

# Algebraic Studies of Kekulé Structures.

## A Semilattice Based on the Sextet Rotation Concept

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A semilattice defined by Ohkami et al. on the set of the Kekulé structures of a benzenoid hydrocarbon is examined and some of its properties are pointed out.

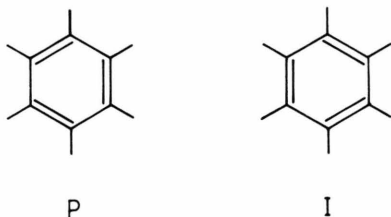
### Introduction

Kekulé structures play a significant role in several theoretical approaches to conjugated molecules and their examination is a subject of contemporary mathematical chemistry [1, 2]. Most of the recent publications on Kekulé structures are concerned with their enumeration [1]. Much less numerous are investigations of the individual properties of Kekulé structures, i.e. properties by which it is possible to discriminate between particular Kekulé structures.

In the present paper we report a few findings about a semilattice defined on the set of Kekulé structures of benzenoid hydrocarbons [3]. This semilattice is important in the theory of Clar's aromatic sextets [3]. Some basic facts about semilattices are given in the Appendix.

Let  $B$  be a benzenoid system possessing  $K$  Kekulé structures  $k_1, k_2, \dots, k_K$ . Their set is denoted by  $K$ , i.e.  $K = \{k_1, k_2, \dots, k_K\}$ . Conventionally we draw  $B$  so that some of its edges are vertical.

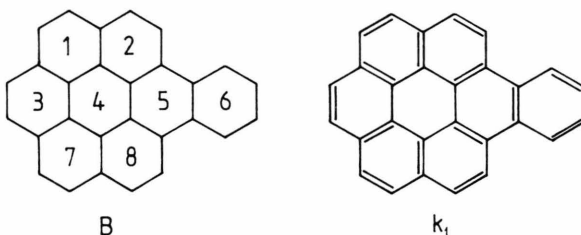
In some of the Kekulé structures of  $B$  three double bonds may belong to the same hexagon and may have the arrangement  $P$  ( $P$ =proper; the vertical double bond is on the right-hand side).



bond is on the right-hand side). This arrangement is to be distinguished from  $I$  ( $I$ =improper; the vertical double bond is on the left-hand side).

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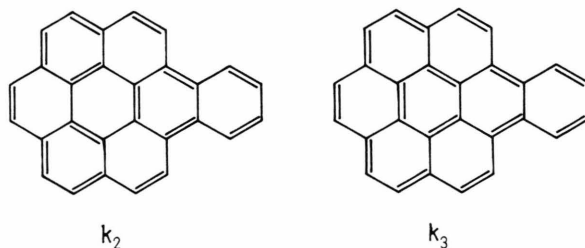
For example, in the Kekulé structure  $k_1$  of benzo-coronene ( $B$ )  $P$ -arrangements of double bonds are in the hexagons 1, 5 and 7 whereas  $I$ -arrangements are in the hexagons 2, 3, 6 and 8.



According to Ohkami et al. [3] the sextet rotation is the transformation of all  $P$ -arrangements into  $I$ -arrangements. Clearly, by a sextet rotation a Kekulé structure is transformed into another Kekulé structure (of the same benzenoid molecule). In other words, the sextet rotation concept defines a mapping of the set  $K$  onto itself:

$$R: K \rightarrow K. \quad (1)$$

For instance, the sextet rotation applied to the Kekulé structure  $k_1$  in the previous example yields  $k_2$ .



This will be written as  $R(k_1)=k_2$ . Further,  $R(k_2)=k_3$  and  $R(k_3)=k_1$ . This latter relation holds because in  $k_3$  there are no  $P$ -type arrangements of double bonds.

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We introduce the following abbreviations:  $R(R(k)) = R^2(k)$ ,  $R(R(R(k))) = R^3(k)$  etc. Let, in addition,  $R^0(k) = k$ .

The mapping (1) has been examined in [3] and [4]. Two of its basic properties are the following.

**Proposition 1** [3]: Every Kekuléan benzenoid system has a Kekulé structure  $k^0$ , such that  $R(k^0) = k^0$ . This Kekulé structure is unique; it is called the root Kekulé structure.

**Proposition 2** [4]: It is not possible to find  $n$  distinct Kekulé structures  $k_1, k_2, \dots, k_n$ ,  $n \geq 2$ , such that  $R(k_i) = k_{i+1}$ ,  $i = 1, \dots, n-1$  and  $R(k_n) = k_1$ . In other words, if  $k$  is not the root Kekulé structure, then for any value of  $p$ ,  $p \geq 1$ ,  $R^p(k) \neq k$ .

