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Interface Theory of Benzenoids

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Abstract

We propose here a novel tool for chemical graph theory, referred to in the following as the *interface theory of benzenoids,* designed for constructing, enumerating, and characterizing Clar covers of arbitrary benzenoids. The presented interface theory uses the new concepts of fragments and interfaces to express an arbitrary Clar cover of a benzenoid $\boldsymbol{B}$ as a collection of covering characters for the interface bonds in $\boldsymbol{B}$. A set of fundamental theorems demonstrates that the interface theory is internally consistent. In particular, we are able to establish the necessary and sufficient conditions required for the existence and uniqueness of a Clar cover in terms of interface bond coverings. The proposed theoretical framework can be conveniently and efficiently used for determining whether a given benzenoid is Kekuléan, for finding its Clar covers and Kekulé structures, for computing its ZZ polynomials, as well as deriving closed forms of ZZ polynomials for whole families of structurally related benzenoids, and for many other interesting applications. We believe that the presented here interface theory of benzenoids opens up new vistas in chemical graph theory and may revolutionize the field in the future.

1 Introduction

Determination and enumeration of Kekulé structures and Clar covers is one of the most important topics in chemical graph theory. Considerable scientific effort [26, 29, 31, 40] has been devoted toward predicting whether a benzenoid is Kekuléan [11, 27, 33, 37, 42, 45, 52, 75], identifying the regions of fixed bonds [14–17, 57, 67, 83], finding what is the maximal number of aromatic sextets that can be accommodated in a benzenoid

[1–5, 7, 8, 12, 38, 43, 50, 51, 60, 73, 74, 76], and finding how many Kekulé structures [6, 10, 28–30, 32, 46, 47, 49, 53, 54, 66, 71] and Clar covers [9, 20, 23, 24, 48, 55, 69, 80, 82, 86–90] can be constructed for a given benzenoid [13, 18, 19, 21, 22, 25, 39, 44, 65, 78, 79, 84, 85]. At the same time, even a casual inspection of the available literature cannot help the impression that the accumulated body of knowledge is surprisingly incomplete and many important results are still missing, despite of many important achievements that have been made. A few of the most important open problems left there to be solved are: finding Clar numbers for an arbitrary benzenoid, enumeration of Clar covers for two most basic classes of benzenoids, hexagons $O(k, l, m)$ [19, 23] and oblate rectangles $Ob(n, m)$ [19, 23], enumeration of Clar covers for n-tier regular benzenoids [28, 78, 79, 85], finding ZZ polynomials for large pericondensed benzenoids [18–25, 61, 65], and efficient algorithms for verification of Kekuléan character of large benzenoids.

In the current paper, we introduce a novel tool for analyzing and characterizing benzenoid structures, which allows one to demonstrate surprisingly many important properties of benzenoids in an easy and efficient fashion. The new framework is based on a concept of *interfaces* and for this reason we refer to it as the *interface theory of benzenoids* [61–63]. The definition of *interfaces* and the closely structurally related *fragments* is based on simple geometrical operations performed on a given benzenoid. We show explicitly that an assignment of covering orders to all the interface bonds uniquely defines a Clar cover for the analyzed benzenoid, provided that the assignment fulfills a certain set of conditions. The necessary and sufficient conditions that need to be satisfied for this purpose are characterized in detail. The new theoretical concepts are accompanied by a complete set of theorems necessary for applying the interface theory to solving practical problems in chemical graph theory. We conclude the paper with an algorithm illustrating how the interface theory can be applied for an automatic generation of Clar covers and with a discussion of applicability of the presented framework to arbitrary benzenoids, including those containing topological holes.

It is our impression that the presented here theory is different from anything that has been proposed to date and for this reason it may bring important new results and breakthroughs to the field of chemical graph theory. In order to show how such new results can be achieved, we accompany the current paper with a sequel paper [64], in which we demonstrate on a collection of examples how the interface theory can be applied for verifying the Kekuléan character of benzenoids, finding Clar numbers of benzenoids, computing their ZZ polynomials, finding essentially disconnected components of benzenoids, and for a couple of other related problems. Another practical application of the presented here interface theory of benzenoids is given in our next work, in which we use it for finding closed form formulas of the ZZ polynomials for the n-tier regular benzenoid strips. We genuinely hope that the reported here technique will be noticed and becomes popular in the community, as we find it very useful and powerful.

