International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075; Impact Factor: RJIF 5.22
Received: 28-02-2019; Accepted: 14-03-2019
www.chemicaljournals.com
Volume 3; Issue 3; May 2019; Page No. 25-31

Enumeration of Kekule structures of polyhex monoradical having only zig-zag assemblies of benzenoid hydrocarbons

Alphonse Emadak[1*], Robert Martin Nemba[2], Leonel Tsassi Djoumessi[3], Jules César Epée N[4]
[1-4] Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, Yaounde, Cameroon

Abstract
A mathematical process of enumeration of Kekule structures of any polybenzenoïd monoradical having only zig-zag assemblies of benzenoid hydrocarbons is given by using a method which consisted of the excision of the radical center C° in order to obtain a conjugated hydrocarbon having a 12-annulene core ring appended to one or more polybenzenoïd fragments and the partition of the resulting conjugated hydrocarbon into smaller independent resonant circuits.

Keywords: polyhex, enumeration, kekule, monoradicals, linear assemblies

1. Introduction
Polycyclic aromatic hydrocarbons are the most abundant class of molecules in the known universe, occurring in meteorites, carbon stars in interstellar space and as pyrolytic products in the combustion engine. The discovery and introduction of the concept of resonance embedding in this chemical compound's family has generated the problem of enumerating Kekule structures of polyhex molecules having several conjugated double bonds. Many publications dealing with the problem of enumeration of resonance structures prove that this problem is far from being exhausted. The enumeration of polyhex hydrocarbons dates back to 1964 [1]. From that day, generation and enumeration of polyhexes has attracted the interest of many researchers. Kekule structures in polyhexes, or particular classes of polyhexes such as cata-condensed or pericondensed benzenoids, coronoids or helicenes have been extensively studied [2-15]. Indeed, a whole book by Cyvin and Gutman [14] is devoted to that topic. It is also discussed at length in several surveys of two recent volumes on Advances in the theory of benzenoid hydrocarbons [16, 17] and in numerous papers cited there. In this work, we are interested in determining the number of Kekule structures of any polybenzenoïd monoradical having only symmetrical zig-zag assemblies of benzenoid hydrocarbons. To simplify the language, we will speak of assemblies of benzenoid hydrocarbons on the acenaphthene moiety. Beyond the direct formulas of computation established, this work provides another insight on the problem of enumeration of Kekule structures of polyhexes monoradicals. This paper contribute to the extensive work done on enumerations of any polybenzenoïd monoradical which still to be documented comparatively to others category of polyhexes such as fusene or perifusene.

2. Generation of polyhex monoradical Skeletons
Polyhex monoradical skeletons examined in this work are obtained from a building up procedure which consists to fuse in different ways the acenaphthene moiety with one or more polybenzenoïd fragments.
Various types of fusion or assembly may occur. The edge to edge fusion which may take place between one edge of A according to the orientations 1,2,3 or 1',2',3' and one terminal edge of a linear polyacene B. Successive repetition of this process generates a monoradical having a trihex core assembled to two or three linear polybenzene fragments located at right angles θ = 60°, 120 or 180° (fig. 1).

