

CHEMICAL GRAPHS. PART 50.*

SYMMETRY AND ENUMERATION OF FIBONACENES (UNBRANCHED CATACONDENSED
BENZENIDS ISOARITHMIC WITH HELICENES AND ZIGZAG CATAFUSENES)

Alexandru T. Balaban

Polytechnic Institute, Organic Chemistry Department,
Splaiul Independentei 313, 77206 Bucharest, Roumania

(Received: January 1989)

Abstract. Formulas for the numbers of fibonacenes (nonbranched catafusenes having no more than two linearly condensed benzenoid rings) have been found, according to the symmetry of the catafusene.

* Preceding part : ref. 21.

Introduction

The enumeration of polycyclic benzenoid hydrocarbons (denoted for brevity *benzenoids* or *polyhexes*) and of their Kekulé structures continues to be a problem of general interest, and the number of books,¹⁻⁷ reviews⁸⁻¹¹ and papers¹²⁻¹⁶ dedicated to this area increases at a rapid pace.

This report will concentrate upon a restricted aspect, connected with both enumerations mentioned above. In a recent paper,¹⁷ we proposed the name "isoarithmic" for those benzenoids which have the same number of Kekulé structures or perfect matchings. The topology of the benzenoid determines this number. In the present paper only catacondensed benzenoids (*catafusenes*) will be considered : in such systems no internal vertex exists. All catafusenes with the same number h of hexagons are isomeric. Two catafusenes with identical sequences of linearly annelated rings are isoarithmic, irrespective of the direction of kinks ; such catafusenes have the same L-transform of their 3-digit codes in our coding system¹⁸ employing symbols 0 and 1 (which is read as digit one for the purpose of ordering lexicographically catafusenes) ; Gutman¹⁹ proposed for the same purpose an equivalent LA sequence. Thus all zigzag catafusenes are isoarithmic and isomeric with helicenes having the same number h of hexagons.

Many recent papers rule out from the enumeration of benzenoids the non-planar heli-cenic systems because such polyhexes are not a part of the graphite lattice : in them, some of the carbon atoms appear several times "on top of one another". However, in the present discussion we shall include them among the benzenoids because formulas for their enumeration are much simpler than for the strictly planar benzenoids.

The first enumeration of nonbranched catafusenes was proposed in 1968 by Balaban and Harary.¹² In the same paper, a new definition for catafusenes

was given on the basis of their dualist graph. This graph has the centers of hexagons as vertices ; the edges of this graph connect vertices corresponding to condensed hexagons, i.e. to rings sharing two carbon atoms. If the dualist graph is acyclic, the polyhex is catacondensed ; if it has 3-membered rings, it is pericondensed ; if, in addition to 3-membered rings and acyclic branches it possesses larger rings, it is corona-condensed (coronoid).

Interestingly, we found out recently that dualist graphs had been described in 1961,²⁰ but no further application for them was proposed till 1967. After that date, dualist graphs served for many other purposes, as described in several reviews.^{10,21} Dualist graphs are a special type of graphs because their geometry is important ; this fact makes them different from normal graphs or from dual graphs defined analogously.²²

Fibonacenes : unbranched catafusenes, isoarithmic with helicenes

A special interest is attached to unbranched catafusenes which are isoarithmic with zigzag catafusenes or with helicenes because the number of their Kekulé structures are Fibonacci numbers.²³⁻²⁶ Such systems have no linearly condensed sequence with more than two condensed hexagons. Among all isomeric catafusenes, they possess thus the maximal number of Kekulé structures, hence the highest stability. We propose for such systems the name fibonacenes.*

In earlier^{12,27} and more recent papers,¹¹ the symmetry of catafusenes

* We are aware that fibonaccenes would be etymologically more suitable but we suppressed one c for simplicity and for similarity with the established name "acenes".

served for classifying them into four classes : α , acenes (e.g. naphthalene 1, anthracene, tetracene, etc.) with linearly condensed rings ; c , centrosymmetric systems (e.g. chrysene 2) ; s , mirror-symmetric systems (phenanthrene 3, picene 4) ; and u , unsymmetrical catafusenes (e.g. tetraphene 5).

Figure 1 presents examples of nonbranched catafusenes together with their dualist graphs. There exists a bijection (one-to-one correspondence) between these catafusenes and the corresponding dualist graphs. Catafusenes 1-4 are fibonacenes, but 5 is not because it has three linearly condensed hexagons.

