Some Benzenoid Hydrocarbons with Extremal Properties *

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Benzenoid systems and their Δ values are studied. Here Δ is the absolute magnitude of the difference between the numbers of black and white vertices. The systems with maximum Δ at a given h (number of hexagons) are treated in particular. TP benzenoids are defined as consisting of fused triangulenes and phenalenes only. All benzenoids with $\Delta = \Delta_{max} = 1, 2, 3, \ldots$ for $h = 3, 6, 9, \ldots$, respectively, are TP benzenoids. By means of a computer program all benzenoid systems with $\Delta = h/3$ up to $h = 15$ are generated. In conclusion, a number of supplementary data to the enumerations of benzenoids are reported.

All benzenoid hydrocarbons are known to be alternant [1–3]. Hence the vertices of benzenoid systems (represented by congruent regular hexagons in a plane [1–3]) may be colored by two colors (say black and white) such that adjacent vertices have different colors. The quantity Δ, sometimes called the color excess, is an important invariant for benzenoid systems. This symbol is used to designate the absolute magnitude of the difference between the numbers of black and white vertices. It is long known that all Kekuléan systems (benzenoids which possess Kekulé structures) have $\Delta = 0$, and that this is not a sufficient condition [4]. Non-Kekuléan benzenoids (without Kekulé structures) with $\Delta = 0$ exist; they are referred to as concealed non-Kekuléans, and all the others ($\Delta > 0$) as obvious non-Kekuléan systems [5]. It has been proved [5] that Δ also is the absolute magnitude of the difference between the numbers of valleys and peaks. Valleys and peaks pertain to a given orientation of a benzenoid, where some of the edges are vertical. They are special vertices on the perimeter (boundary). A valley (resp. peak) lies below (resp. above) its two nearest neighbouring vertices.

In the present work we are primarily studying the obvious non-Kekuléan benzenoid systems where Δ has its maximum value for a given h, which designates the number of hexagons.

It is well known that non-Kekuléan benzenoid systems correspond to hydrocarbon radicals rather than normal molecules.

Possible Values of Δ and its Maximum

It has been pointed out [4] that all integer values (in addition to zero) for Δ are possible in benzenoids. The statement is seen to be sound by virtue of the existence of the phenalene-triangulene homologs. For these particular systems [4] one has

$$\Delta = \tfrac{1}{2}[(8h+1)^{1/2} - 3], \tag{1}$$

where h is the number of hexagons. Equation (1) gives $\Delta = 0, 1, 2, 3, \ldots$ for $h = \tfrac{1}{2}(\Delta + 1)(\Delta + 2) = 1, 3, 6, 10, \ldots$.

The values (1) do not in general give the maximum Δ value for a given h, as is easily shown by counterexamples (for $h \geq 15$).

Theorem 1: The maximum Δ value in benzenoids is

$$\Delta_{max} = [\tfrac{h}{3}], \tag{2}$$

which gives $\Delta_{max} = 0$ for $h = 1, 2$; $\Delta_{max} = 1$ for $h = 3, 4, 5$; $\Delta_{max} = 2$ for $h = 6, 7, 8$; etc.

In order to prove *Theorem 1* it is sufficient to show that for all benzenoid systems

$$3\Delta \leq h. \tag{3}$$

For this purpose we focus our attention upon the benzenoids having a certain value of Δ and the minimum possible number of hexagons.

The inner dual D(B) of benzenoid systsm B is the graph spanned by the internal vertices of B. The inner dual is, of course, a bipartite graph. It is a well-known fact the Δ value of B is equal to the absolute magnitude of the difference between the numbers of black and white vertices of D(B) [6].