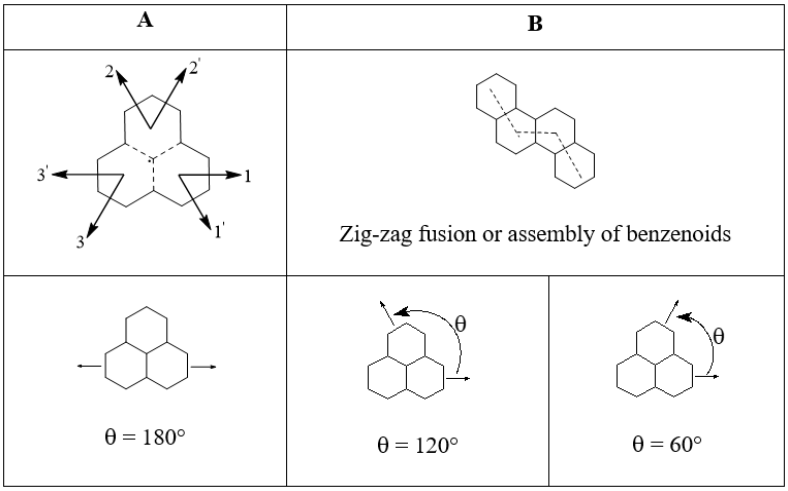


Fig 1: Acenaphtyl moiety and orientation of zig-zag fusion

3. Enumeration of Kekule structures of a polybenzenoïd monoradical

3.1 Mathematical formulation

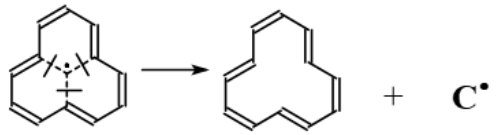
The enumeration of Kekule structures of any polybenzenoïd monoradical utilizes two steps:

- The deletion of the radical center in order to obtain a conjugated hydrocarbon having a 12-annulene core ring appended to one or more polybenzenoïd fragments and
- The partition of the resulting conjugated hydrocarbon into smaller independent resonant circuits.

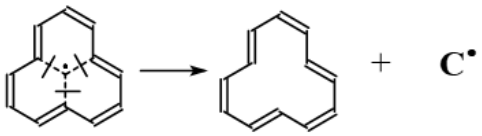
The computation as prescribed by the literature [15] of the number of Kekule structures of these independent circuits identified in step two aforementioned.

The determination of the number of Kekule structure of the monoradical using the principle of combination and taking into account the possibly independent resonant circuits.

The deletion of the radical center $C^{\bullet}$ in AI and AII is depicted on the following diagrams:



A_I $\quad G_0^+$



A_{II} $\quad G_0^-$

Where the resulting substructures G_0^+ and G_0^- are planar 12-annulene rings containing six double bonds rotating in the clockwise (+sign) and anti clockwise (-sign) directions.

Such a distinction between G_0^+ and G_0^- generates the following theorems:

Theorem 1: The number of Kekule structures of the unidirectional circuits G_0^+ and G_0^- are respectively:

$$K(G_0^+)=K(G_0^-)= 1 \quad (1)$$

Theorem 2: The number of Kekule structures of a single monoradical center $C^{\bullet}$ which exhibit an invariant electronic structure is $K(C^{\bullet})= 1$

If we claim that the two mesomeric forms of the trihex monoradical result from the interactions of G_0^+ and G_0^- with $C^{\bullet}$ therefore:

$$K(A_I) = K(G_0^+)xK(C^{\bullet}) = 1 \quad (2)$$

$$K(A_{II}) = K(G_0^-)xK(C^{\bullet})= 1 \quad (3)$$

The excision of $(C^{\bullet})$ of a monoradical suppresses 3 internal edges and generates a parent conjugated hydrocarbon contains a planar 12 annulene ring possessing a resonant circuit of type G_0^+ or G_0^-.

The dissection of the parent conjugated circuits of type G_0^+ and G_0^- into smaller independent benzenoïd fragments is operated at a second step, with respect to the following conditions:

- To position the cutting lines, one may start from the core of the structure and move toward the terminal edges of each polybenzenoïd branch.
- The orientation of each cutting line follows adjacent hexagonal rings and non-adjacent single bonds inside each hexagonal ring.
- A cutting dissection line does not bissect a double bond.
- The benzenoïd fragment to retain during a cutting in any direction is one which has a maximum number of hexagonal rings in resonance.

If the previous conditions are satisfied during the dissection of the parent conjugated circuit one may obtain the solution of the problem of the enumeration of Kekule structures of any monoradical G_0 by applying the following principles.

Now let G_0 denote any polyhex monoradical having a trihex core appended to one or more polybenzenoïd fragments.