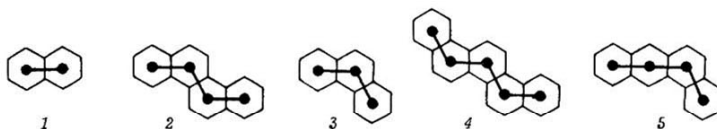


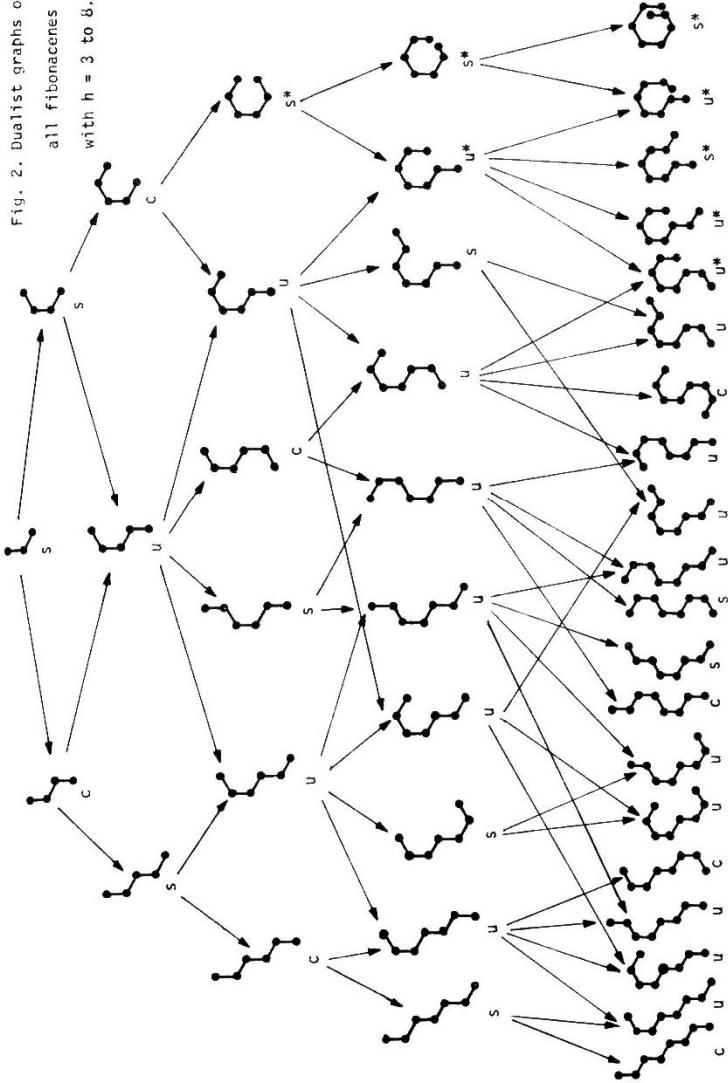
Figure 1. Catafusenes and their dualist graphs.

Enumeration of fibonacenes

We shall present the dualist graphs of fibonacenes with with $h = 3$ to 8 condensed hexagons, and the modes of their formation by annelation at a marginal vertex. The symmetry of the system is indicated by letters c , s , and u , with the significance indicated above. Asterisks denote nonplanar fibonacenes.

Figure 2 presents the derivation of fibonacenes on increasing the number of hexagons by one (annelation). It is evident that for obtaining distinct and nonisomorphic fibonacenes by this procedure, each centrosymmetric or mirror-symmetric has two "successors" and one "predecessor" ; each unsymmetric fibonacene has four "successors" and two "predecessors".

Fig. 2. Dualist graphs of
all fibonaccies
with $h = 3$ to 8 .



This follows naturally from the facts that (i) the two endpoints are topologically equivalent in c - and s -type fibonacenes and nonequivalent in u -type fibonacenes and (ii) at a given endpoint annelations can occur in two and only two kinked directions in order to afford a fibonacene with one more hexagon.