As an illustration we present a benzenoid system and its inner dual in Figure 1. The vertices of D(B) in this example are colored black and white, and it is easy to see that $\Delta = 7 - 6 = 1$. The same example shows than an inner dual may be a disconnected graph.
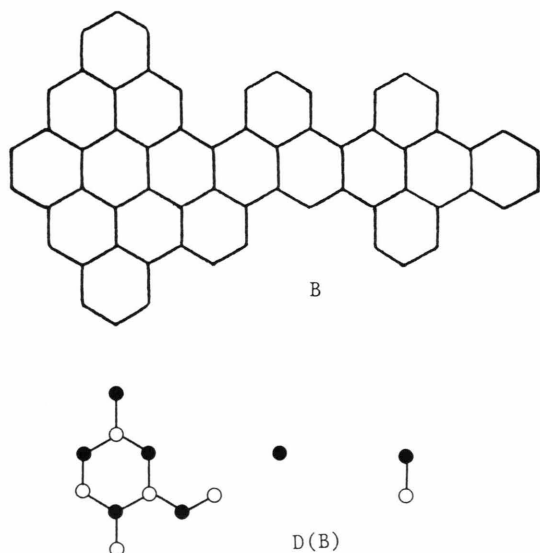
For $\Delta = 1$ it is elementary to conclude that there is a unique inner dual D_1 (Fig. 2), requiring at least three hexagons in the corresponding benzenoid system, B_1. For $\Delta = 2$ we have two different possibilities, namely D_2 and D_2', both requiring at least six hexagons in the respective benzenoids, B_2 and B_2' (cf. Figure 2). For $\Delta > 2$, the inner duals of the benzenoids with minimum h values must be composed of D_1 and/or D_2 components. In order to see this, note first that if an inner dual is composed of disconnected D_1 and/or D_2 units, then we can easily associate to it a benzenoid system with 3Δ hexagons. (Such systems are called TP benzenoids; see below.)

An attempt to construct a connected inner dual for $\Delta = 3$, requiring as few hexagons as possible, would lead to D_3^* of Figure 3. The graph D_3^* can not, however, be an inner dual of any benzenoid system. The occurrence of the fragment D_3^* in an inner dual implies the existence of one more (white) vertex, as depicted in D_3^{**}. But D_3^{**} is no more compatible with $\Delta = 3$, and in order to maintain this condition, we have to introduce an additional (black) vertex, as depicted in D_3. Benzenoid systems whose inner dual is D_3 must possess at least 10 hexagons, cf. B_3. Therefore by means of D_3 we can not construct $\Delta = 3$ benzenoids with minimum number of hexagons. Analogous arguments show that it is not possible to find a connected inner dual compatible with $\Delta = 4$, $h = 12$ or $\Delta = 5$, $h = 15$, etc.

Thus we come to the conclusion that 3Δ is the least number of hexagons necessary to construct a benzenoid system whose number of black vertices exceeds by Δ the number of white vertices. Hence the inequality (3) follows.
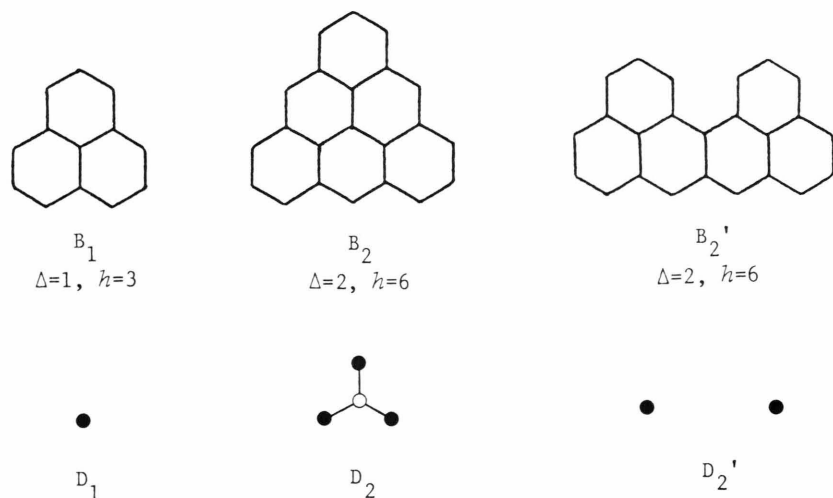

Fig. 1. Benzenoid system, B, and its inner dual, D(B).

