CCA-1829

Enumeration of Kekulé Structures for Helicenic Systems

Milan Randić

Department of Mathematics and Computer Science, Drake University, Des Moines, Iowa 50311 and Ames Laboratory-DOE*, Iowa State University, Ames, Iowa 50011, USA

and

Sonja Nikolić and Nenad Trinajstić

The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

The logo of Dresdner bank (West Germany)

Enumeration of Kekulé structures is reported for five classes of helical benzenoids using the Gordon-Davison counting algorithm or its variants and the two-step decomposition procedure based on the concept of partial essential single and double bonds.

The number of Kekulé valence structures (K) for conjugated hydrocarbons is an important structural parameter.[1-7] In the case of benzenoid hydrocarbons log K appears to be a convenient measure of their aromatic stabilities.[8-10] Finding K is not difficult for smaller benzenoid systems,[11-13] but as the size increases, the enumeration of K may become rather intricate,[14-17] unless certain special structural features of the system are employed in order to make the enumeration simple.[18-22]

In the present note we report the enumeration of Kekulé structures for special kinds of helical benzenoids called helicenic systems.[23,24] Theoretically, there are several classes of helicenic systems possible.[25,26] We consider the following five classes: (a) [N]helicenes, (b) double helicenes, (c) branched helicenes, (d) cyclohelicenes and (e) helicenes condensed with circulenes.

The enumerations are based on the Gordon-Davison algorithm[27] or its variants: the Cyvin algorithm[19] and our algorithm,[22,28] and the convenient

two-step reduction procedure[29] which breaks up the molecule into fragments for which the Kekulé counts are known or could easily be obtained.

The enumeration algorithm of Gordon and Davison is applicable to unbranched cata-condensed chains of benzene rings. It may be presented as follows: Insert 2 in the first hexagon (because the Kekulé count for benzene is 2), inscribe 3 in the adjacent hexagon (because the Kekulé count for naphthalene is 3). Subsequent hexagons, if fused linearly, increase the inscribed value by 1, but if the direction of fusion changes, one has to add, instead of 1, the value in the preceding ring. The process continues by adding this number for each subsequent linearly annelated hexagon until the next change of fusion direction appears when the process is repeated in the same manner. The process ends when all available hexagons in the molecule are exhausted.

Recently, an alternative algorithm to the Gordon-Davison algorithm has been proposed by Cyvin *et al.*[19.30] The following is a description of the Cyvin algorithm: Start with 1 which is placed outside the first hexagon (because for the trivial case with no rings $K = 1$). Insert 1 in the first ring and inscribe 1 in all adjacent linearly fused hexagons. If the direction of fusion changes, then add the sum of all numbers in the linearly annelated part of the molecule preceding the kink. The same number is placed in the next ring if linearly fused, otherwise the summing process is repeated. When all the hexagons in the benzenoid chain are exhausted, the above process ends. The Kekulé count is then equal to the sum of all numbers inscribed in individual hexagons.

It has been shown[31] that the Cyvin algorithm is just a reformulation of the original Gordon-Davison algorithm. However, the work by Cyvin *et al.*[19.30] has stimulated further work on the reformulation of the Gordon--Davison procedure.[22,28,32]

Our approach is more general and it represents the two-step reduction procedure[29] based on the concept of partial essential single and double bonds. Partial essential single and double bonds are those bonds which remain unchanged in a certain subset of Kekulé structures for the molecule. The enumeration is carried out in the following way. We first delete partial essential single and double bonds in an arbitrary selected angularly annelated benzene (the first step). This will break up the structure into two smaller fragments if it is a benzenoid chain or into a single fragment if it is a cycloarene. Branching will increase the number of created fragments in both cases. The Kekulé structures for fragments can be counted either by the Gordon-Davison procedure or by the Cyvin procedure. The resulting number of Kekulé structures is denoted by $K(A)$.