From Propositions 1 and 2 it immediately follows that the mapping (1) induces a semilattice on the set  $\mathbf{K}$  (cf. the Appendix). Indeed, if one writes  $k_a \succ k_b$  whenever for some  $p \geq 0$ ,  $R^p(k_a) = k_b$ , then  $\langle \mathbf{K}, \succ \rangle$  is a semilattice.

The relation  $\succ$  is reflexive because for any  $k_a \in \mathbf{K}$ ,  $R^0(k_a) = k_a$ .

The relation  $\succ$  is antisymmetric because the existence of two Kekulé structures  $k_a$  and  $k_b$ ,  $k_a \neq k_b$ , such that  $R^p(k_a) = k_b$  and  $R^q(k_b) = k_a$  would imply  $R^{p+q}(k_a) = k_a$ ,  $R^{p+q}(k_b) = k_b$  and would therefore contradict Proposition 2.

The relation  $\succ$  is transitive because if  $R^p(k_a) = k_b$  and  $R^q(k_b) = k_c$ , then  $R^{p+q}(k_a) = k_c$ .

Since  $\mathbf{K}$  is a finite set, from Propositions 1 and 2 it follows that for an arbitrary Kekulé structure  $k \in \mathbf{K}$  and for some sufficiently large value of  $p$ ,  $R^p(k) = k^0$ , where  $k^0$  denotes the root Kekulé structure. Therefore, for any  $k \in \mathbf{K}$ ,  $k \succ k^0$ . This means that  $\inf \{k_a, k_b\}$  exists for any pair of Kekulé structures  $k_a, k_b \in \mathbf{K}$ .

This proves that  $\langle \mathbf{K}; \succ \rangle$  is a semilattice.

It is easy to demonstrate that in the general case  $\langle \mathbf{K}; \succ \rangle$  is not a lattice. For example,  $\sup \{k_1, k_3\}$  does not exist in the case when  $k_1$  and  $k_3$  are the Kekulé structures of benzo[a]pyrene, presented in Figure 1.

Figure 1 contains the nine Kekulé structures of benzo[a]pyrene. For this molecule the mapping (1) has the following specific form:

$$\begin{aligned} R(k_1) &= k_2; & R(k_2) &= k_5; & R(k_3) &= k_5; \\ R(k_4) &= k_8; & R(k_5) &= k_9; & R(k_6) &= k_9; \\ R(k_7) &= k_8; & R(k_8) &= k_9; & R(k_9) &= k_9. \end{aligned}$$

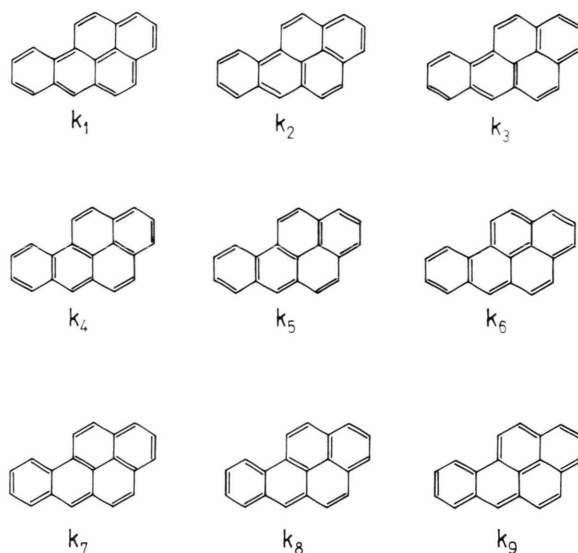


Fig. 1. The nine Kekulé structures of benzo[a]pyrene.

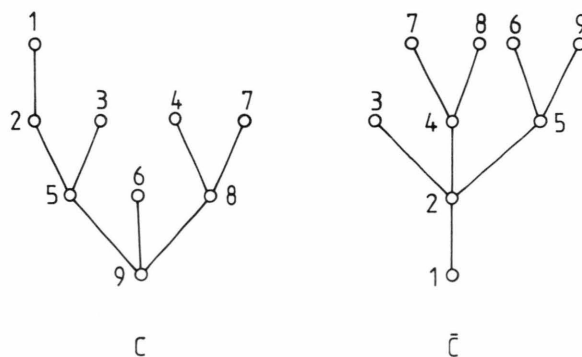


Fig. 2. The coral (C) of benzo[a]pyrene.  $\bar{C}$  is the dual of the coral C. The vertices of C and  $\bar{C}$  are labeled according to Figure 1.