2 Preliminaries

A *benzenoid* $\boldsymbol{B}$ is defined as a finite plane graph embedded in a hexagonal lattice [40]. An example of $\boldsymbol{B}$ is shown in Fig. 1 (a). Here, we treat the definition of $\boldsymbol{B}$ quite generally, allowing benzenoids with inner perimeters and with vertices of degree 1. A *Kekulé structure* $\boldsymbol{K}$ is a spanning subgraph of $\boldsymbol{B}$ whose components are K_2 [56] and a *Clar cover* $\boldsymbol{C}$ is a spanning subgraph of $\boldsymbol{B}$ whose components are either K_2 or C_6 [26]; examples of $\boldsymbol{K}$ and $\boldsymbol{C}$ are shown in Figs. 1 (b) and (c), respectively. For convenience, we establish the following correspondences: a vertex $\equiv$ an atom, an edge $\equiv$ a bond, an edge belonging to a complete graph on 2 vertices $K_2 \equiv$ a double bond, a cycle graph on 6 vertices $C_6 \equiv$ an aromatic ring, and an edge belonging to $C_6 \equiv$ an aromatic bond. The maximal number of aromatic rings C_6 that can be accommodated in $\boldsymbol{C}$ is referred to as the *Clar number* Cl of $\boldsymbol{B}$ [26, 43]. The Clar covers with Cl aromatic sextets C_6 are referred to as the *Clar structures* of $\boldsymbol{B}$. [26, 43] The Clar covers with k aromatic sextets C_6 are referred to as the Clar covers of order k. If we represent the number of Clar covers

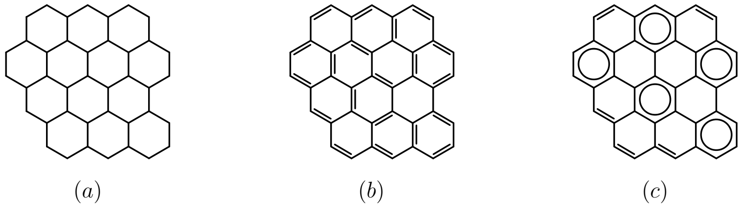

(a) (b) (c)

Figure 1. Example of (a) a benzenoid $\boldsymbol{B}$, (b) a Kekulé structure of $\boldsymbol{B}$, and (c) a Clar cover of $\boldsymbol{B}$ (which is also a Clar structure, since it has the maximum possible number of rings). The benzenoid shown here allows a total of 125 Kekulé structures and one Clar structure. The total number of Clar covers is 847.

of order k for $\boldsymbol{B}$ by c_k, we can define a combinatorial polynomial

$$\mathrm{ZZ}\left(\boldsymbol{B},x\right)=\sum_{k=0}^{Cl}c_kx^k \tag{1}$$

usually referred to as the *Clar covering polynomial* of $\boldsymbol{B}$ or the *Zhang-Zhang polynomial* of $\boldsymbol{B}$ or, shortly, the *ZZ polynomial* of $\boldsymbol{B}$ [82, 87–89]. In the ZZ polynomial, the number of Clar structures is given by the coefficient c_{Cl}, and the number of Kekulé structures is given by the coefficient c_0. For example, the benzenoid shown in Fig. 1 has the ZZ polynomial (which is easily calculated using the ZZDecomposer [24, 91, 92])

$$\mathrm{ZZ}(\boldsymbol{B},x)=x^5+19x^4+112x^3+280x^2+310x+125, \tag{2}$$

where the polynomial degree is the Clar number $Cl=5$, the coefficient $c_0=\mathrm{ZZ}(\boldsymbol{B},0)=125$ is the number of Kekulé structures, $c_5=1$ is the number of Clar structures, and $c_0+c_1+c_2+c_3+c_4+c_5=\mathrm{ZZ}(\boldsymbol{B},1)=847$ is the total number of Clar covers.

