

Determining the Number of Resonance Structures in Concealed Non-Kekuléan Benzenoid Hydrocarbons

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The number of resonance structures (SC) for previously published concealed non-Kekuléan benzenoid hydrocarbons is determined. Using a simple computer program, analytical expressions for determining SC for various classes of non-Kekuléan (free-radical) benzenoid hydrocarbons are derived, and some properties of concealed non-Kekuléan benzenoid hydrocarbons are studied.

INTRODUCTION

Schlenk hydrocarbon¹ is a diradical synthesized in 1915, some 15 years after Gomberg discovered triphenylmethyl monoradical, whereupon he declared that he "...wished to reserve the field for ..." himself.² When all the $p\pi$ -electrons in a benzenoid hydrocarbon can be paired, it is said to be Kekuléan; otherwise it is non-Kekuléan. The number of distinct ways in which the maximum number of $p\pi$ -electrons can be paired in the valence-bond picture corresponds to the number of resonance structures in a polycyclic conjugated hydrocarbon. Since 1972, concealed non-Kekuléan (diradical) benzenoid hydrocarbons have intrigued various researchers.³ The study of diradicals and higher polyradicals is important to our understanding, both fundamentally and because of their potential use in the fabrication of organic ferromagnetic materials.^{1,4}

In this paper, analytical expressions for the number of resonance structures (SC) in series of radical benzenoid hydrocarbons are derived with the aid of a computer. The construction of concealed non-Kekuléan benzenoid hydrocarbons from smaller obvious non-Kekuléan benzenoids is discussed and illustrated. The SC values for these systems were determined from the tail coefficients of their matching (or acyclic) polynomials. In general, the x^n coefficient of the matching polynomial is the number of "near-perfect" matchings that leave n sites unmatched. Since diradicals have two sites unmatched, the tail coefficient is that of x^2 .

Rapid Recognition of Hydrocarbon Radicals. A benzenoid structure can be oriented three different ways with some of its edges (approximately 1/3) in a vertical direction. A benzenoid structure so oriented has peaks (upward pointing vertexes on the upper periphery) denoted by \wedge and valleys (downward pointing vertexes on the lower periphery) denoted by \vee . Whenever $\wedge \neq \vee$, then the corresponding benzenoid structure is a radical. Odd-carbon benzenoid structures always

have $\wedge \neq \vee$. For well-behaved benzenoid systems, $\wedge - \vee = 1$ for monoradicals, $\wedge - \vee = 2$ for diradicals, etc. When $\wedge = \vee$ the benzenoid structure may or may not be a radical. If it is a radical, it is called a concealed (hidden) non-Kekuléan benzenoid ($K = 0$). Many of this type of radicals have a narrow isthmus of fewer vertical edges than peaks or valleys.⁵ Also, partially concealed benzenoid radicals are possible. For example, a partially concealed triradical would have $\wedge - \vee = 1$.

Any alternant hydrocarbon (not just benzenoids) may be separated into s starred sites and u unstarred sites such that no two members of s are adjacent, and no two members of u are adjacent. By convention, the sets are chosen so that the structure is "maximally starred," i.e., $s \geq u$. For a well-behaved, maximally starred radical benzenoid system, it can be shown that the unpaired electrons are only found on starred sites. Concealed non-Kekuléan benzenoids formally have the same number of starred and unstarred carbon vertexes, have the same number of peaks and valleys ($\wedge - \vee = 0$), and are made by joining together two (obvious) radical benzenoid systems having the same $\wedge - \vee$ value through their unstarred peaks either directly or through a nonradical spacer group. Such constructed concealed non-Kekuléan benzenoids are essentially disconnected (disjoint) $p\pi$ -electronic systems, and the unstarred sites one of the components become formally starred though the unpaired electrons do not travel these sites.⁵ A partially concealed triradical can be formed by similarly joining a well-behaved benzenoid monoradical with a well-behaved benzenoid diradical. Nevertheless, all non-Kekuléan benzenoids can be recognized from the tail coefficient of their matching polynomials.