Employing the usual graphical representation of a semilattice [3], [5] we arrive at the diagram C depicted on Figure 2.

The semilattice associated with a benzenoid system has a number of distinguished features. Because of the form of its diagram we propose to call such a semilattice a coral.

## Introduction to the Theory of Corals

A coral consists of  $K$  vertices, where  $K$  is the number of Kekulé structures of the associated benzenoid

molecule. These vertices are labeled by  $1, 2, \dots, K$  so that the  $i$ -th vertex corresponds to the Kekulé structure  $k_i$ ,  $i = 1, 2, \dots, K$ . If  $R(k_i) = k_j$  then the  $i$ -th vertex is drawn above the  $j$ -th vertex and connected with it by a line. In accordance with Proposition 2, there are  $K-1$  such connecting lines.

As a consequence of the above construction, the vertex corresponding to the root Kekulé structure will be on the bottom of the coral. It will be called the *root* of that coral.

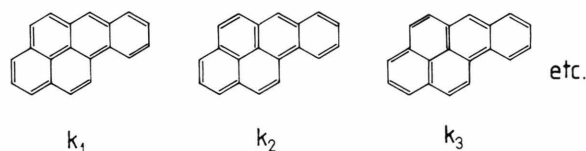
It is convenient to arrange the vertices of the coral in distinct layers. The number of these layers (not counting the bottom layer which consists of a unique vertex – the root) is the *height* of the coral. This terminology fully matches the notion of the height of a semilattice, as defined in the Appendix.

Certain vertices of a coral are maximal in the sense that they are not connected to any vertex lying above them. We shall call them *buds*. It is clear that the buds form an antichain (cf. the Appendix) and that their number is the width of the respective semilattice. Hence the number of buds will be called the *width* of the coral.

In the example given in Fig. 2 the vertex 9 is the root of the coral  $C$  whereas the vertices 1, 3, 4, 6, and 7 are its buds. The height and the width of this coral are 3 and 5, respectively.

In the general case the coral associated with a benzenoid system is not unique. Namely the structure of the coral depends on the way in which the benzenoid system is drawn.

For instance, if instead as in Fig. 1 we draw the Kekulé structures of benzo[a]pyrene as



then the mapping (1) results in

$$\begin{aligned} R(k_1) &= k_1; & R(k_2) &= k_1; & R(k_3) &= k_2; \\ R(k_4) &= k_2; & R(k_5) &= k_2; & R(k_6) &= k_5; \\ R(k_7) &= k_4; & R(k_8) &= k_4; & R(k_9) &= k_5. \end{aligned}$$

The corresponding coral is just  $\bar{C}$  from Figure 2. We call it the *dual* of the coral  $C$ .

Denote by  $\varrho_n$  the rotation of a benzenoid system in the horizontal plane by  $n \cdot 60^\circ$ . Denote by  $\sigma$  the reflection of a benzenoid system in a plane perpendicular to the horizontal plane, which contains a vertical edge.

From the definition of the mapping (1) or, more precisely, from the choice that the P-arrangements of double bonds are transformed into I-arrangements, it follows that the form of the coral remains unchanged by applying  $\varrho_n$ ,  $n$  even, or by applying  $\sigma$  followed by  $\varrho_n$ ,  $n$  odd. On the other hand the coral will be changed by applying  $\varrho_n$ ,  $n$  odd, or by applying  $\sigma$  followed by  $\varrho_n$ ,  $n$  even. In these latter cases the dual of the original coral will be obtained.

What is important is that irrespective of the way in which the formula of the benzenoid system is drawn we obtain either the coral or its dual. This finding can be formulated also in the following manner.

**Proposition 3.** Let  $C$  be a coral associated with a benzenoid system  $B$ , and let  $\bar{C}$  be the dual of the coral. Then the pair  $(C, \bar{C})$  is uniquely determined by  $B$ .

It is clear that the dual of the dual of a coral  $C$  is identical to  $C$ :  $\bar{\bar{C}} = C$ .

Proposition 3 can be further extended.

**Proposition 4.** The pair  $(C, \bar{C})$  remains the same if the sextet rotation is defined so to transform the I-arrangements of double bonds into P-arrangements.