3 Interface theory formalism

3.1 Definitions and preliminary observations

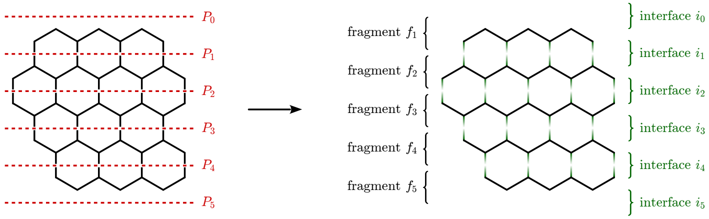


Figure 2. Dividing a benzenoid $\boldsymbol{B}$ into fragments f_k. Sets of vertical bonds of a fragment f_k form interfaces, namely the upper interface i_{k-1} and the lower interface i_k of f_k. Note that the first and last interface, i_0 and i_5, are necessarily empty.

Take an arbitrary benzenoid $\boldsymbol{B}$ in the orientation shown in Fig. 2 (i.e., with some of its edges oriented vertically) and introduce a system of horizontal partition lines P_k (shown in red in Fig. 2). In cases where a line P_k intersects the periphery of $\boldsymbol{B}$ in exactly two places, it is usually referred to in the existing literature as an elementary cut [41, 72] or an orthogonal edge cut [34, 59]. Note, however, that each of our partition lines can intersect the periphery of $\boldsymbol{B}$ in more than two places (for details, see Fig. 4 and Section 3.5), depending on the actual shape of $\boldsymbol{B}$. The partition lines P_k divide $\boldsymbol{B}$ into stripes. The set of bonds (edges) and atoms (vertices) within the stripe located (at least partially) between the lines P_{k-1} and P_k is called a *fragment* f_k. Each fragment f consists of vertices v_j (sometimes referred to as atoms of f), vertical edges e_j (referred to as *interface bonds* or *interface edges* of f), and the remaining non-vertical edges s_j (referred to as *spine bonds* or *spine edges* of f). The intersection $i_k = f_k \cap f_{k+1}$, consisting of interface bonds belonging simultaneously to both fragments f_k and f_{k+1}, is called the *interface* i_k. The fragment f_k has i_{k-1} as its *upper interface* and i_k as its *lower interface*. It is convenient to augment the set of interfaces with two additional empty sets: the upper interface i_0 of the first fragment f_1 and the lower interface i_K of the last fragment f_K.

The vertices v_j within a given fragment f are enumerated from left to right. The enumeration of spine bonds simply follows from the relation $s_j = v_j v_{j+1}$. Take now an interface bond $e = v'_i v''_j$ located between the vertex v'_i of the fragment f' and the vertex v''_j of the fragment f''. Depending on our needs, we will refer to e as e_i (when we discuss fragment f') or as e_j (when we discuss fragment f''). We are careful in the following that this double enumeration scheme does not lead to inconsistencies or ambiguities. This labeling system is illustrated in Fig. 3.

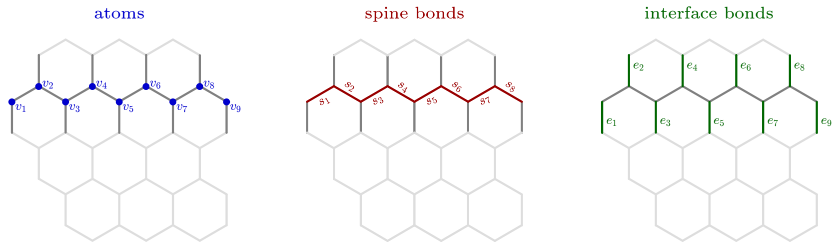


Figure 3. Detailed label assignment for the atoms and bonds in the fragment f_2 of the benzenoid $\boldsymbol{B}$ from Fig. 2. Spine bonds s_j have the same index as the atom v_j to their left, and interface bonds e_j have the same index as the atom v_j to their top or bottom. Here, the bonds e_2, e_4, e_6 and e_8 form the interface i_1, which is the upper interface of f_2. The bonds e_1, e_3, e_5, e_7 and e_9 form the interface i_2, which is the lower interface of f_2.