B_1
$\Delta=1$, $h=3$

B_2
$\Delta=2$, $h=6$

B_2'
$\Delta=2$, $h=6$

D_1

D_2
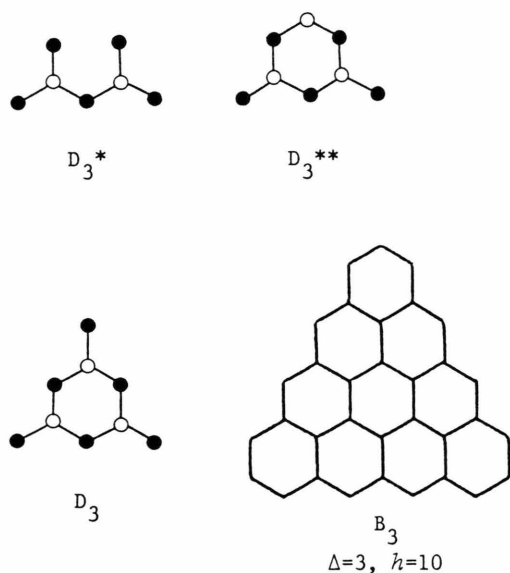
D_2'

Fig. 2. Some benzenoids and their inner duals.

Fig. 3. The benzenoid B_3 and its inner dual D_3. The graphs D_3^* and D_3^{**} are not inner duals.
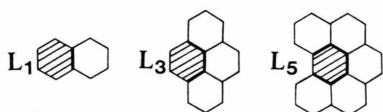

Fig. 4. Additional modes of a hexagon, where the addition does not change the Δ value of the system.
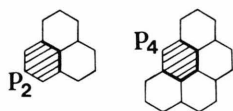

Fig. 5. Addition modes of a hexagon, where the addition shifts the Δ value by one unit.

Selection Rules for Δ

Generating Benzenoids

All benzenoids of $h + 1$ hexagons may obviously be generated by adding one hexagon each time to the existing benzenoids with h hexagons. The new hexagon is added to the perimeter in different modes, where five cases are distinguished, viz. $\{i\}$; $i = 1, 2, 3, 4, 5$. This symbol indicates that the new hexagon shares i connected edges with the old perimeter.

Rules for Changes in Δ

Theorem 2: Assume a benzenoid generated in the described way from an original benzenoid with parameters h and Δ. The corresponding parameters for the new benzenoid are $h + 1$ and Δ'. The new benzenoid may only acquire the values $\Delta' = \Delta$ and $\Delta \pm 1$ (not -1 for $\Delta = 0$).

The theorem is easily proved by inspecting all the possibilities of adding a hexagon to a benzenoid [7]. More specific rules are also detected:

(i) On adding the hexagon in the modes $\{1, 3, 5\}$ the Δ value does not change. This means an annelation (catacondensation) $\{1\}$, imbedding into a bay $\{3\}$, or immersing into a fjord $\{5\}$ [7]. The features are illustrated in Fig. 4, where the added hexagon is hatched. It is implied that the new (hatched) hexagon does not share more than the heavy-drawn edges with the old perimeter. We refer to modes of a hexagon in a benzenoid according to its environments. The modes of the hatched hexagons (denoted L_1, L_3, and L_5; cf. Fig. 4) are three different addition modes.

(ii) On adding the hexagon in the modes $\{2, 4\}$ the Δ values shift by one unit (± 1). This means an addition into a fissure or a cove, corresponding to $\{2\}$ and $\{4\}$, respectively; cf. Figure 5. The corresponding addition modes are designated P_2 and P_4, respectively.