The dual needs not differ from the coral. For instance, the coral and its dual coincide in symmetric benzenoid systems which are not affected by the action of the symmetry operators  $\sigma$  and  $\varrho_n$ ,  $n$  odd. However, the property  $C = \bar{C}$  was observed also in the case of some non-symmetric benzenoid systems.

Bearing in mind Propositions 3 and 4 we see that chemically relevant could be only those structural features which are common to the coral and its dual. In the following propositions we summarize a number of findings of this kind.

**Proposition 5.** The coral and its dual have equal heights.

**Proposition 6.** The coral and its dual have equal widths. The coral and its dual have equal numbers of buds.

**Proposition 7.** The root of the coral is a bud of its dual. The root of the dual is a bud of the coral.

### On Possible Chemical Applications of Coral

As already explained, the vertices of the coral correspond to the Kekulé structures of the respective benzenoid molecule. Therefore the structure of the coral

reflects certain relations between these Kekulé structures and offers a possibility to make distinctions between them. One obvious option of this kind would be to classify the Kekulé structures into those which correspond to buds and those which do not correspond to buds. Proposition 6 reveals that such an idea is mathematically sound. Kekulé structures corresponding to buds of the coral are those which cannot be obtained from any other Kekulé structure using one or more sextet rotations. Thus these Kekulé structures may be considered as a (minimal) basis set from which all the other Kekulé structures of the same benzenoid molecule are generated by means of sextet rotations.

Examining a large number of examples we observed that the height and the width of coral roughly parallel the chemical stability of the respective benzenoid molecule. The smaller the height and the greater the width of a coral (i.e. the larger the number of its buds), the greater is the stability of the benzenoid system considered.

The two extremes in this sense are the linear polyacenes and the polyphenylenes. The linear polyacene with  $h$  hexagons has  $h+1$  Kekulé structures. Its coral has height  $h$  and width 1 (i.e. just one bud). Linear polyacenes, on the other hand, are known to be the least stable among the Kekulé benzenoid hydrocarbons.

The polyphenylenes are highly aromatic conjugated systems. The coral of a polyphenylene with  $h$  hexagons has the minimum possible height ( $=1$ ) and the maximum possible width ( $=2^h - 1$ ).

The rule which we are putting forward is the following. If two benzenoid hydrocarbons have equal (or nearly equal) numbers of Kekulé structures, then the hydrocarbon whose coral has a larger number of buds is more stable. It is, of course, irrelevant whether we count the buds of the coral or the buds of the dual coral.

A characteristic example is provided by the pair dibenzo[*e, l*]pyrene, coronene. Both of these  $C_{24}$ -benzenoid hydrocarbons have 20 Kekulé structures. On the other hand, the coral of dibenzo[*e, l*]pyrene has 17 buds whereas the coral of coronene has only 13 buds. It is well known that dibenzo[*e, l*]pyrene – being a fully benzenoid hydrocarbon – exhibits a substantially higher chemical stability than coronene.

The following result gives a further support for the above observation.

Let  $B_{ab}$  be a benzenoid system composed of two parts  $B_a$  and  $B_b$ , connected by essentially single and

double bonds. Then, as well known [1],

$$K\{B_{ab}\} = K\{B_a\} K\{B_b\}, \quad (2)$$

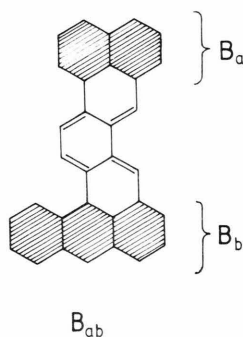
where  $K\{B\}$  stands for the number of Kekulé structures of the benzenoid system  $B$ . Note that  $K\{B\}$  is also the number of vertices of the coral (or its dual) associated with  $B$ .

*Proposition 8.* Let the coral associated with the benzenoid system  $B$  have  $F\{B\}$  vertices which are not buds. Then

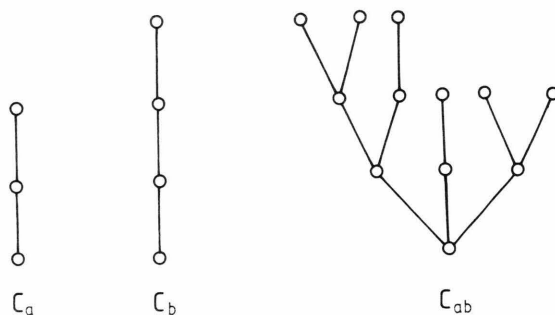
$$F\{B_{ab}\} = F\{B_a\} F\{B_b\}. \quad (3)$$

There is a remarkable analogy between (2) and (3).