For now, let us require that the benzenoid has no holes, in the sense that all spine bonds $s_1, \ldots, s_{m-1}$ in all fragments exist. Allowing holes makes the formalism only slightly more complicated; this case will be covered later. On the other hand, whether or not any of the interface bonds are missing is irrelevant for the derivations that follow.

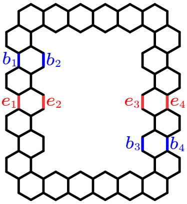
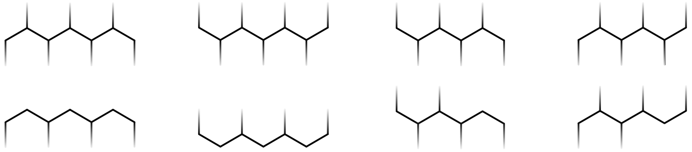


Figure 4. Two equivalence classes of the Θ^* relation, $\{e_1, e_2, e_3, e_4\}$ and $\{b_1, b_2, b_3, b_4\}$, demonstrate that for benzenoids with an inner perimeter (here, a fenestrene) the Θ^* equivalence classes might or might not coincide with the interfaces defined in the current work.

We believe that it can be possible to define the notions of fragments and interfaces in a more formal way using the theory of elementary cuts [34, 41, 58, 59, 72, 81] and employing the equivalence classes of the Θ^* relation [35, 68, 77]. Such a task seems rather straightforward for the benzenoid shown in Fig. 2 (we thank the referees for bringing it to our attention), but for benzenoids with holes certain problems must be resolved first. To explicate the problems, let us recapitulate the relevant definitions. An elementary cut of $\boldsymbol{B}$ is a straight line segment, passing through the centers of some edges of $\boldsymbol{B}$, being orthogonal to these edges, and intersecting the perimeter of $\boldsymbol{B}$ exactly twice. However, often in our considerations we are forced to consider partition lines cutting through holes inside benzenoids, i.e., cuts that intersect the—outer or inner—perimeter(s) of $\boldsymbol{B}$ more than twice, and such a partition line does not conform to any of the definitions of an elementary cut that we could find in the literature. It should be possible to introduce a new definition of an elementary cut that will be applicable also to such a situation; this task is not attempted here because of the other, more serious problem. Assuming that a suitable definition of an elementary cut has been introduced, we could define an interface i_k as an equivalence class of the Θ^* relation induced by elementary cuts in one direction, where Θ^* is the transitive closure of the Djoković-Winkler relation Θ relation defined as follows. Two edges $e_1 = u_1w_1$ and $e_2 = u_2w_2$ of the graph $\boldsymbol{B}$ are in the Θ relation, $e_1 \Theta e_2$, if $d_{\boldsymbol{B}}(u_1, u_2) + d_{\boldsymbol{B}}(w_1, w_2) \neq d_{\boldsymbol{B}}(w_1, u_2) + d_{\boldsymbol{B}}(u_1, w_2)$, where the distance $d_{\boldsymbol{B}}(u_1, u_2)$ between the vertices u_1 and u_2 is the number of edges on the shortest u_1,u_2-path. Consider now the fenestrene [25] shown in Fig. 4. Some of the Θ^* equivalence classes, for example $\{e_1, e_2, e_3, e_4\}$, coincide with interfaces of this structure. However, other Θ^* equivalence classes, for example $\{b_1, b_2, b_3, b_4\}$, contain interface bonds belonging to multiple interfaces. This example shows that the interface theory of benzenoids constructed in the current work cannot be currently expressed in a general case by the existing theory of elementary cuts and the equivalence classes of the Θ^* relation, but we would not be surprised if such a generalization is discovered in the future.