As previously observed the core of G_0 contains two central resonant circuits G_0^+ and G_0^-, which may induce two mesomeric resonant forms G_0^+ and G_0^- containing a 12-annulene ring in clockwise (+sign) and anticlockwise (-sign) rotation respectively.

The mesomeric forms G_0^+ and G_0^- generated the following instantaneous equilibria.

$$G_0^+ \leftrightarrow G_0 \leftrightarrow G_0^- \quad (4)$$

Let $K(G_0)$, $K(G_0^+)$ and $K(G_0^-)$ denote the number of kekule structures of G_0, G_0^+, G_0^-. From (4) one way may deduce the following relationship:

$$K(G_0) = K(G_0^+) + K(G_0^-) \quad (5)$$

The excision and dissections processes applied to the resonant forms G_0^+ and G_0^- of the polyhex are collected in the following set of dissections or partitions:

$$G_0^+ = \{D_{01}, D_{02},\ldots, D_{0i},\ldots, D_{0j}, C^{\bullet}, \delta\}$$

$$G_0^- = \{D_{01}', D_{02}',\ldots,D_{0r}',\ldots,D_{0k}', C^{\bullet}, \delta'\}$$

The elements D_{0i} $(1\leq i \leq j)$ and D_{0r}' $(1\leq r \leq k)$ have polybenzenoïd classical structures, $C^{\bullet}$ is the radical center, while δ and δ' are residual non resonance fragments (possessing one or more non conjugated double bonds)

If G_0^+ and G_0^- contain respectively j and k independent polybenzenoïd substructures, therefore:

$$K(G_0^+) = \prod_{i=1}^{j} K(D_{0i}) \quad (6)$$

$$K(G_0^-) = \prod_{r=1}^{k} K(D'_{0r}) \quad (7)$$

$$K(G_0) = \prod_{i=1}^{j} K(D_{0i}) + \prod_{r=1}^{k} K(D'_{0r}) \quad (8)$$

The enumeration of Kekule structures for numerous conjugated hydrocarbons is intensively documented in chemical literature [15]. However, we recall that the number of Kékulé structures of zig-zag polybenzenoids G_i, also named fibonaccene is:

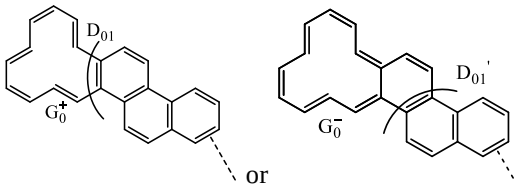
$$K(G_i) = F_{h_i+1} \quad (9)$$

Where h_i is the number of benzenoids. F_{h_i+1} is a Fibonacci number which respects following recurrence rules:

$$F_0 = F_1 = 1 \text{ and } F_n = F_{n-1} + F_{n-2}$$

where n is an integer number. [xxx]
In equation (1)–(14), $K(D_{0i})$ and $K(D_{0r}')$ are the number of Kekule structures of the polybenzenoïd with one or many dissections D_{0i} and D_{0r}' respectively.
We have applied the partition processes and (9)–(14) to the enumeration of Kekule structures for the following series of polyhex monoradicals having linear assemblies.

Case 1: One edge zig-zag assemblies

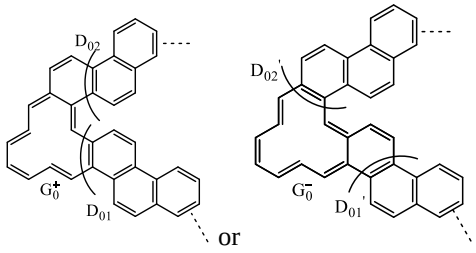


We have one dissection D_{01} on G_0^+ and one D_{01}' on G_0^-, therefore:

$$K(G_0) = K(D_{01}) + K(D_{01}') \quad (10)$$

$$K(G_0) = F_{h_1+1} + F_{h_1} = F_{h_1+2}$$

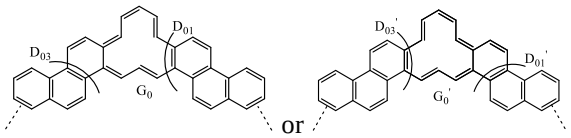
Case 2: Two zig-zag linear assemblies
We will distinguish here the various possible assemblies. These assemblies can be at 60 °, 120 °, 180 ° from each other.
For assemblies of 60°:



$$K(G_0) = K(D_{01})\,K(D_{02}) + K(D_{01}')\,K(D_{02}') \quad (11)$$

$$K(G_0) = F_{h_1+1} F_{h_2} + F_{h_1} F_{h_2+1}$$

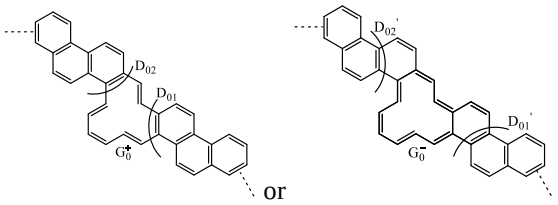
For asemblies of 180°:



$$K(G_0) = K(D_{01})\,K(D_{03}) + K(D_{01}')\,K(D_{03}') \quad (12)$$

$$K(G_0) = F_{h_1+1} F_{h_2} + F_{h_1} F_{h_2+1}$$

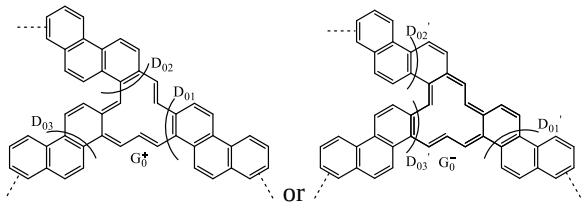
For an assemblies of 120°:



$$K(G_0) = K(D_{01})K(D_{02}) + K(D_{01}')K(D_{02}') \quad (13)$$

$$K(G_0) = F_{h_1+1} F_{h_2+1} + F_{h_1} F_{h_2}$$

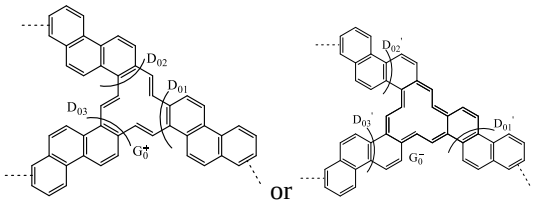
Case 3: Three edges zig-zag assemblies
The three linear branches can be positioned in two different ways on the various assembly sites offered by the perinaphthyl.
First way:



$$K(G_0) = K(D_{01})K(D_{02})K(D_{03}) + K(D_{01}')K(D_{02}')K(D_{03}') \quad (14)$$

$$K(G_0) = F_{h_1+1} F_{h_2+1} F_{h_3} + F_{h_1} F_{h_2} F_{h_3+1}$$

Second way:



$$K(G_0) = K(D_{01})K(D_{02})K(D_{03}) + K(D_{01}')K(D_{02}')K(D_{03}') \quad (15)$$

$$K(G_0) = F_{h_1+1} F_{h_2+1} F_{h_3+1} + F_{h_1} F_{h_2} F_{h_3}$$

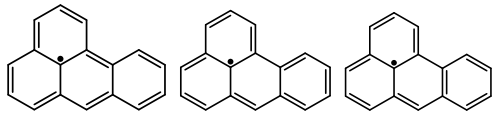
3.2 Application, results and graphical representations
The application is focusing on the enumeration of Kekule structures of any polybenzenoïd monoradical having only symmetrical zig-zag assemblies of benzenoid hydrocarbons. Therefore $h_i=h$. The results of computation obtained is

followed by graphical representations of Kekule structures.

