Enumeration of Kekule Structures of Polyhex Monoradical Having Only Linear Assemblies of Benzenoid Hydrocarbons

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Abstract: A mathematical process of enumeration of Kekule structures of any polybenzenoïd monoradical having only linear assemblies of benzenoid hydrocarbons is given by using a method which consisted of the excision of the radical center $C^{\bullet}$ in order to obtain a conjugated hydrocarbon having a 12-annulene core ring appended to one or more polybenzenoïd fragments, the partition of the resulting conjugated hydrocarbon into smaller independent resonant circuits. Polyhex monoradical skeletons are obtained from a building up procedure which consists to fuse in different ways the acenaphtyl moiety with one or more polybenzenoïd fragments. Mathematical formulas are established for three cases of assemblies, one edge linear assemblies, two edges linear assemblies with two linear polybenzenoid fragments located at right angles $\theta = 60°$, 120° or 180° and three edges linear assemblies with three linear polybenzenoid fragments located at right angles $\theta = 60°$, 120° or 180°. Results show that the number of Kekule structures of any polybenzenoïd monoradical having only linear assemblies of benzenoid hydrocarbons increases with the number of fused benzenoids according to results compiled in the table for h equal 1, 2, 3 and 4. Difficulty to represent graphs when the number of structures increases with the number of benzenoids cannot be neglected.

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 compounds 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 linear assemblies of benzenoid hydrocarbons. To simplify the language, we will speak of assemblies of benzenoid hydrocarbons on the acenaphtyl 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 acenaphtyl 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 polybenzenoid fragments located at right angles θ = 60°, 120° or 180° (figure 1).
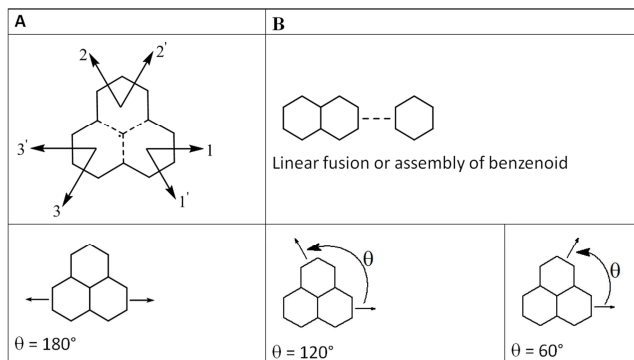

Figure 1. *Acenaphtyl moiety and orientation of linear fusion.*

3. Enumeration of Kekule Structures of a Polybenzenoïd Monoradical
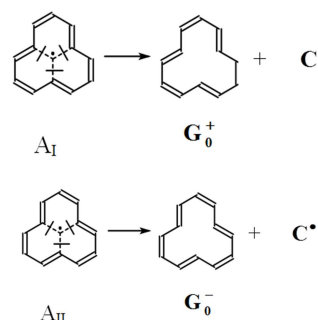
3.1. Mathematical Formulation

The enumeration of Kekule structures of any polybenzenoïd monoradical utilizes two steps:
(1) the deletion of the radical center $C^{\bullet}$ in order to obtain a conjugated hydrocarbon having a 12-annulene core ring appended to one or more polybenzenoïd fragments and
(2) 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 A_I and A_{II} is depicted on the following diagrams:

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:

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

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:

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

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

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:
a) To position the cutting lines, one may start from the core of the structure and move toward the terminal edges of each polybenzenoïd branch.
b) The orientation of each cutting line follows adjacent hexagonal rings and non-adjacent single bonds inside each hexagonal ring.
c) A cutting dissection line does not bissect a double bond.
d) 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.