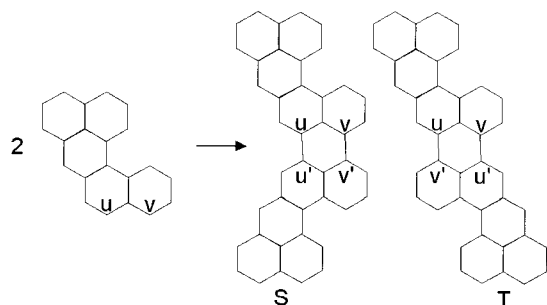
CONSTRUCTION OF CONCEALED NON-KEKULEAN BENZENOIDS

The smallest concealed non-Kekuléan benzenoid ($C_{38}H_{18}$), called Clar's goblet by Cyvin and co-workers,³ is a diradical produced by joining the unstarred peaks of two $C_{19}H_{11}$ benzo-

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Table 1. Matching Polynomials for Application of Polanski and Zander's Theorem to the Two $h = 11$ Concealed Non-Kekuléan Benzenoids in Figure 1^a

power of x (e/o)	G (o)	$G - u$ (e)	$G - v$ (e)	$G - u - v$ (o)	S (e)	T (e)
42					1	1
40					-52	-52
38					1 244	1 244
36					-18 172	-18 172
34					181 420	181 420
32					-1 312 812	-1 312 812
30					7 126 183	7 126 183
28					-29 624 587	-29 524 586
26					95 459 320	95 459 292
24					-239 805 080	-239 804 736
22/21	1				469 966 888	469 964 446
20/19	-25	1	1	1	-715 715 438	-715 704 344
18/17	263	-23	-23	-21	839 771 307	839 737 593
16/15	-1521	220	220	180	-748 827 985	-748 758 504
14/13	5299	-1140	-1411	-817	497 462 511	497 366 309
12/11	-11 454	3490	3504	2128	-239 399 921	-239 313 406
10/9	15 245	-6449	-6523	-3214	80 223 102	80 175 904
8/7	-11 986	7039	7224	2695	-17 674 051	-17 660 346
6/5	5109	-4243	-4462	-1111	2 341 600	2 339 984
4/3	-999	1234	1335	161	-159 286	-159 222
2/1	62	-129	-137		3 844	3 844

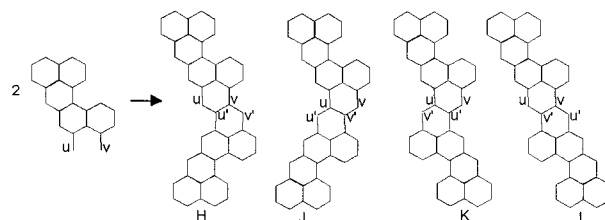
^a Powers of x are for structures with (even/odd) vertex count.**Figure 1.** The construction of graphs S and T corresponding to concealed benzenoid diradicals with the same SC from isomorphic fragments G and G' in the sense of Polansky and Zander.

[cd]pyrenyl monoradicals. All the concealed non-Kekuléan benzenoid diradicals up to 16 rings were enumerated by Cyvin and co-workers³ and can be constructed by joining two monoradicals via their appropriate unstarred peaks, either directly or through a spacer group.⁵ As will be shown, the SC values of concealed non-Kekuléan benzenoid hydrocarbons can be determined two ways: from the tail coefficient of their matching polynomials and as the product of the SCs of their construction components.

A theorem described in a book by Cvetković, Doob, Gutman, and Torgašev⁶ but ultimately due to Polansky and Zander⁷ is relevant to the determination of the matching polynomials of certain related isomeric systems such as a pair of $h = 11$ concealed non-Kekuléan benzenoid structures from Guo et al.³ as illustrated in Figure 1. Start with two isomorphic graphs, G and G' . Designate two vertexes in G as u and v , and the two corresponding vertexes in G' as u' and v' . Form a new graph S by joining u to u' with an edge and v to v' with another edge. Form a second new graph T by starting with fresh copies of G and G' and joining instead u to v' and v to u' . Polansky and Zander's theorem⁷ states that the matching polynomials of S and T are related by

$$\alpha(T) - \alpha(S) = (\alpha(G - u) - \alpha(G - v))^2 \quad (1)$$

Explicit calculation of the four polynomials confirms this relation for the two structures in Figure 1.