An atom v can have two possible orientations. If its interface bond points up and its spine bonds point down (e.g., ˪, ⅄, ˩), v is called an *upper atom.* Otherwise (e.g., ᒥ, Y, ᒣ), it is called a *lower atom.* Based on this classification, each fragment can be assigned to one of four shapes depicted schematically in Fig. 5.



shape `W` shape `N` shape `R` shape `L`

Figure 5. Fragments can have four possible shapes, `W` (wide), `N` (narrow), `R` (right), or `L` (left). Note that, for the shape assignment, it is entirely irrelevant whether or not all interface bonds are present.

Definition 1. The function *shape* of a fragment f with m atoms is defined as follows

$$\operatorname{shape}(f) = \begin{cases} \texttt{W} \quad \text{(wide)} & \text{if } v_1 \text{ is a lower atom,} \quad \text{and } v_m \text{ is a lower atom.} \\ \texttt{N} \quad \text{(narrow)} & \text{if } v_1 \text{ is an upper atom,} \quad \text{and } v_m \text{ is an upper atom.} \\ \texttt{R} \quad \text{(right)} & \text{if } v_1 \text{ is an upper atom,} \quad \text{and } v_m \text{ is a lower atom.} \\ \texttt{L} \quad \text{(left)} & \text{if } v_1 \text{ is a lower atom,} \quad \text{and } v_m \text{ is an upper atom.} \end{cases}$$

Equivalently, we can say that the shape of a fragment with m atoms is

$$\begin{array}{lcll} \texttt{W} & \text{(wide)} & \text{if } m \text{ is odd,} & \text{and the upper atoms } v_j \text{ have even indices } j. \\ \texttt{N} & \text{(narrow)} & \text{if } m \text{ is odd,} & \text{and the upper atoms } v_j \text{ have odd indices } j. \\ \texttt{R} & \text{(right)} & \text{if } m \text{ is even,} & \text{and the upper atoms } v_j \text{ have odd indices } j. \\ \texttt{L} & \text{(left)} & \text{if } m \text{ is even,} & \text{and the upper atoms } v_j \text{ have even indices } j. \end{array}$$

Following this classification, we can easily find that in the benzenoid $\boldsymbol{B}$ depicted in Fig. 2, f_1 and f_2 have shape `W`, f_3 and f_5 have shape `N`, and f_4 has shape `R`.

Remark 2. Fragment shapes can be used to uniquely specify the structure of regular benzenoid strips, i.e. merged rows of hexagons where two adjacent rows differ at each end by $\pm\frac{1}{2}$ hexagon unit [31, 36, 78]. For example, $[\texttt{W}, \texttt{W}, \texttt{N}, \texttt{R}, \texttt{N}]$ with $n = 3$ hexagons in the first row denotes the benzenoid $\boldsymbol{B}$ given in Fig. 2, $[\texttt{W}, \texttt{R}, \texttt{R}, \texttt{N}]$ with $n = 3$ denotes the parallelogram $\boldsymbol{M}(3,3)$ , and $[\texttt{W}, \texttt{L}, \texttt{R}, \texttt{N}]$ with $n = 2$ denotes the chevron $\boldsymbol{Ch}(2,2,2)$ .

An attentive reader might further notice that the number of occurrences of `W`-shaped fragments is identical to the number of `N`-shaped fragments in all of these examples. This is, in fact, not a coincidence, but, as we will soon see, one of the requirements for a benzenoid structure $\boldsymbol{B}$ to be Kekuléan.

Definition 3. Let b be a bond in $\boldsymbol{B}$ and let $\boldsymbol{C}$ denote some Clar cover of $\boldsymbol{B}$. The *covering order* of the bond b, $\text{ord}_{\boldsymbol{C}}(b)$, in the Clar cover $\boldsymbol{C}$ is a number assigned as follows:

$$\text{ord}_{\boldsymbol{C}}(b) = \begin{cases} 1 & \text{if } b \text{ is a double bond} \\ 1/2 & \text{if } b \text{ is an aromatic bond} \\ 0 & \text{if } b \text{ is a single bond} \end{cases}$$

Alternatively, we can say that

$$\text{ord}_{\boldsymbol{C}}(b) = \begin{cases} 1 & \text{if } b \in E\left(K_2\right), K_2 \subset \boldsymbol{C} \\ 1/2 & \text{if } b \in E\left(C_6\right), C_6 \subset \boldsymbol{C} \\ 0 & \text{otherwise} \end{cases}$$

From now on, the bond covering orders will be referred to as bond orders and a shorthand notation $\text{ord}(b) \equiv \text{ord}_{\boldsymbol{C}}(b)$ will be used for the bond covering orders as long as the underlying Clar cover $\boldsymbol{C}$ is clear from the context. A bond b is said to be *covered* if $\text{ord}(b) > 0$.