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

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:

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

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:

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

$$K(G_0^-) = \prod_{r=1}^{k} K(D_{0r}') \qquad (7)$$

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

The enumeration of Kekule structures for numerous conjugated hydrocarbons is intensively documented in chemical literature. [15]. However, we recalled that the number of Kékulé structures of linear polybenzenoids G_i is
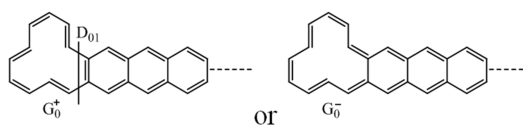
$$K(G_i) = h_i + 1 \qquad (9)$$

Where h_i is the number of benzenoids.

In equation (1)–(15), 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)–(15) to the enumeration of Kekule structures for the following series of polyhex monoradicals having linear assemblies.

Case 1: One edge linear assemblies

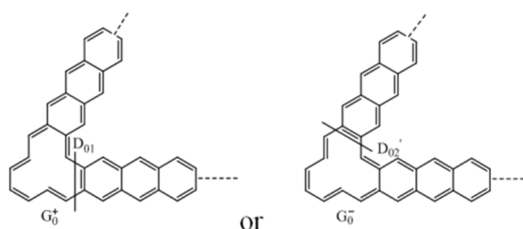We have one dissection D_{01} on G_0^+

$$K(G_0) = K(D_{01}) + 1 \qquad (10)$$

$$K(G_0) = h_1 + 1 + 1 = h_1 + 2$$

Case 2: Two edges linear assemblies

We will distinguish here the various possible assemblies. These assemblies can be at 60 °, 120 °, 180 ° from each other.
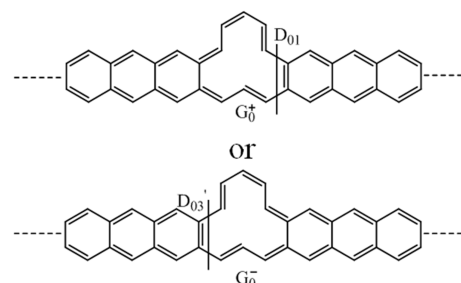
For assemblies of 60°:

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

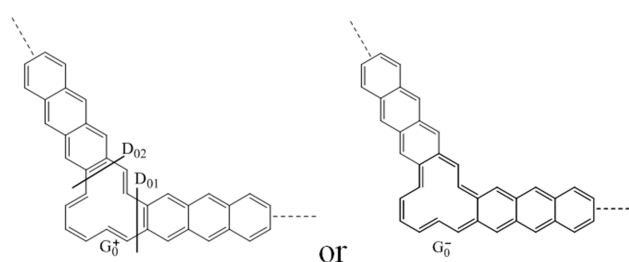$$K(G_0) = h_1 + 1 + h_2 + 1 = h_1 + h_2 + 2$$

For assemblies of 180°:

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

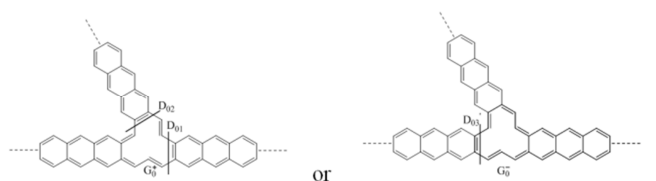$$K(G_0) = h_1 + 1 + h_3 + 1 = h_1 + h_3 + 2$$

For an assemblies of 120°:

$$K(G_0) = K(D_{01}) \times K(D_{02}) + 1 \qquad (13)$$

$$K(G_0) = (h_1 + 1)(h_2 + 1) + 1$$

Case 3: Three edges linear assemblies

The three linear branches can be positioned in two different ways on the various assembly sites offered by the perinaphthyl.
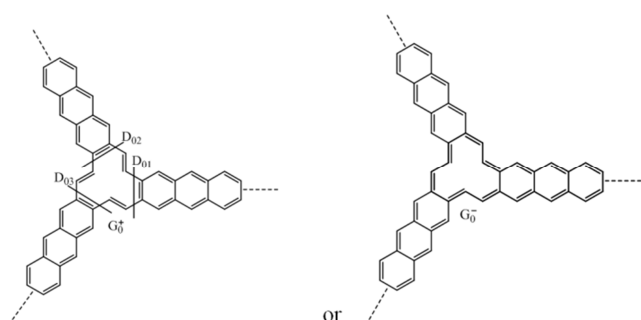
First way:

or

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

$$K(G_0)=(h_1+1)(h_2+1)+(h_3+1)$$

Second way:

or

$$K(G_0)=K(D_{01})xK(D_{02})xK(D_{03})+1 \qquad (15)$$
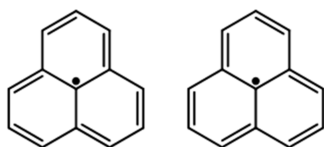
$$K(G_0)=(h_1+1)(h_2+1)(h_3+1)+1$$

3.2. Application, Results and Graphical Representations

The application is focusing on the enumeration of Kekule structures of any polybenzenoïd monoradical having only symmetrical linear assemblies of benzenoid hydrocarbons. Therefore $h_i=h$. The results of computation obtained is followed by graphical representations of Kekule structures.
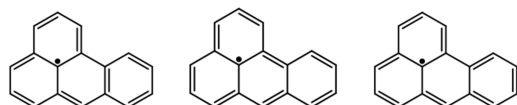
Case 1: One edge linear assemblies

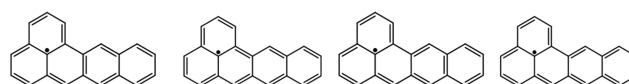Series of a single linear assembly are enumerate using (10) where $h_i=h$ and $K(G_0)=h_1+1+1=h_1+2=h+2$

For *h=0*, $K(G_0)=2$

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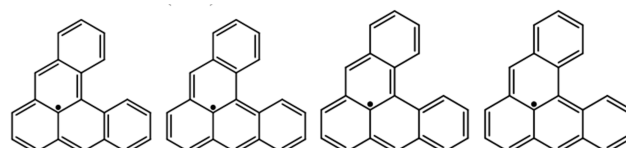

For *h=2*, $K(G_0)=4$

Case 2: Two edges linear assemblies

Series of a two linear assemblies are enumerate using (11), (12) and (13) where $h_i=h$.

For 60° assemblies, we have

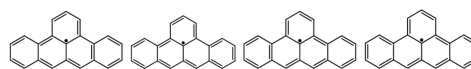$$K(G_0)=h_1+1+ h_2+1=h_1+h_2+2=2(h+1)$$

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

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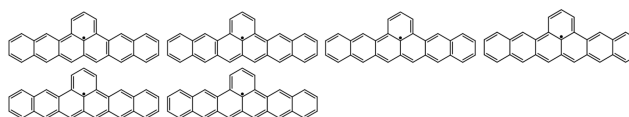

For 180° assemblies, we have

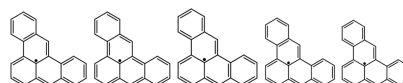$$K(G_0)= K(G_0)=h_1+1+ h_3+1=h_1+ h_3+2=2(h+1)$$

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

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

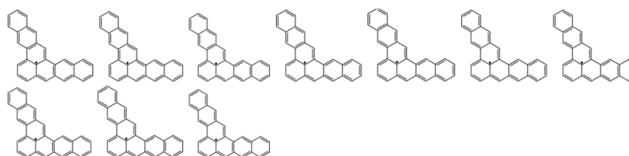

For 120° assemblies, we have

$$K(G_0)=(h_1+1)(h_2+1)+1= (h+1)^2+1$$

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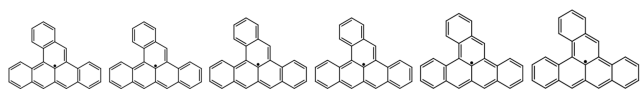

For *h=2*, $K(G_0)=10$

Case 3: Three edges linear assemblies

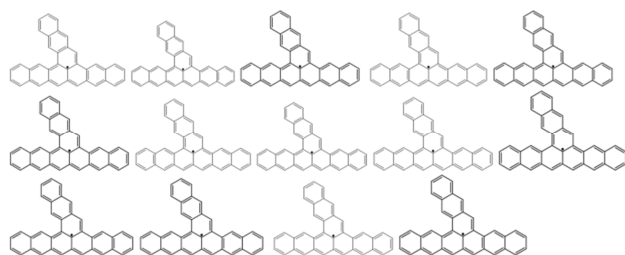Series of a three linear assemblies are enumerate using (14) and (15) where $h_i=h$.