**Figure 2.** Construction of graphs H , J , K , and L corresponding to concealed benzenoid diradicals with the same SC from isomorphic fragments G and G' . If G and G' are isomorphic, then H and J are also isomorphic and therefore have the same matching polynomial.

We observe that eq 1 is also derivable from a general relation published much more recently by Babić et al.,⁸ namely

$$\alpha(G) = \sum_{F \subseteq E} (-1)^{|F|} \alpha[G_1 - V_1(F)] \alpha[G_2 - V_2(F)] \quad (2)$$

The meaning of the symbols in eq 2 is as follows: Separate a graph G into two components G_1 and G_2 by deleting a set of edges E . V_1 and V_2 are the sets of vertexes in G_1 and G_2 that terminate the edges in E and are ordered in the same way as E . The summation is over all possible subsets of E , including the empty set and E itself. $G_i - V_i$ is the component G_i with the vertexes corresponding to each subset F deleted in turn. $|F|$ is the number of edges in each F . For the structures S and T in Figure 1, only two edges need be deleted to separate S or T into two components, so the summation in eq 2 would have only four terms and

$$\alpha(S) = \alpha(G)^2 - \alpha(G - u)^2 - \alpha(G - v)^2 + \alpha(G - u - v)^2 \quad (3)$$

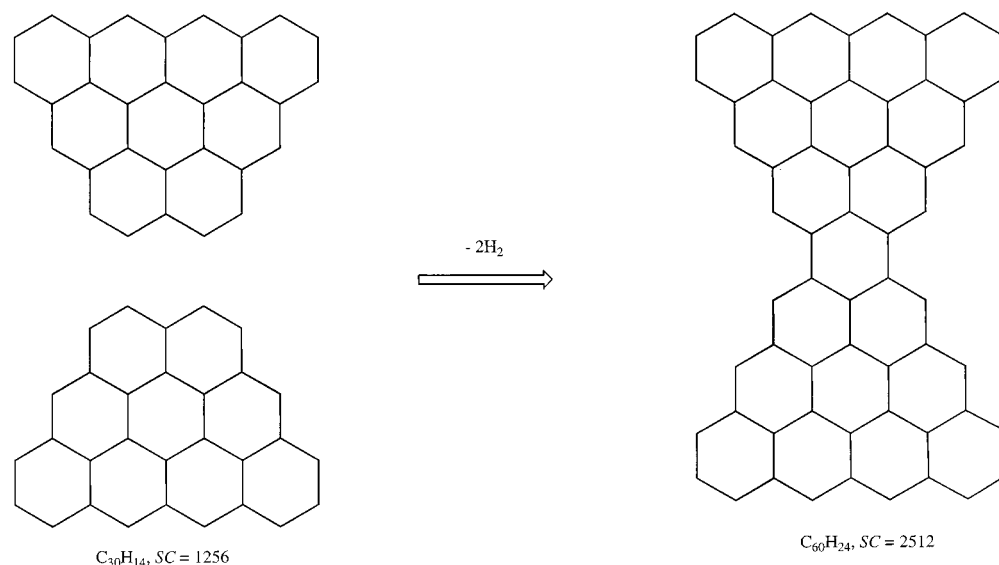
and

$$\alpha(T) = \alpha(G)^2 - 2\alpha(G - u) \alpha(G - v) + \alpha(G - u - v)^2 \quad (4)$$

Table 2. SCs for the Concealed Non-Kekuléan Benzenoids Enumerated in ref 3^a

description	structure count											
h = 11	3844	3025	3844	3410	3410	3224	2860	2704				
h = 12, C ₄₆ H ₂₄	3844	3844	6014	6448	6634	6820	6448	6634	5642	6696	6820	
	3025	3025	4235	5005	5335	5500	5280	5335	5335			
	3844	6014	6634	6448	5642	6634	6448	6820	6820	6696	3410	3410
	5335	5720	5885	4774	6014	5642	5940	6050	6050	5720		
	5885	6014	6014	5952	6200	4774						
h = 12, C ₄₄ H ₂₂	3410	3410	5335	5885	4774	6014	5642	5005				
	5885	5720	6050	6050	5940	6014	6014	5952	6200	4774		
	3224	3224	5044	5408	5564	5564	4732	5394	5766	5766	5394	
	5616	5720	5720	5408	2860	2860	4004	5044	4732			
	4785	5115	5115	4785	5044	5044	4992	5200	4004			
h = 12, C ₄₂ H ₂₀	2704	4836	4524									

^a Entries in this table correspond to the placement of structures in Figure 1 of ref 3. In every case, the SC for the whole structure is the product of the SCs of the two fragments, as expected.