Definition 4. Let v be an atom in $\boldsymbol{B}$ and let $b_1, \ldots, b_n$ be all the bonds connected to v in some Clar cover $\boldsymbol{C}$ of $\boldsymbol{B}$. The *covering order* of the atom v, $\text{ord}_{\boldsymbol{C}}(v)$, in the Clar cover $\boldsymbol{C}$ is defined as

$$\text{ord}_{\boldsymbol{C}}(v) = \text{ord}_{\boldsymbol{C}}(b_1) + \ldots + \text{ord}_{\boldsymbol{C}}(b_n).$$

Lemma 5. *Since for a given Clar cover* $\boldsymbol{C}$ *of* $\boldsymbol{B}$*, every vertex* v *is matched (i.e.,* $v \in V\left(K_2\right), K_2 \subset \boldsymbol{C}$ *or* $v \in V\left(C_6\right), C_6 \subset \boldsymbol{C}$ *), the atom covering order* $ord(v) \equiv ord_{\boldsymbol{C}}(v)$ *is constant and independent of* $\boldsymbol{C}$*:*

$$ord(v) = \left\{ \begin{array}{c} 1 \;+\; 0 \;+ 0 \\ 1/2 + 1/2 + 0 \end{array} \right\} = 1. \tag{3}$$

Proof. A graphical justification of this fact, up to a rotation, is given in Fig. 6. Formal proof relies on the observation that the Clar cover $\boldsymbol{C}$ is a perfect matching of $\boldsymbol{B}$ and every vertex of $\boldsymbol{B}$ is matched exactly once, either belonging to one K_2 component of $\boldsymbol{C}$ or to one C_6 component of $\boldsymbol{C}$. In the first situation, one of the edges incident to v has order 1 and all others have order 0, therefore their sum is 1. In the second situation, two of the edges incident to v have order $1/2$ and all others have order 0, thus their sum is also 1. ■

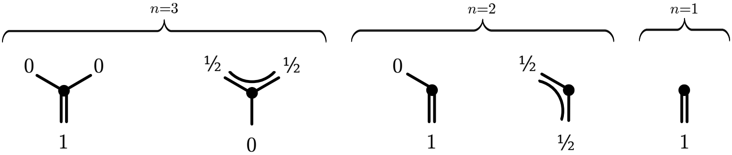


Figure 6. Possible bonding situations for an atom in a Clar cover. The number n denotes the number of bonds connected to C, and the numbers 0, $1/2$ and 1 denote the covering order of each bond.

Definition 6. Let i be an interface consisting of the bonds b_1, …, b_n. The *interface order* $\mathrm{ord}_{\boldsymbol{C}}(i)$ of the interface i is defined as

$$\mathrm{ord}_{\boldsymbol{C}}(i) = \mathrm{ord}_{\boldsymbol{C}}(b_1) + \ldots + \mathrm{ord}_{\boldsymbol{C}}(b_n).$$

The order of an empty interface (such as the upper interface i_0 of f_1) is obviously zero. In the following, we will often resort to a shorthand notation $\mathrm{ord}(i) \equiv \mathrm{ord}_{\boldsymbol{C}}(i)$ as long as the underlying Clar cover $\boldsymbol{C}$ is clear from the context. The orders of spine bonds are of secondary importance for the development of interface theory thanks to Lemma 8.