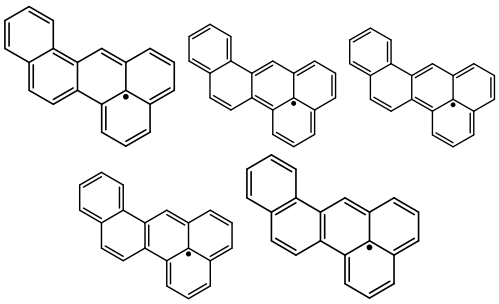
Case 1: One edge zig-zag assemblies
Series of a single zig-zag assembly are enumerate using (10) where $h_i=h$ and

$$K(G_0)= F_{h+1}+F_h = F_{h+2}$$

For *h=1*, $K(G_0)=3$



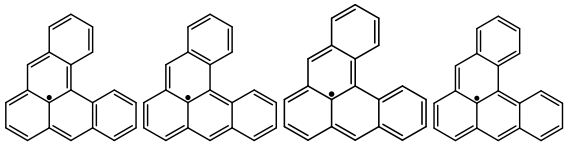
For *h=2*, $K(G_0)=5$



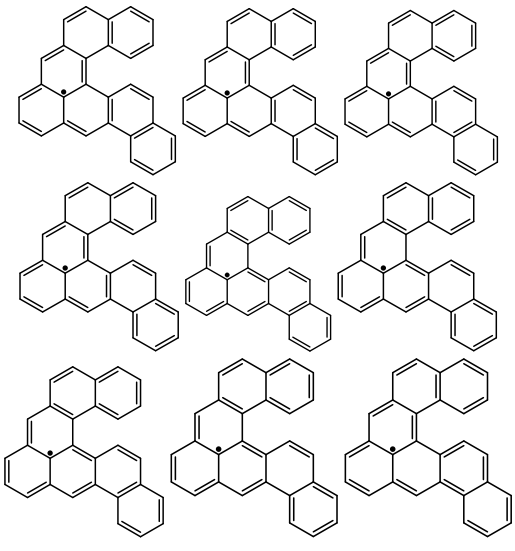
Case 2: Two edges zig-zag assemblies
Series of a two zig-zag assemblies are enumerate using (11), (12) and (13) where $h_i=h$.
For 60° assemblies, we have