Benzenoids with $\Delta = \Delta_{max}$

First Results of Enumerations

Throughout this section we assume $\Delta \geq 1$. In other words we consider only obvious non-Kekuléan systems.

The benzenoids with $h \leq 10$ have all been enumerated and classified in detail [8]. Figure 6 displays all systems with $\Delta = \Delta_{max} = 1$ and 2. Within each h value ($h = 3, 4, 5, 6, 7, 8$) the systems are classified according to their numbers of internal vertices (n_{int}). The value $\Delta = 3$ occurs for the first time (lowest h value) at $h = 9$. These systems, along with those of $h = 10$, $\Delta = 3$ are displayed in Figure 7. Also for $h = 11$ Δ has its maximum value equal to 3. In this case ($h = 11$, $\Delta = 3$) there are 374 benzenoid systems [8], which are well known, but not depicted here for the sake of brevity.

TP Benzenoids and Their Properties

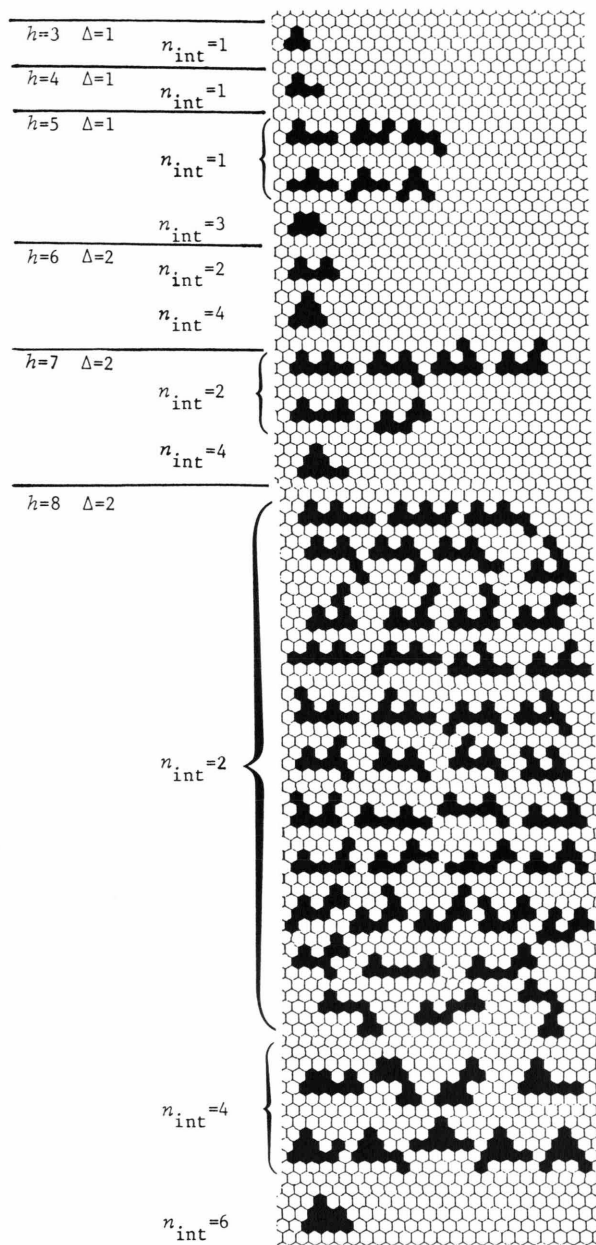*Definition:* A Triangulene-Phenalene (TP) benzenoid consists of phenalene, triangulene, or any number of

Fig. 6. Benzenoid systems with $\Delta = \Delta_{\max}$ for $h = 3, 4, 5, 6, 7, 8$, classified according to their numbers of internal vertices (n_{int}).

Fig. 7. Benzenoid systems with $\Delta = \Delta_{\max}$ for $h = 9, 10$, classified according to their numbers of internal vertices (n_{int}).

two benzenoid units are said to be fused (in a restricted sense as used here) when they share exactly one edge.