For the first type of assemblies, we have

$$K(G_0)=(h_1+1)(h_2+1)+(h_3+1)=(h+1)(h+2)$$
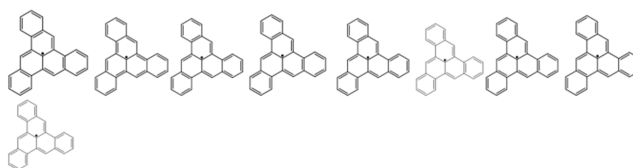
For *h=1*, $K(G_0)=6$

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

For the second type of assemblies, we have

$$K(G_0)=(h_1+1)(h_2+1)(h_3+1)+1=(h+1)^3+1$$
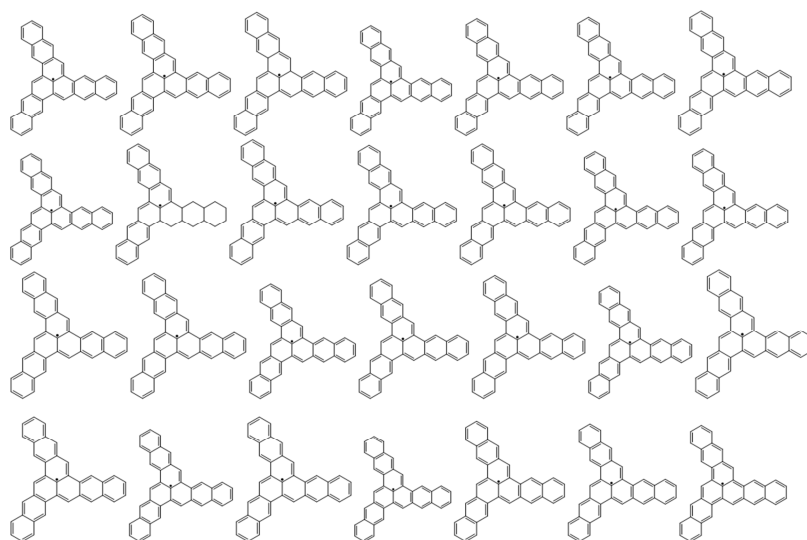
For $h=1$, $K(G_0)=9$

For $h=2$, $K(G_0)=28$

Table 1. *Results summary of the enumeration polyhex monoradical with linear assembled polybenzenoïds.*

General graph of polyhex monoradicals	Mathematical formula	h	K(G₀)
		0	2
		1	3
	$h+2$	2	4
		3	5
		4	6
		1	5
		2	10
	$(h+1)^2+1$	3	17
		4	26
		1	4
		2	6
	$2h+2$	3	8
		4	10
		1	4
		2	6
	$2h+2$	3	8
		4	10
		1	9
		2	28
	$(h+1)^3+1$	3	65
		4	126
		1	6
		2	12
	$(h+1)(h+2)$	3	20
		4	30

According to the above table of results, the mathematical formulas of the number of kekule structures of polyhexes monoradical having identical two edges linear polybenzenoids are invariant when the two linear polybenzenoid fragments are located at angles $\theta = 60°$ or $180°$. For h =3 and above, it is observed more than 50% gap between numbers kekule of the two cases of structures of polyhexes monoradical having identical three edges linear polybenzenoids with different angles. In general, the number of kekule structures increases with h for any cases.

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 identical linear polybenzenoids. We did not carry out the computation of cases where $h_1 \neq h_2 \neq ... \neq h_i$ 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 papers 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

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