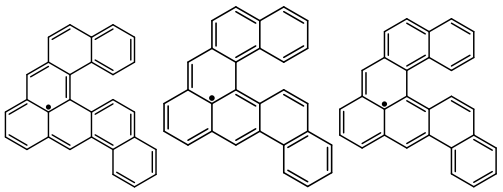
$$K(G_0)= 2F_{h+1}F_h$$

For *h=1*, $K(G_0)=4$



For *h=2*, $K(G_0)=12$

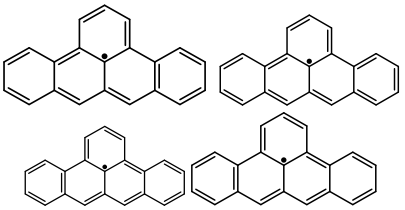




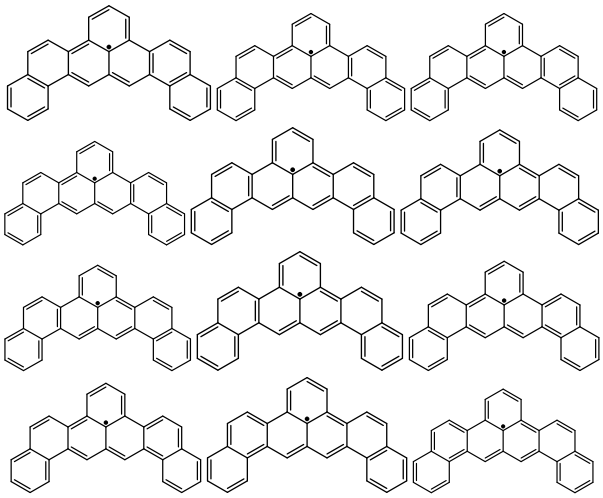
For 180° assemblies, we have

$$K(G_0)= 2F_{h+1}F_h$$

For *h=1*, $K(G_0)=4$



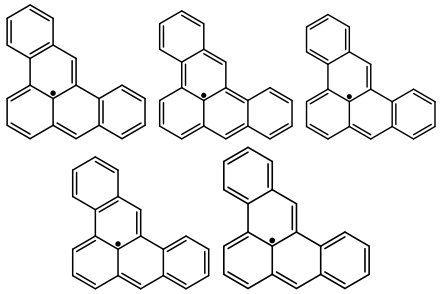
For *h=2*, $K(G_0)=12$



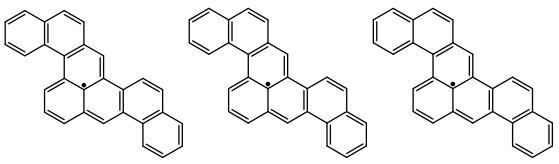
For 120° assemblies, we have

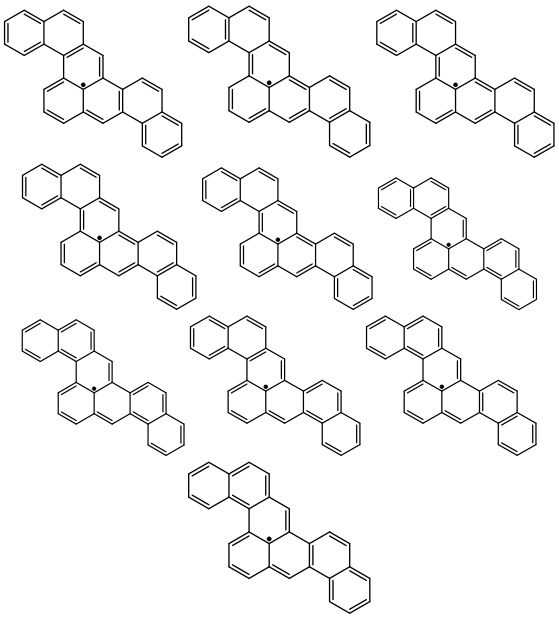
$$K(G_0)= F_{h+1}^2+F_h^2$$

For *h=1*, $K(G_0)=5$



For *h=2*, $K(G_0)=13$





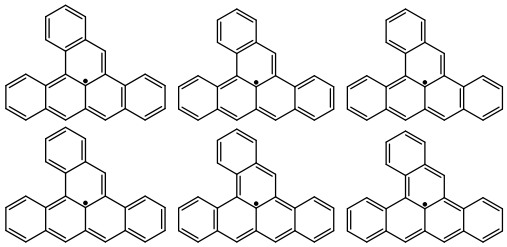
Case 3: Three edges zig-zag assemblies

Series of a three linear assemblies are enumerate using (14) and (15) where $h_i=h$.

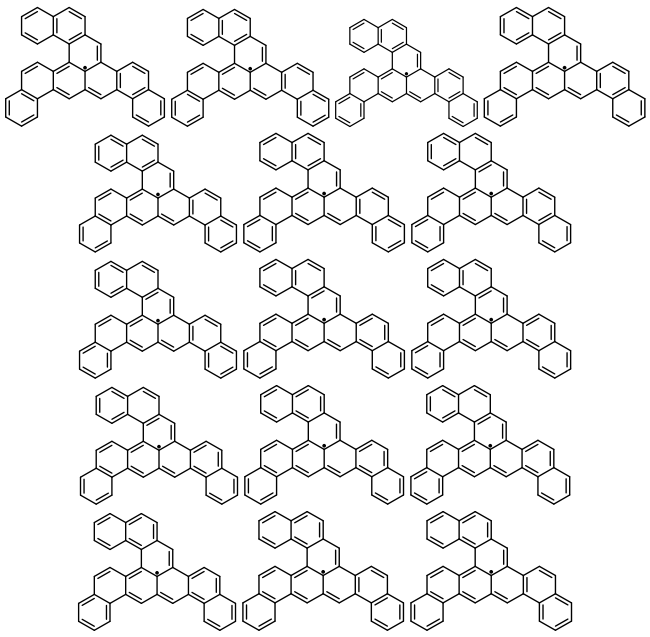
For the first type of assemblies, we have