In the second step we delete partial essential single and double bonds in the previously selected benzene ring and in the adjacent angularly anne-leted benzenes. This process will break up the structure into even smaller fragments. The Kekulé counts for fragments can be obtained again by the Gordon-Davison algorithm or by the Cyvin algorithm and the resulting number is denoted by $K(B)$.

The total number of Kekulé structures depends on whether the considered molecule was a (branched) benzenoid chain or a cycloarene (corona--condensed benzenoid):

$$K \text{ (benzenoid)} = K \text{ (A)} + K \text{ (B)} + \text{correction} \qquad (1)$$

where:

$$\text{correction} = \begin{cases} 2 \text{ for cycloarenes} \\ 0 \text{ for (branched) chains} \end{cases} \qquad (2)$$

For branched cycloarenes the value of the correction factor depends on the number and sizes of the attached benzenoid chains.

(a) [N]helicenes

[N]helicenes are *ortho*-condensed benzene rings, with the molecular formula $C_m H_{(m+6)/2}$, which give rise to a regular cylindrical helix.[24] We give an example of a N[helicenic] structure [7]helicene (1), prepared some twenty years ago.[33]

1
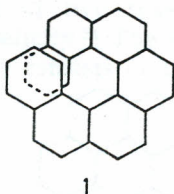
An inspection of the Kekulé numbers (obtained either by the Gordon--Davison algorithm or the Cyvin algorithm) for the first few members of the [N]helicene class:

[N]helicene	1	2	3	4	5	6	7	8
K	2	3	5	8	13	21	34	55

reveals that these numbers belong to the Fibonacci series:[34] 1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 144, ... The same Kekulé numbers appear for poly-phenanthrenes, the »zig-zag« shaped benzenoid hydrocarbons.[35] The regularity in the shape of [N]helicenes (or poly-phenanthrenes) can be »translated« into a regularity in the recursive expression for K:[18,36,37]

$$K_N = K_{N-1} + K_{N-2}; \quad N = 2, 3, \dots \qquad (3)$$

$$K_o = 1 \text{ (by definition)} \qquad (4)$$

$$K_1 = K \text{ (benzene)} = 2 \qquad (5)$$

where N is the number of benzene rings in a [N]helicene.

The above result can also be obtained from the generalization of the Gordon-Davison procedure.[32] Each non-terminal ring in a chain of benzene rings may be classified according to the parity of the number of steps along a path between the two points of attachment to the neighbouring hexagons. For an even-length path the end-points are *like* and both are starred or unstarred, whereas for an odd-length path the end-points are *unlike* and one is starred and the other unstarred. Thus, the hexagons in a benzenoid chain are partitioned into like-linked (denoted by l) and unlike-linked (denoted by u), with linking paths of even and odd parity, respectively. For example, [7]helicene 1 may be represented by the following sequence of ring types: u, u, u, u, u.
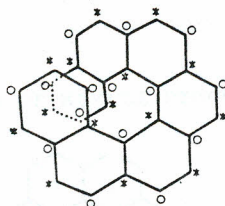
It appears that the benzene rings in [N]helicenes will always only be unlike-
-linked and consequently the sequence of ring types will contain only u
entries. The count of Kekulé structures can then be expressed as the
recursion:

$$K_i = K_{i-1} + K_{i-2} \qquad (6)$$

with both ring $i - 1$ and ring $i - 2$ of u-type and with initial conditions
$K_o = 1$ and $K_1 = 2$. Expressions (3) and (6) are identical, though they have
been reached in different ways.

(b) *Double Helicenes*

Double helicenes consist of two fused distinct [N]helicenes which can
be of the same or opposite helicity.[21] The smallest double helicene: diphenan-
thro[3.4-c; 3.'4'-1]-chrysene (2) consists of two fused [6]helicenes.[38]
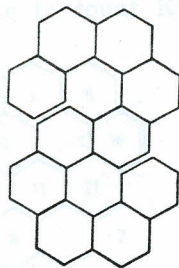
2

The number of Kekulé structures for double helicenes can be obtained
by the Gordon-Davison procedure[27] or by the Cyvin procedure[19] or by our
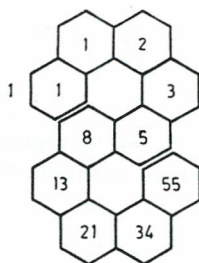procedure.[22,28,29] Below we apply all these three procedures to 2.