A TP benzenoid has obviously $h = 3, 6, 9, \ldots$. Furthermore, it has

$$h = 3\,\Delta, \qquad \Delta = \Delta_{\max} = \tfrac{h}{3}. \qquad (4)$$

Phenalene and triangulene with $\Delta = 1$ and $\Delta = 2$, respectively, are the trivial TP benzenoids. For $\Delta = 2$ another system, two fused phenalenes, exists; cf. Figure 6. The three existing TP benzenoids with $\Delta = 3$ are found in Figure 7.

Theorem 3: Benzenoids with $h = 3, 6, 9, \ldots$ and $\Delta = \Delta_{\max} = h/3$ consist exclusively of TP benzenoids.

The statement formulated here as *Theorem 3* has already been deduced within the proof of *Theorem 1*.

The results of enumeration displayed in Figs. 6 and 7 illustrate *Theorem 3* for $h = 3, 6$ and 9. In subsequent parts of this paper we give analogous data for $h = 12$ and $h = 15$.

these two units fused together so that a triangle apex of each unit points the same way (conventionally upwards).

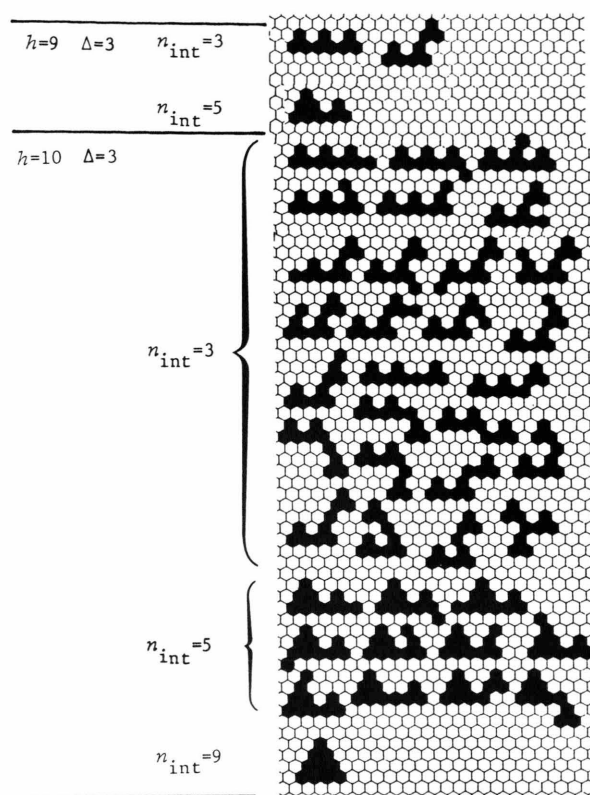Phenalene is the smallest ($h = 3$) triangular benzenoid. Triangulene is the $h = 6$ triangle. By definition

In Figs. 6 and 7 numbers of internal vertices are taken into account. Consider the TP benzenoids with a given h. Assume that a member consists of P phenalenes and T triangulenes. Then

$$h = 3\Delta = 3P + 6T, \quad \Delta = P + 2T, \quad (5)$$

and the number of internal vertices is

$$n_{\text{int}} = P + 4T. \quad (6)$$

We look for the TP systems with the maximum number of internal vertices, $(n_{\text{int}})_{\text{max}}$, for a given h. Such a system is evidently one with $P = 0$ or $P = 1$. This results can also be found analytically by a manipulation of (5) and (6), which leads to

$$n_{\text{int}} = 2\Delta - P. \quad (7)$$

Consequently,

$$(n_{\text{int}})_{\text{max}} = 2\Delta - 1; \quad \Delta = 1, 3, 5, \ldots; \quad h = 3, 9, 15, \ldots,$$
$$(n_{\text{int}})_{\text{max}} = 2\Delta; \qquad \Delta = 2, 4, 6, \ldots; \quad h = 6, 12, 18, \ldots,$$
$$(8)$$

The systems among TP benzenoids with $n_{\text{int}} = (n_{\text{int}})_{\text{max}}$ for a given Δ or h are referred to as the restricted TP benzenoids.