**Figure 3.** Construction of a concealed non-Kekuléan (tetraradical) benzenoids by joining two diradical benzenoids through their unstarred peaks.

Subtracting eq 3 from eq 4 gives eq 1. Coefficients for the relevant polynomials are given in Table 1.

We further observe that eq 2 can be adapted to a more complicated connectivity between u, v and u', v' that is relevant to a trio of $h = 12$ structures from Guo et al. as illustrated in Figure 2. Since three edges are removed to separate structures H , J , K , or L in Figure 2 into two components, the summations in eq 2 will have $2^3 = 8$ terms. Without explicitly writing out the derivations, the relevant results are

$$\alpha(H) - \alpha(K) = -\alpha(G - v)^2 + \alpha(G - u) \alpha(G - v) \quad (5)$$

$$\alpha(H) - \alpha(L) = -\alpha(G - u)^2 + \alpha(G - u) \alpha(G - v) \quad (6)$$

$$\alpha(K) - \alpha(L) = \alpha(G - v)^2 + \alpha(G - u)^2 \quad (7)$$

Again, for the structures shown, the relationships in eqs 5–7 were confirmed by explicit calculation of the relevant polynomials. Overall, it should be noted that S and T (Figure 1) are constructed without any spacer group whereas H – L (Figure 2) are each constructed with a butadiene spacer group and that H and J are identical (isomorphic).

While the diradical structures in Guo et al.³ are small enough to enable calculation of the matching polynomials

directly, the above relationships may be useful for much larger structures. In general, when two large components are connected by a narrow isthmus of a few edges, the summation in eq 2 will have a manageable number of terms.

STRUCTURE COUNT DETERMINATION OF CONCEALED NON-KEKULEAN BENZENOIDS

Since concealed non-Kekuléan benzenoids are essentially disconnected systems all their SCs are simply the product of the SCs of the component parts. Thus all concealed non-Kekuléan benzenoid diradicals enumerated by Cyvin and co-workers³ can be determined from the SCs of the monoradical components, the values of which many can be obtained from analytical expressions previously published.⁵ Table 2 summarizes the SCs for all these systems.

The smallest concealed non-Kekuléan benzenoid tetraradical is the C₆₀H₂₄ structure (19 rings) given in Figure 3 produced by joining the unstarred peaks of two C₃₀H₁₄ dibenzo[*bc,hi*]coronene (first structure in Figure 4) diradicals. Numerous other concealed non-Kekuléan benzenoid tetraradicals can be generated by this procedure using any combination of the diradicals shown in Figure 4. SCs for all concealed non-Kekuléan benzenoid tetraradicals generated