Lemma 7. *Let C be a Clar cover of a benzenoid $\boldsymbol{B}$. Consider a fragment f of $\boldsymbol{B}$ together with its upper interface i_{upper} and its lower interface i_{lower}. Then*

$$\sum_{e_j \in i_{upper}} (1 - \mathit{ord}(e_j)) = \sum_{e_j \in i_{lower}} (1 - \mathit{ord}(e_j)) \tag{4}$$

Proof. The fragment f consists of atoms $v_1, \ldots, v_m$, interface bonds $e_1, \ldots, e_m$, and spine bonds $s_1, \ldots, s_{m-1}$. By applying Lemma 5 to each atom v_j in f, we find the system of equations:

$$\begin{array}{rrcrcrcll} \text{Atom } v_1: & & & \mathrm{ord}(e_1) & + & \mathrm{ord}(s_1) & = & 1, & \\ \text{Atom } v_j: & \mathrm{ord}(s_{j-1}) & + & \mathrm{ord}(e_j) & + & \mathrm{ord}(s_j) & = & 1 & \text{for } 1 < j < m, \\ \text{Atom } v_m: & \mathrm{ord}(s_{m-1}) & + & \mathrm{ord}(e_m) & & & = & 1. & \end{array} \tag{5}$$

Multiplying these equations by a weight $(-1)^j$ and summing them together eliminates the orders of spine bonds and produces

$$\sum_{j=1}^{m} (-1)^j \mathrm{ord}(e_j) = \sum_{j=1}^{m} (-1)^j.$$

Regrouping of these terms results in Eq. (4), where i_{upper} consists of e_j with odd indices and i_{lower} consists of e_j with even indices, or *vice versa.* ■

Lemma 8. *The orders of the spine bonds in a Clar cover* $\boldsymbol{C}$ *of a benzenoid* $\boldsymbol{B}$ *are uniquely determined by the orders of the interface bonds.*

Proof. Consider a fragment f of $\boldsymbol{B}$ consisting of atoms $v_1, \ldots, v_m$, interface bonds $e_1, \ldots,$ e_m, and spine bonds $s_1, \ldots, s_{m-1}$. For a given Clar cover $\boldsymbol{C}$, the interface bond orders $\operatorname{ord}(e_1), \ldots, \operatorname{ord}(e_m)$ are by assumption all known. (Whenever an interface bond e_j is missing, $\operatorname{ord}(e_j)$ is taken to be zero.) The spine bond orders $\operatorname{ord}(s_1), \ldots, \operatorname{ord}(s_{m-1})$ can be determined from Eqs. (5), which are an overdetermined system of m linear equations for $m-1$ unknown variables $\operatorname{ord}(s_j)$. For $1 \leq j < m$, Eqs. (5) have a unique solution

$$\begin{aligned}
\operatorname{ord}(s_j) &= \sum_{i=1}^{j} (-1)^{(i+j)} (1 - \operatorname{ord}(e_i)) &(6)\\
&= -\sum_{i=j+1}^{m} (-1)^{(i+j)} (1 - \operatorname{ord}(e_i)) &(7)
\end{aligned}$$

provided that

$$\sum_{j=1}^{m} (-1)^{j} (1 - \operatorname{ord}(e_j)) = 0. \tag{8}$$

But now by assumption $\boldsymbol{C}$ is a Clar cover and Eq. (8) is satisfied by Lemma 7. ■

Remark 9. It is obvious from Lemma 7 that a Clar cover $\boldsymbol{C}$ of a given benzenoid $\boldsymbol{B}$ is uniquely and fully determined by its interface bond orders.

Remark 10. Note that a complete set of interface bond orders for a given benzenoid $\boldsymbol{B}$ can only correspond to a Clar cover of $\boldsymbol{B}$ if it satisfies the necessary (but not sufficient) conditions given by Lemma 7 for every fragment f_k of $\boldsymbol{B}$. Sufficient conditions will be derived later.

3.2 First rule of interface theory

Theorem 11. (First rule of interface theory: interface order criterion) *Let* $\boldsymbol{C}$ *be some Clar cover of a benzenoid* $\boldsymbol{B}$*. Let* f_k *be a fragment of* $\boldsymbol{B}$*, and let* i_{k-1} *and* i_k *be the upper and lower interfaces of* f_k*, respectively. The following conditions are always satisfied.*

(*a*) *If* f_k *has the shape* `W`*, then* $\operatorname{ord}(i_k) = \operatorname{ord}(i_{k-1}) + 1$.