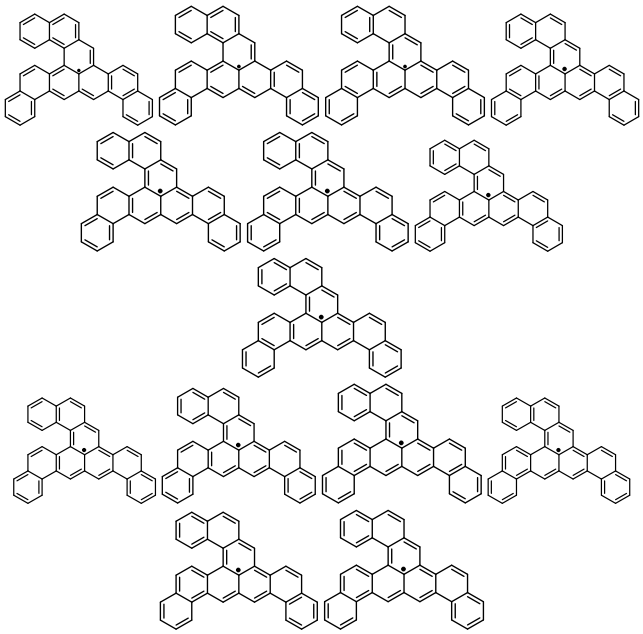
$$K(G_0)= F_{h+1}^2F_h + F_h^2F_{h+1}=F_h\ F_{h+1}F_{h+2}$$

For $h=1$, $K(G_0)=6$



For $h=2$, $K(G_0)=30$

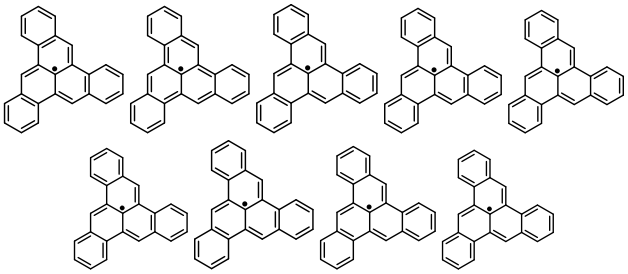




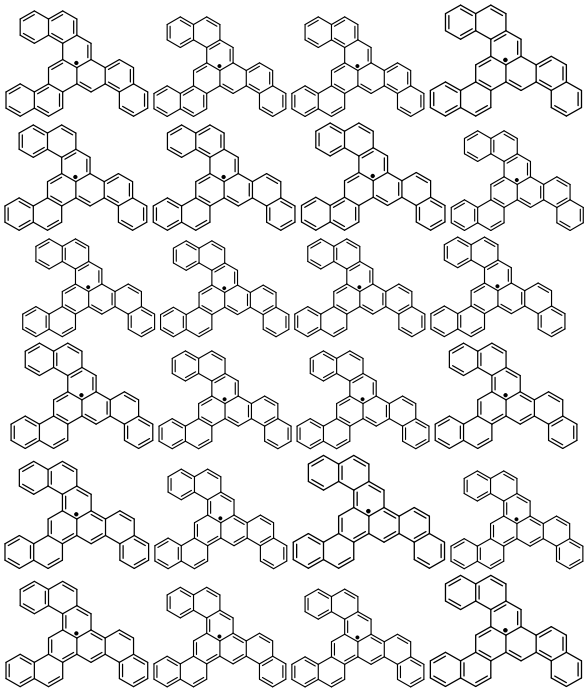
For the second type of assemblies, we have

