may be written [39]

$$F_N = \frac{1}{\sqrt{5}}\left[\left[\frac{1+\sqrt{5}}{2}\right]^{N+1} - \left[\frac{1-\sqrt{5}}{2}\right]^{N+1}\right] \qquad \text{(B17)}$$

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