On this basis, it is possible to find formulas for the numbers $C(h)$, $S(h)$ and $U(h)$ of fibonacenes belonging to symmetry classes c , s , u with h hexagons, as well as for their total,

$$T(h) = U(h) + S(h) + C(h)$$

One can obtain easily explicit formulas for C and S :

$$\begin{aligned}C(2k+1) &= 0 \\C(2k) &= S(2k) = 2^{k-2} \\S(2k+1) &= 2^{k-1}\end{aligned}$$

The following recurrence can be found on the basis of the above predecessor-successor relationships :

$$U(k+1) = \frac{1}{2} [2C(h) + 2S(h) + 4U(h) - C(k+1) - S(h+1)]$$

On substituting the above values we obtain the recurrence relationships for U and T :

$$\begin{aligned}U(2k) &= 2U(2k-1) \\U(2k+1) &= 2U(2k) + 2^{k-2} \\T(2k) &= 2U(2k-1) + 2^{k-1} \\T(2k+1) &= 2U(2k) + 2^{k-2} + 2^{k-1} \\T(2k) &= 2T(2k-1)\end{aligned}$$

Finally, one obtains explicit formulas for U and T :

$$\begin{aligned}
 U(2k) &= 2^{2k-4} - 2^{k-2} = 2^{k-2}(2^{k-2} - 1) \\
 U(2k+1) &= 2^{2k-3} - 2^{k-2} = 2^{k-2}(2^{k-1} - 1) \\
 T(2k) &= 2^{2k-4} + 2^{k-2} = 2^{k-2}(2^{k-2} + 1) \\
 T(2k+1) &= 2^{2k-3} + 2^{k-2} = 2^{k-2}(2^{k-1} + 1)
 \end{aligned}$$

Table 1 presents numerical data for numbers C, S, U and T as functions of the number h of hexagons. The values in brackets indicate how many of the corresponding systems are nonplanar. It is easy to see the regular trend for numbers of nonplanar centrosymmetric and mirror-symmetric fibonacenes.

TABLE 1. Numbers of all fibonacenes with h = 3 to 10 according to their symmetry. Bracketed numbers denote nonplanar systems.

h	Centrosymm.	Mirror-symm.	Unsymm.	Total
	C(h)	S(h)	U(h)	T(h)
3	0	1	0	1
4	1	1	0	2
5	0	2	1	3
6	2	2(1)	2	6(1)
7	0	4(1)	6(1)	10(2)
8	4	4(2)	12(3)	20(5)
9	0	8(2)	28(9)	36(11)
10	8(1)	8(4)	56(21)	72(26)

The numbers found in TABLE 1 and with the above formulas agree with those found from computer simulations of benzenoid structures (these, however, do not include nonplanar systems^{2,3}).

References

1. S.J. Cyvin and I. Gutman, "*Kekulé Structures in Benzenoid Hydrocarbons*", Lecture Notes in Chemistry No. 46, Springer, Berlin, 1988.
2. J.V. Knop, W.R. Müller, K. Szymanski and N. Trinajstić, "*Computer Generation of Certain Classes of Molecules*", Kemija u industriji, Zagreb, 1985.
3. K. Szymanski, "*Polyhexagons der Ordnungen 1-10 klassifiziert nach der Anzahl der inneren Knoten*", Univ. Düsseldorf, Rechenzentrum.
4. J.R. Dias, "*Handbook of Polycyclic Hydrocarbons*", Elsevier, Amsterdam, Part A, 1987 ; Part B, 1988.
5. I. Gutman and O.E. Polansky, "*Mathematical Concepts in Organic Chemistry*", Springer, Berlin, 1986.
6. F. Harary and E.M. Palmer, "*Graphical Enumeration*", Academic Press, New York, 1973.
7. N. Trinajstić, "*Chemical Graph Theory*", CRC Press, Boca Raton, Florida, 1983.
8. A.T. Balaban, in "*Chemical Applications of Graph Theory*", Academic Press, London, 1976, p. 63.
9. A.T. Balaban, *J. Chem. Inf. Comput. Sci.*, 25, 334 (1985) ; *J. Mol. Struct. (Theochem)* 120, 117 (1985).
10. A.T. Balaban, *Pure Appl. Chem.*, 52, 1409 (1980) ; 54, 1075 (1982).
11. A.T. Balaban, J. Brunvoll, J. Ciosłowski, B.N. Cyvin, S.J. Cyvin, I. Gutman, He Wenchen, He Wenje, J.V. Knop, M. Kovačević, W.R. Müller, K. Szymanski, R. Tošić and N. Trinajstić, *Z. Naturforsch.*, 42A, 863 (1987).
12. A.T. Balaban and F. Harary, *Tetrahedron*, 24, 2505 (1968).
13. F. Harary and R.C. Read, *Proc. Edinburgh Math. Soc. Sci.*, II, 17, 1 (1970).