As an illustration of Proposition 8 consider the essentially disconnected benzenoid system  $B_{ab}$ , composed of a naphthalene ( $B_a$ ) and an anthracene ( $B_b$ ) unit:



The corresponding corals are  $C_a$ ,  $C_b$  and  $C_{ab}$ , respectively:



The corals  $C_a$ ,  $C_b$  and  $C_{ab}$  have 1, 1, and 6 buds, respectively. Therefore  $F\{B_a\} = K\{B_a\} - 1 = 2$ ,  $F\{B_b\} = K\{B_b\} - 1 = 3$  and  $F\{B_{ab}\} = K\{B_{ab}\} - 6 = 6$ , in harmony with (3).

We note in passing that in the above example  $C_a = \bar{C}_a$ ,  $C_b = \bar{C}_b$  and  $C_{ab} = \bar{C}_{ab}$ .

**Appendix: Definition of a Semilattice**

Let  $S$  be a set and  $>$  a binary relation on this set. This relation is said to be *partial ordering* if it is

- |                |  |
|----------------|--|
| reflexive,     | i.e. $a > a$ ;                             |
| antisymmetric, | i.e. $a > b$ and $b > a$ implies $a = b$ ; |
| transitive,    | i.e. $a > b$ and $b > c$ implies $a > c$ . |

Here  $a, b, c$  denote elements of  $S$ .

A set together with partial ordering is called a *partially ordered set*.

Let  $\langle S; > \rangle$  be a partially ordered set and  $a, b \in S$ . The *supremum* of  $a$  and  $b$ , denoted as  $\sup\{a, b\}$ , is another element  $c$  of  $S$ , such that  $c > a$  and  $c > b$ ; if for some  $x \in S$   $x > a$  and  $x > b$ , then  $x > c$ .

The *infimum* of  $a$  and  $b$ , denoted as  $\inf\{a, b\}$ , is an element  $d$  of  $S$ , such that  $a > d$  and  $b > d$ ; if for some  $y \in S$   $a > y$  and  $b > y$ , then  $d > y$ .

Neither  $\sup\{a, b\}$  nor  $\inf\{a, b\}$  need to exist in the general case.

If  $\langle S, > \rangle$  is a partially ordered set, such that for any  $a, b \in S$  both  $\sup\{a, b\}$  and  $\inf\{a, b\}$  exist, then

$\langle S; > \rangle$  is said to be a *lattice*. If for any  $a, b \in S$  only  $\inf\{a, b\}$  exists, then  $\langle S; > \rangle$  is a *semilattice*.

Let  $\langle S; > \rangle$  be a partially ordered set and  $L = \{a_0, a_1, a_2, \dots, a_n\}$  be a subset of  $S$ . We say that  $L$  is a chain of  $\langle S; > \rangle$  if  $a_i > a_{i-1}$  for all  $i = 1, 2, \dots, n$ . The length of this chain is  $n$ .

If  $S$  is a finite set, then the length of  $\langle S; > \rangle$  is equal to the length of the longest chain contained in  $\langle S; > \rangle$ . In the same sense we speak about the *length of a* (finite) *lattice or semilattice*.

Let  $\langle S; > \rangle$  be a partially ordered set and  $M = \{b_1, b_2, \dots, b_n\}$  be a subset of  $S$ . We say that  $M$  is an antichain of  $\langle S; > \rangle$  if for all values of  $i, j = 1, 2, \dots, n$ ,  $i \neq j$ , neither  $b_i > b_j$  nor  $b_j > b_i$  hold. The size of this antichain is  $n$ .

If  $S$  is a finite set, then the width of  $\langle S; > \rangle$  is equal to the size of the greatest antichain contained in  $\langle S; > \rangle$ . In the same sense we speak about the *width of a* (finite) *lattice or semilattice*.

More details on the theory of semilattices can be found in pertinent textbooks (see e.g. [5]).

- [1] Details on the enumeration of Kekulé structures can be found in: S. J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer-Verlag, Berlin 1988 and the numerous references cited therein.
- [2] Details of the application of Kekulé structures in resonance theory, Clar's aromatic sextet theory, conjugated circuit theory, etc. can be found in: I. Gutman and S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydro-*

*carbons*, Springer-Verlag, Berlin 1989 and the references cited therein.

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