Definition: A restricted Triangulene-Phenalene (TP) benzenoid consists of phenalene, triangulene, or a number of triangulenes with one or zero phenalene fused together so that a triangle apex of each unit points the same way (conventionally upwards).

Restricted TP benzenoids form a subset of the TP benzenoids. They are the systems with the maximal number of triangulenes for a given h.

Application of the Selection Rules for Δ

The benzenoids with $\Delta = \Delta_{\text{max}} = h/3$ were computer-generated also for $\Delta = 4$ and $\Delta = 5$, i.e. $h = 12$ and 15, respectively. The complete enumeration of the benzenoids with such a high h value as 15 is a formidable task even for the strongest computers accessible at present [8]. This was avoided by means of the selection rules of Δ (see above).

The existence of 14 benzenoids with $h = 12$, $\Delta = 4$ was reported previously [8]. The forms are displayed in Figure 8. They are all TP benzenoids in accord with *Theorem 3* and have a unique restricted TP benzenoid (with $n_{\text{int}} = 8$) among them.
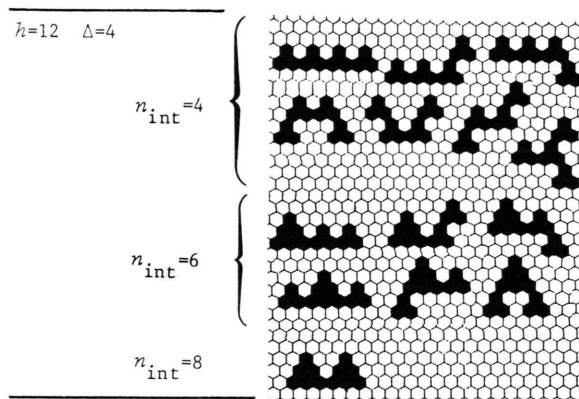

Fig. 8. Benzenoid systems with $\Delta = \Delta_{\text{max}}$ for $h = 12$, classified according to their numbers of internal vertices (n_{int}).
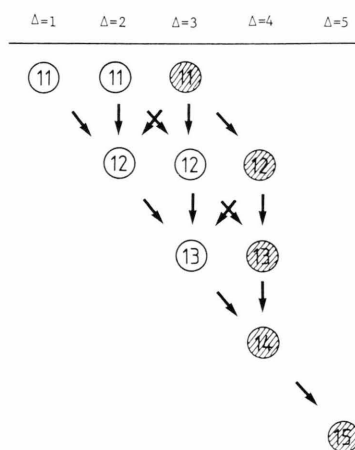

Fig. 9. Scheme for the generation of benzenoids with $\Delta = \Delta_{\text{max}}$, represented by the hatched circles. The numerals inscribed into the circles are h values.

In order to generate the benzenoids with $h = 15$, $\Delta = 5$ we followed the scheme of Fig. 9, where it is presupposed that the $h = 11$ benzenoids with $\Delta \geq 1$ are accessible. They have been generated before and their numbers reported elsewhere [8].