14. J. Brunvoll, S.J. Cyvin and B.N. Cyvin, *J. Comput. Chem.*, 8, 189 (1987).
15. J.V. Knop, K. Szymanski, Z. Jericevic and N. Trinajstić, *J. Comput. Chem.*, 4, 23 (1983) ; *Math. Chem.*, 16, 119 (1984).
16. R. Tosić and M. Kovacevic, *J. Chem. Inf. Comput. Sci.*, 20, 29 (1988).
17. A.T. Balaban and I. Tomescu, *Math. Chem.*, 14, 155 (1983).
18. A.I. Balaban, *Rev. Roum. Chim.*, 22, 45 (1987).
19. I. Gutman, *Theoret. Chim. Acta*, 45, 309 (1977).
20. F.T. Smith, *J. Chem. Phys.*, 34, 793 (1961).
21. A.T. Balaban, *Rev. Roum. Chim.*, 33, 699 (1988).
22. F. Harary, "Graph Theory", Addison-Wesley, Reading, Mass. 1971.
23. M. Gordon and W.H.T. Davison, *J. Chem. Phys.*, 20, 428 (1952).
24. T.F. Yen, *Theoret. Chim. Acta*, 20, 339 (1983).
25. S.J. Cyvin, *Math. Chem.*, 13, 167 (1982).
26. A.T. Balaban and I. Tomescu, *Croatia Chem. Acta*, 54, 391 (1984).
27. A.T. Balaban, *Tetrahedron*, 25, 2949 (1969) ; B. Dzonova-Jerman-Blazić and N. Trinajstić, *Computers and Chemistry*, 6, 121 (1982).

Appendix

An alternative approach for finding the explicit formulas for U and T consists in using the 3-digit notation¹² of catafusenes : on starting at one end one assigns digit 1 for a 120° kinked annelation, digit 2 for a 240° kink, and digit 0 for a 180° straight-on annelation (in the case of fibonacenes, the notation cannot contain digit 0). Among all possible notations involving either end of the unbranched fibonacene or either convention for the 120°/240° kink, one chooses as canonical the notation which corresponds to the smallest number when the digits are read sequentially.

Figure 3 presents the notation of all fibonacenes with 3 to 6 hexagons, arranged in the same order as in the upper part of Fig. 2.

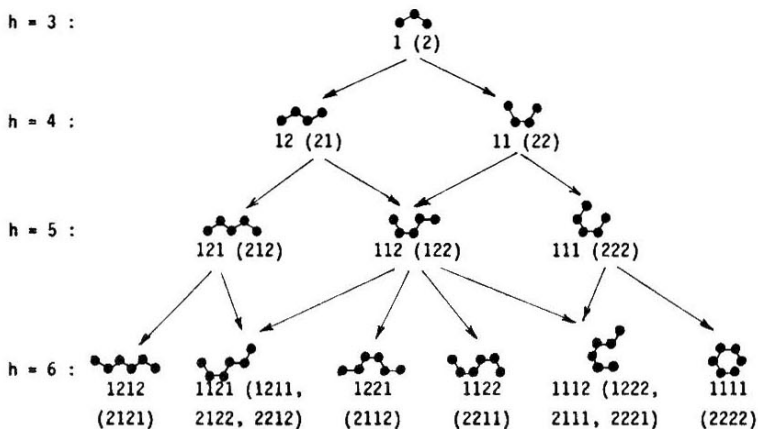


Fig. 3. The fibonacenes with $h = 3$ to 6 arranged as in Fig. 2. The correct notation is without brackets ; in brackets is the alternative notation to be discarded.

It will be seen that the mirror-symmetrical and the centrosymmetrical fibonacenes have one correct and one alternative notation, whereas the unsymmetrical fibonacenes have one correct and three alternative codes.

Taking into account that the notation of a fibonacene with h hexagons consists of a string with $h-2$ digits, that the number of binary numbers having $h-2$ digits is 2^{h-2} , and that the numbers of symmetrical fibonacenes obey the simple relationships indicated by the explicit formulas for C and S (see also TABLE 1), one obtains the explicit formulas for U and T.

Finally, mention should be made that in a forthcoming paper by A.T. Balaban and C. Arteni, the explicit formulas for the number of fibonacenes result as a particular case ($s = 2$) for the nonbranched catafusenes with h hexagons whose longest linearly condensed portion consists of s benzenoid rings.