(i) The Gordon-Davison procedure
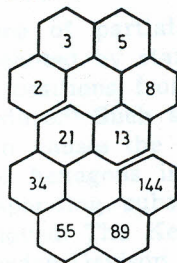
K = 144

The Kekulé count obtained is the same as for [10]helicene. [10]Helicene
and 2 represent isoconjugated (isoarithmic) systems.

(ii) The Cyvin procedure

The number of Kekulé structures (K = 144) is equal to the sum of numbers inscribed in individual rings plus one placed outside the ring at which the enumeration started.

(iii) Our procedure

We first delete partial essential single and double bonds (thick lines in the structure below) in an arbitrary angularly annelated hexagon and use the Gordon-Davison procedure to count Kekulé structures in the fragments.


2A

The Kekulé count for 2A is given by:

$$K(2A) = 5 \cdot 21 = 105. \tag{7}$$

Now we delete the sequence of partial essential single and double bonds from 2. In the hexagon denoted by star (see structure 2B below) we place double bonds in different positions from those they occupied in 2A, according to the reduction procedure.[29] Such an assignment of double bonds in the hexagon labelled by a star causes the placement of double bonds in the adjacent angularly annelated hexagons in positions which will remain unchanged in the whole corresponding subset of Kekulé structures and, therefore, these can also be removed. The Kekulé counts for the fragments are again determined by the Gordon-Davison algorithm.
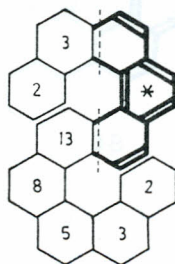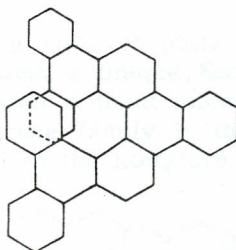

2B

The Kekulé count for *2B* is given by:

$$K\,(2B) = 3 \cdot 13 = 39. \tag{8}$$

The total number of Kekulé structures for *2* represents the sum of (7) and (8):

$$K\,(2) = K\,(2A) + K\,(2B)$$
$$= 144. \tag{9}$$

(c) *Branched Helicenes*

Branched helicenes possess at least one hexagon with three neighbours. An example of a branched helicene is tribenzo[f,l,r]heptahelicene (3).[39]

3

The Kekulé structures can be simply enumerated for branched helicenes by our procedure. To illustrate the procedure for this class of helicenic systems we will consider 3. We will generate two subsets of Kekulé structures for 3. The partial essential single bonds are removed from the benzene ring at which branching occurs (the first step) and the partial essential single and double bonds are also removed from this benzene ring and all angularly annelated rings (the second step). The Kekulé counts for the fragments so created are all known.[40]
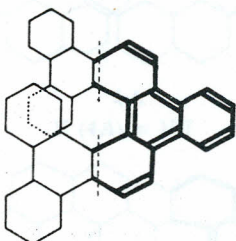
(i) First step

3A
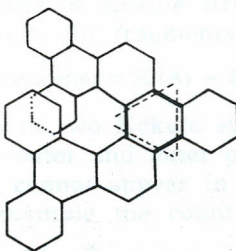
$$K\,(3A) = [K\,(\text{triphenylene})]^2 \cdot K\,(\text{benzene})$$
$$= 162. \tag{10}$$

(ii) Second step

3 B

$$K\ (3B) = [K\ (\text{phenanthrene})]^2$$
$$= 25.$$

(11)

(iii) The total Kekulé count for *3*

$$K\ (3) = K\ (3A) + K\ (3B)$$
$$= 187.$$

(12)