In the scheme of Fig. 9 the vertical arrows symbolize additions where Δ is unshifted; in these cases only the $\{1, 3, 5\}$ additions need to be executed, i.e. the L-type additions illustrated in Figure 4. For the additions symbolized by skew arrows Δ shifts by one unit; then only the $\{2, 4\}$ or P-type additions (cf. Fig. 5) need to be executed. Thus, for instance, the 14 systems of Fig. 8 ($h = 12$, $\Delta = 4$), which all are TP benzenoids, may easily be generated by a suitable computer pro-
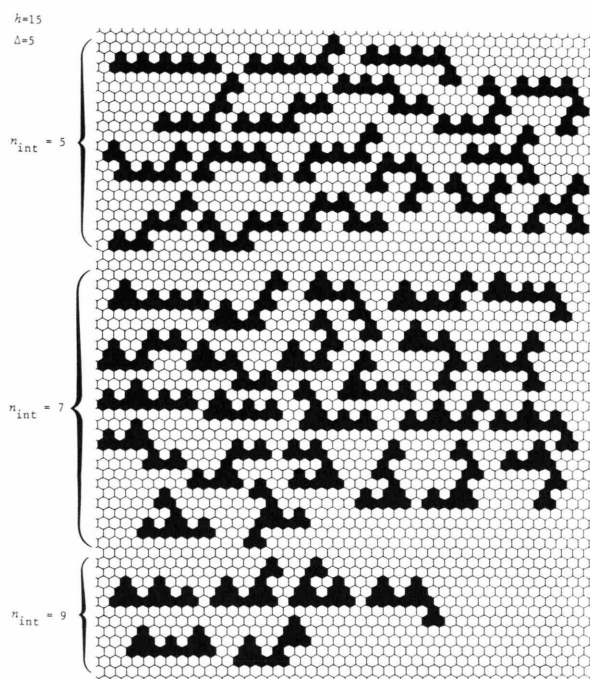
Fig. 10. Benzenoid systems with $\Delta = \Delta_{max}$ for $h = 15$, classified according to their numbers of internal vertices (n_{int}).

Table 1. Numbers of benzenoids with different Δ values (* Unknown).

h	$\Delta = 0$	$\Delta = 1$	$\Delta = 2$	$\Delta = 3$	$\Delta = 4$	$\Delta = 5$
1	1	0	0	0	0	0
2	1	0	0	0	0	0
3	2	1	0	0	0	0
4	6	1	0	0	0	0
5	15	7	0	0	0	0
6	51	28	2	0	0	0
7	190	134	7	0	0	0
8	764	619	52	0	0	0
9	3 223	2 957	322	3	0	0
10	14 107	14 024	1 916	39	0	0
11	62 887	67 046	10 922	374	0	0
12	285 016	320 859	60 705	2 990	14	0
13	*	*	*	21 675	211	0
14	*	*	*	*	2 588	0
15	*	*	*	*	*	48

gram [9] from the 374 systems with $h = 11$, $\Delta = 3$. These 374 systems are also needed, together with the 10 922 systems with $h = 11$, $\Delta = 2$, in order to generate the $h = 12$ systems with $\Delta = 3$. Among the $h = 12$ systems we also need to generate those with $\Delta = 2$ in order to complete the task. This is the hardest part of the schedule; one needs to start with 374 ($h = 11$, $\Delta = 3$) + 10 922 ($h = 11$, $\Delta = 2$) + 67 046 ($h = 11$, $\Delta = 1$) systems. After each series of runs of this type a special procedure of the computer program [9] was used to eliminate duplicated (isomorphic) systems, which are generated in large amounts.

The process was continued through the scheme of Fig. 9 until the systems with $h = 15$, $\Delta = 5$ eventually were generated. Their number was found to be 48. Furthermore, they were all found to be TP benzenoids (in consistence with *Theorem 3*) with 6 restricted TP benzenoids ($n_{int} = 9$) among them. The forms are displayed in Figure 10.

Summary of Enumeration Results

The recent consolidated report on enumerations of benzenoids contains a table where the benzenoids are classified according to their Δ values (Table 7, [8]). The computations described above provide significant supplements to this table. We have also access to the number for $h = 12$, $\Delta = 0$. It is the number of 284 917 [10] Kekuléan benzenoids + 98 [11] concealed non-Kekuléans with $h = 12$. Then the number for $h = 12$, $\Delta = 1$ is obtainable by subtraction since the total number of benzenoids with $h = 12$ also is accessible [10].

Table 1 gives the number of benzenoids classified according to Δ values with all supplements of the present knowledge.

Acknowledgement

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