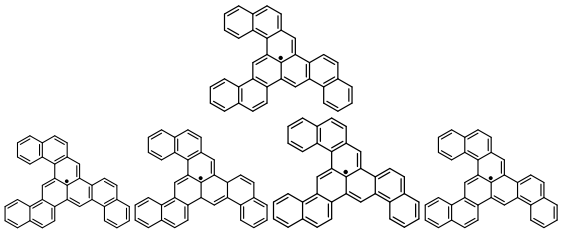
$$K(G_0)= F_{h+1}^3+F_h^3$$

For $h=1$, $K(G_0)=9$



For $h=2$, $K(G_0)=35$





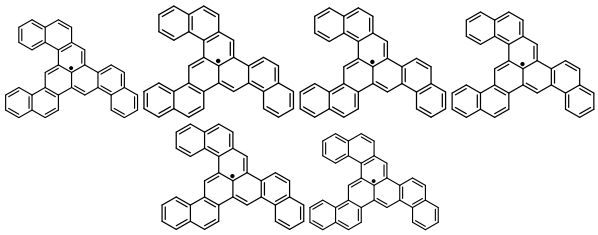
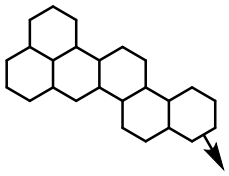
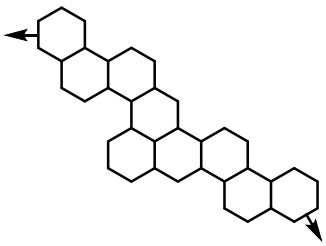
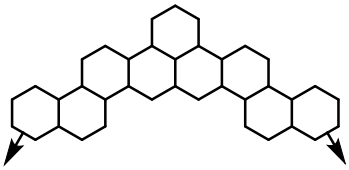
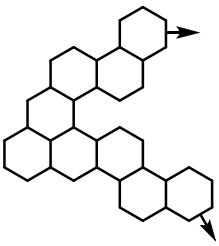
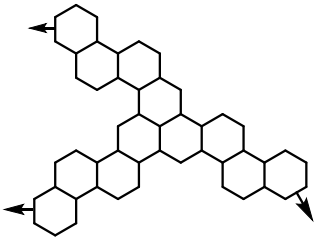
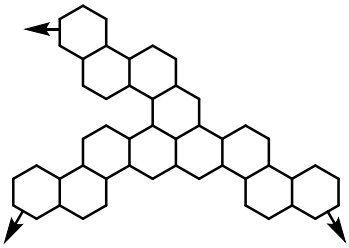


Table 1: Results summary of the enumeration polyhex monoradical with zig-zag assembled polybenzenoïds

General graph of polyhex monoradicals	Mathematical formula	h	K(G_0)
	F_{h+2}	1	3
		2	5
		3	8
		4	13
	$F_{h+1}^2 + F_h^2$	1	5
		2	13
		3	34
		4	89
	$2F_{h+1}.F_h$	1	4
		2	12
		3	30
		4	80
	$2F_{h+1}.F_h$	1	4
		2	12
		3	30
		4	80
	$F_{h+1}^3 + F_h^3$	1	9
		2	35
		3	152
		4	637
	$F_h.F_{h+1}.F_{h+2}$	1	6
		2	30
		3	120
		4	520

4. Conclusion

The results summarized in this paper are expected to eventually lead to a better understanding of how compute the number of kekule structures of polyhexes monoradical having only symmetrical linear poly benzenoids. We did not carry out the computation of cases where h1≠h2≠…≠hi

because formulas derived can be used to obtain the number of those monoradical polycyclic aromatic hydrocarbons. However, this case is relevant to be studied in future publication with the involvement of combinatorial methodology combined with group theory approach. We noticed the difficulty to represent graphs when the number of structures increases with the number of benzenoids. This complexity challenges us to develop easy and appropriate methods that can generate all the structures without duplication whatever the size of the graphs.

Acknowledgements

This research was supported by the Ministry of Higher Education of the Republic of Cameroon through the modernization research allowances. Authors also thank the University of Yaounde´ I and High Teacher Training College (Cameroon) for the use of their infrastructural facilities.

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