(d) *Cyclohelicenes*

Cyclohelicenes represent a class of postulated helicenes.[41] If they are ever prepared, they will possess a unique Escher-type[42] structural feature: A twisted loop overlapping itself without intersection. The smallest member of the hypothetical cyclohelicene family is the »figure-eight« structure *4*. Cyclohelicene *4* was discussed in the literature for the first time in a paper by Balaban.[43]
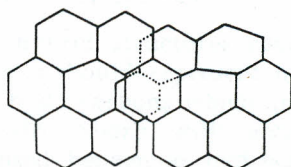

4

The same type of two-step reduction procedure that has been used earlier in this note to enumerate Kekulé structures for unbranched cycloarenes[19] can be employed for the enumeration of the Kekulé structures for unbranched cyclohelicenes. The total number of Kekulé structures for a cyclohelicene is given in terms of Kekulé counts for fragments A and B:

$$K\ (\text{cyclohelicene}) = K\ (A) + K\ (B) + 2$$

(13)

where the correction 2 refers to two Kekulé structures in which the double bonds are placed only on the outer and inner periphery of the cyclohelicene. These two Kekulé structures cannot appear in either of the two fragments.

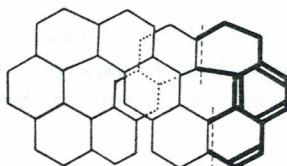Let us consider as an example the count of Kekulé structures for *4*.

(i) First step
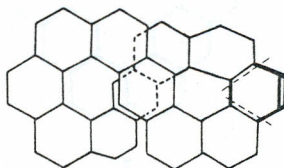
4 A

$$K\ (4A) = 177$$

(14)

(ii) Second step

4 B

$$K (4B) = 81 \tag{15}$$

(iii) The total Kekulé count for 4

$$K (4) = K (4A) + K (4B) + 2$$

$$= 260. \tag{16}$$

The two Kekulé structures of 4 with double bonds on the outer and inner peryphery are shown below.

(e) *Helicenes Condensed With Circulenes*

There is a possibility of hybrid structures consisting of helicenes fused to circulenes. Such combinations should represent members of a very special class of non-planar benzenoid hydrocarbons which are termed heli-circulenes.[44] Circulenes are benzenoid hydrocarbons with annulene-like holes.[45] Other names such as corona-condensed benzenoid hydrocarbons, corannulenes, cycloarenes or coronoid hydrocarbons have also been used for circulenes.[19,25,46,47]

The enumeration of Kekulé structures for heli-circulenes also proceeds in two steps. However, care must be taken during the determination of the correction term in (1). The procedure will be illustrated for 5.
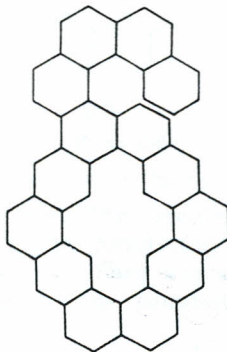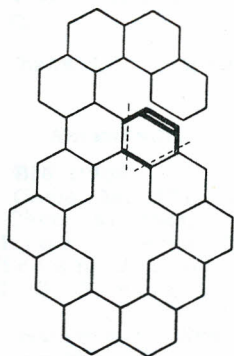

5

(i) First step

We will remove partial essential single and double bonds from that hexagon which, upon deletion, creates immediately a chain fragment. The Kekulé count for a benzenoid fragment is determined, as usual, by the Gordon-Davison algorithm.
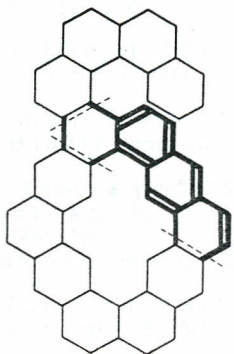
5 A