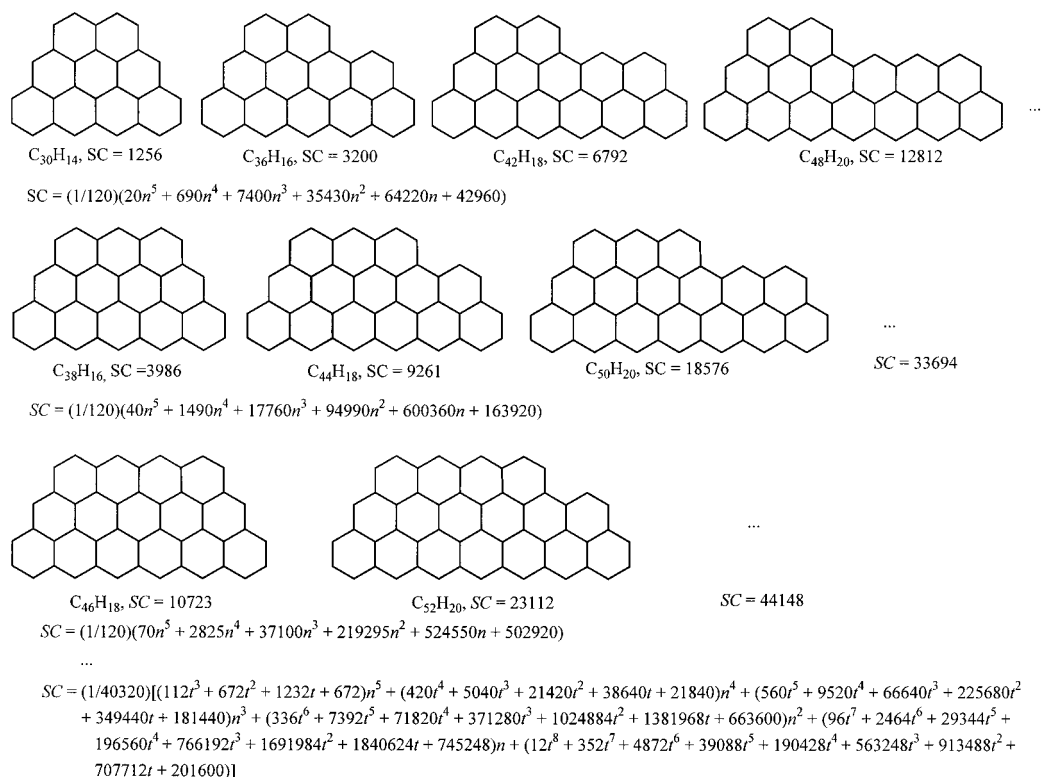


Figure 4. Two-dimensional array of diradical benzenoid series with analytical expressions for counting the number of resonance structures (SC).

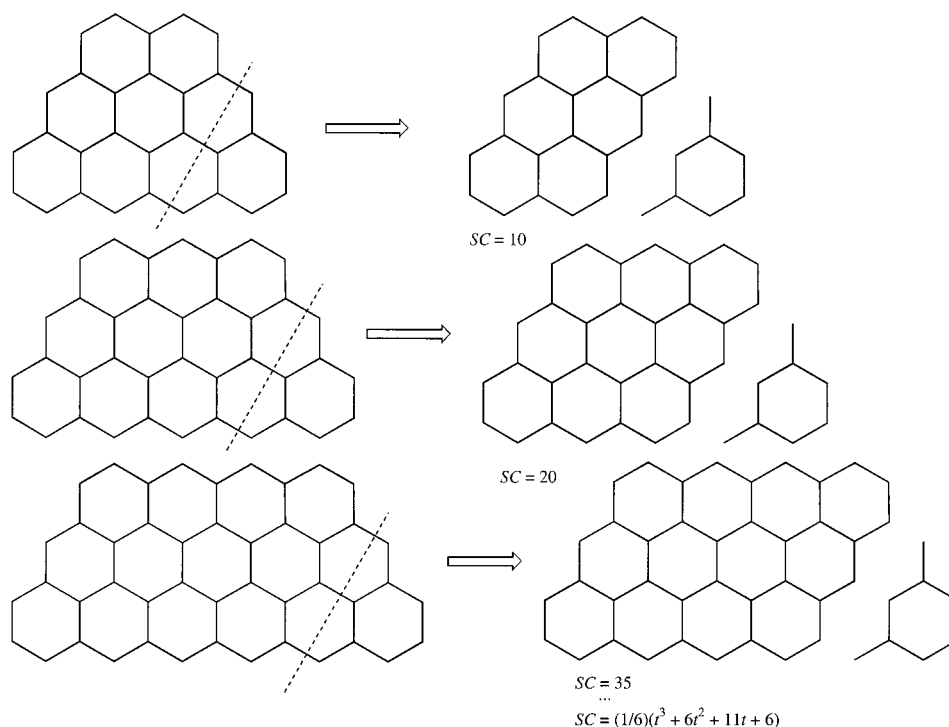


Figure 5. Pruning off *m*-quinodimethane from the lower right-hand corner of the first generation structure in the row series of Figure 3 to give structures having SCs which when multiplied by 2 give values corresponding to the first coefficient of the analytical expressions.

using the diradicals in Figure 4 can be determined from the analytical expressions given therein.

COMPUTER DETERMINATION OF THE STRUCTURE COUNT OF NON-KEKULEAN BENZENOIDS

The tail coefficient (last nonzero coefficient) of the matching polynomial of radical benzenoids gives their SC.