K (5A) = 455

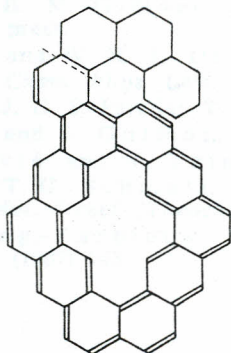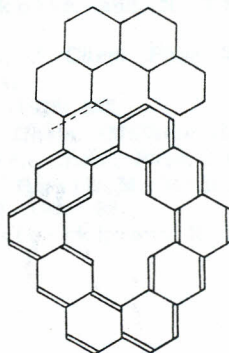(ii) Second step

5 B

K (5B) = 152

(iii) Determination of the correction term

The correction term arises from the circulene part of 5. There will be two Kekulé structures for circulene containing double bonds on the outer and inner periphery of the molecule. They are attached to the helicene part for which Kekulé structures should be counted.

5 C

K (5C) = 5

5 D

K (5D) = 8

$$\text{Correction} = K\ (5C) + K\ (5D)$$
$$= 13. \tag{17}$$

(iv) The total Kekulé count for 5

$$K\ (5) = K\ (5A) + K\ (5B) + \text{correction}$$
$$= 620. \tag{18}$$

REFERENCES

1. L. Pauling, *Acta Cryst.* **B36** (1980) 1898.
2. D. J. Klein, *Pure Appl. Chem.* **55** (1983) 299.
3. M. Randić, *Pure Appl. Chem.* **55** (1983) 347.
4. S. E. Stein and R. L. Brown, *Carbon* **23** (1985) 105.
5. S. E. Stein and R. L. Brown, *J. Amer. Chem. Soc.* **109** (1987) 3721.
6. S. A. Alexander and T. G. Schmalz, *J. Amer. Chem. Soc.* **109** (1987) 6933.
7. D. J. Klein and T. G. Schmalz, *Pauling-Wheland Resonance Theory of Benzenoid Hydrocarbons,* preprint.
8. P. G. Carter, *Trans. Faraday Soc.* **45** (1949) 597.
9. I. Gutman, N. Trinajstić, and C. F. Wilcox, Jr., *Tetrahedron* **31** (1975) 143.
10. P. Swinbourne-Sheldrake, W. C. Herndon, and I. Gutman, *Tetrahedron Lett.* (1975) 755.
11. W. C. Herndon, *J. Chem. Educ.* **51** (1974) 10.
12. N. Trinajstić, *Chemical Graph Theory,* CRC, Boca Raton, FL 1983, Vol. II, Chapter 2.
13. S. J. Cyvin and I. Gutman, *Comput. Math. Appls.* **12B** (1986) 859.
14. B. Džonova-Jerman-Blažič and N. Trinajstić, *Comput. Chem.* **6** (1982) 121.
15. R. L. Brown, *J. Comput. Chem.* **4** (1983) 556.
16. J. V. Knop, K. Szymanski, N. Trinajstić, and P. Křivka, *Comput. Math. Appls.* **10** (1984) 369.
17. D. J. Klein, T. G. Schmalz, and G. E. Hite, *J. Comput. Chem.* **7** (1986) 443.
18. A. T. Balaban and I. Tomescu, *Croat. Chem. Acta* **57** (1984) 391.
19. J. L. Bergan, S. J. Cyvin, and B. N. Cyvin, *Chem. Phys. Lett.* **125** (1986) 218.
20. S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, *Chem. Phys. Lett.* **140** (1987) 124.
21. J. L. Bergan, B. N. Cyvin, and S. J. Cyvin, *Acta Chim. Hung.* **124** (1987) 299.
22. M. Randić, L. L. Henderson, and R. Stout, *Croat. Chem. Acta,* in press.
23. H. Wynberg, *Acc. Chem. Res.* **4** (1971) 65.
24. R. H. Martin, *Angew. Chem. Int. Edit. Engl.* **13** (1974) 649.
25. J. V. Knop, W. R. Müller, K. Szymanski, and N. Trinajstić, *Computer Generation of Certain Classes of Molecules,* SKTH, Zagreb 1985, p. 91.
26. M. Randić, B. M. Gimarc, S. Nikolić, and N. Trinajstić, *Gazz. Chim. Ital.,* in press.
27. M. Gordon and W. H. T. Davison, *J. Chem. Phys.* **20** (1952) 428.
28. M. Randić, *Chem. Phys. Lett.,* in press.
29. M. Randić, *J. C. S. Faraday Trans. II* (1976) 232.
30. S. J. Cyvin and I. Gutman, *Math. Chem. (Mülheim/Ruhr)* **19** (1986) 229.
31. T. P. Živković and N. Trinajstić, *Chem. Phys. Lett.* **136** (1987) 141.
32. D. J. Klein, T. G. Schmalz, S. El-Basil, M. Randić, and N. Trinajstić, *J. Mol. Struct. (Theochem)* **179** (1988) 99.
33. M. Flammang-Barbieux, J. Nasielski, and R. H. Martin, *Tetrahedron Lett.* (1967) 743.

34. D. T. A. Cohen, *Basic Techniques of Combinatorial Theory*, Wiley, New York 1978, p. 63.
35. W. A. Seitz, D. J. Klein, T. G. Schmalz, and M. A. Garcia-Bach, *Chem. Phys. Lett.* **115** (1985) 139.
36. A. T. Balaban and I. Tomescu, *Math. Chem. (Mülheim/Ruhr)* **14** (1983) 155.
37. A. T. Balaban, *J. Mol. Struct. (Theochem)* **120** (1985) 117.
38. W. H. Laarhoven and T. J. H. M. Cuppen, *Tetrahedron Lett.* (1971) 163.
39. T. E. M. van den Hark, J. H. Noordik, and P. T. Beurskens, *Cryst. Struct. Comm.* **3** (1974) 443.
40. Ref. 25, the appendix.
41. M. Randić, B. M. Gimarc, S. Nikolić, and N. Trinajstić, *Gazz. Chim. Ital.* in press.
42. C. H. MacGillavry, *Symmetry Aspects of M. C. Escher's Periodic Drawings*, Oosthoek, Utrecht 1965.
43. A. T. Balaban, *Tetrahedron* **25** (1969) 2949.
44. Ref. 25, p. 93.
45. J. H. Dopper and H. Wynberg, *J. Org. Chem.* **40** (1975) 1957.
46. M. Randić and N. Trinajstić, *J. Amer. Chem. Soc.* **106** (1984) 4428.
47. A. T. Balaban, J. Brunvoll, J. Cioslowski, B. N. Cyvin, S. J. Cyvin, I. Gutman, H. Wenchen, H. Wenjie, J. V. Knop, M. Kovačević, W. R. Müller, K. Szymanski, R. Tošić, and N. Trinajstić, *Z. Naturforsch.* **42a** (1987) 863.

SAŽETAK

Prebrojavanje Kekuléovih struktura helicenskih sustava

M. Randić, S. Nikolić i N. Trinajstić

Prikazano je prebrojavanje Kekuléovih struktura za specijalnu vrstu helikoidnih benzenoida nazvanih [N]heliceni (N = broj šesteročlanih prstenova). Identificirano je pet skupina helicena: [N]heliceni, dvostruki heliceni, razgranani heliceni, cikloheliceni i helicirkuleni. Broj Kekuléovih struktura kod [N]helicena i dvostrukih helicena određuje se ili Gordon-Davisonovim postupkom ili Cyvinovim postupkom. Kekuléovi brojevi za [N]helicene (2, 3, 5, 8, 13, 21, 34, 55, 89, 144, . . .) pripadaju Fibonoccijevu redu (1, 1, 2, 3, 5, 8, 13, 21, 34, 55, 144, . . .). Isti Kekuléovi brojevi javljaju se i kod poli-fenantrena.

Međutim, za određivanje Kekuléova broja razgrananih helicena, ciklohelicena i heli-cirkulena uveden je novi postupak od dva koraka, u kojima se molekula razlaže na manje fragmente za koje se zna Kekuléov broj ili ga je lakše dobiti.