As explained above, the tail coefficient is associated with the power of x that gives the multiplicity of the radical: x for monoradicals, x^2 for diradicals, etc. In general, the coefficients of the matching polynomial $a_{n-i}x^i$ are the number of “almost perfect” matchings that leave i vertexes unmatched. A previously published program that uses Mathematica was employed.⁹

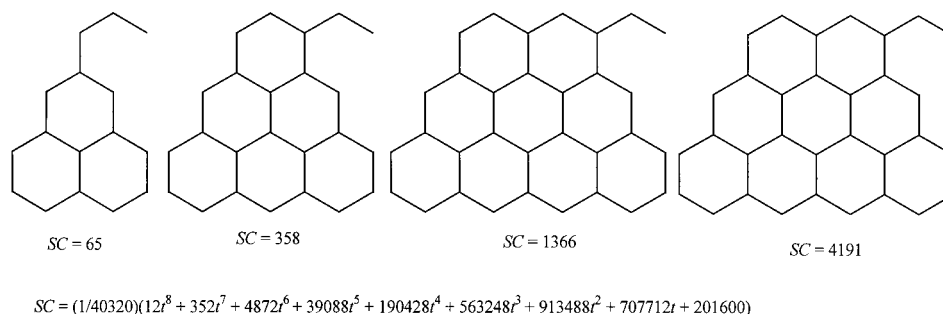


Figure 6. Zero generation members to the series in Figure 4.

Mathematica was also able to give the analytical expressions for the diradical series in Figure 4 by means of the built-in function `InterpolatingPolynomial[{list},n]`. If `{list}` is a list of k integers, the function finds a polynomial in n of at most order $k - 1$ that evaluates to the list of integers when $n = 1, 2, 3, \dots$. For these calculations, a polynomial was known to be complete when adding another element to `{list}` no longer increased the order of the polynomial. The polynomials in n for each value of t were obtained thus. The final polynomial in n and t was obtained from `InterpolatingPolynomial[{list},t]`, where `{list}` was a list of polynomials in n , rather than a list of integers. The correctness of this polynomial was confirmed by its prediction of the correct SC value (7 640 798) for the $n = 7, t = 10$ structure.

STRUCTURAL ORIGIN OF SOME OF THE COEFFICIENTS IN THE ANALYTICAL EXPRESSIONS TO THE DIRADICAL SERIES IN FIGURE 4

Figure 4 presents a two-dimensional array consisting of rows and columns of infinite series of benzenoid diradicals with analytical expressions for counting their number of resonance structures (SC). The first series ($t = 1$) which starts with triangulene ($C_{22}H_{12}$) is not shown in Figure 4. Members of the row series are generated by successively attaching the C_6H_2 aufbau unit, and the column members by successively attaching the C_8H_2 aufbau unit. The SC analytical expressions for each row series is in terms of n , which denotes the generation of the structure for which the number of resonance structures is sought. The overall analytical expression which generalizes these row analytical expression is given at the bottom of Figure 4, where t identifies the row. The denominator number is the factorial of the highest exponent of t . Setting $n = 1$ in the overall analytical expression of Figure 4 gives an expression identical with that derived previously for the triangulene column series.⁵

Figure 5 summarizes the structural origin of the first coefficient to the row analytical expressions. By pruning off m -quinodimethane from the lower right-hand corner of the first-generation member ($n = 1$) to each row, a benzenoid structure is obtained that has a SC which when multiplied by two equals the value of the coefficient of the n term

having the largest exponent value. The last coefficient is equal to the SC of the zero-generation member multiplied by $5!$, which is shown in Figure 6. The second structure has a SC = 358 which when multiplied by $5! = 120$ gives 42 960, corresponding to the last coefficient in the analytical expression for the first row series ($t = 2$) given in Figure 4.

CONCLUSION

While determining the number resonance structures (SC) of previously published³ concealed non-Kekuléan benzenoid hydrocarbons, two methods for their calculation have been verified. A general analytical expression for determining the SC of diradical benzenoid members belonging to a two-dimensional array has been established. These results can be used to determine the SC of tetradical concealed non-Kekuléan benzenoids constructed from the diradical members of this two-dimensional array. Some properties of these systems and a previous theorem have been pointed out.

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