(*b*) *If* f_k *has the shape* $\mathtt{N}$, *then* $\mathrm{ord}(i_k) = \mathrm{ord}(i_{k-1}) - 1$.

(*c*) *If* f_k *has the shape* $\mathtt{R}$ *or* $\mathtt{L}$, *then* $\mathrm{ord}(i_k) = \mathrm{ord}(i_{k-1})$.

Proof. Eq. (4) can be rewritten in the following form.

$$\sum_{j \text{ odd}} \mathrm{ord}(e_j) - \sum_{j \text{ even}} \mathrm{ord}(e_j) \quad = \quad -\sum_{i=1}^{m} (-1)^i = \begin{cases} 0 & \text{if } m \text{ is even} \\ 1 & \text{if } m \text{ is odd} \end{cases} \tag{9}$$

Note now that the bonds e_j with even j form either the upper (for $\mathrm{shape}(f_k) = \mathtt{R}$ or $\mathtt{N}$) or the lower (for $\mathrm{shape}(f_k) = \mathtt{L}$ or $\mathtt{W}$) interface of f_k. Similarly, the bonds e_j with odd j form either the upper (for $\mathrm{shape}(f_k) = \mathtt{L}$ or $\mathtt{W}$) or the lower (for $\mathrm{shape}(f_k) = \mathtt{R}$ or $\mathtt{N}$) interface of f_k. Therefore, by Definition 6,

$$\begin{aligned} \sum_{j \text{ even}} \mathrm{ord}(e_j) \quad &= \quad \begin{cases} \mathrm{ord}(i_{k-1}) & \text{if shape}(f_k) = \mathtt{L} \text{ or } \mathtt{W}, \\ \mathrm{ord}(i_k) & \text{if shape}(f_k) = \mathtt{R} \text{ or } \mathtt{N}, \end{cases} \\ \sum_{j \text{ odd}} \mathrm{ord}(e_j) \quad &= \quad \begin{cases} \mathrm{ord}(i_{k-1}) & \text{if shape}(f_k) = \mathtt{R} \text{ or } \mathtt{N}, \\ \mathrm{ord}(i_k) & \text{if shape}(f_k) = \mathtt{L} \text{ or } \mathtt{W}. \end{cases} \end{aligned}$$

In either case, Eq. (9) can be rewritten as

$$\mathrm{ord}(i_k) - \mathrm{ord}(i_{k-1}) = \begin{cases} 0 & \text{if } m \text{ is even, i.e. if shape}(f_k) = \mathtt{R} \text{ or } \mathtt{L}, \\ 1 & \text{if } m \text{ is odd and shape}(f_k) = \mathtt{W}, \\ -1 & \text{if } m \text{ is odd and shape}(f_k) = \mathtt{N}. \end{cases}$$

■

Corollary 12. *If the conditions given by Theorem 11 are satisfied, then so is Eq. (8); i.e., the system of equations (5) can be solved for the spine bond orders.*

Remark 13. The orders of spine bonds obtained in Corollary 12 may be ill-defined, in the sense that Eq. (6) predicts spine bond orders other than 0, 1/2 or 1. Therefore, Theorem 11 provides us with a necessary condition for admissible values of interface and spine bonds, but this condition is not sufficient. We will see soon that a sufficient condition will be provided by Theorem 16.

Example 14. Theorem 11 provides an easy tool for predicting the number of double bonds or aromatic rings in each interface. Applying the theorem to the benzenoid $\boldsymbol{B}$ originally introduced in Fig. 2 produces the interface orders shown in Fig. 7, which can be computed as follows:

- The interface i_0 does not contain any bonds, and therefore, by Def. 6, its order must be $\mathrm{ord}(i_0) = 0$.

- The fragment f_1 has shape $\mathtt{W}$, therefore $\mathrm{ord}(i_1) = \mathrm{ord}(i_0) + 1 = 1$. This signifies that interface i_1 contains either one double bond or one aromatic ring.

- The fragment f_2 has shape $\mathtt{W}$, therefore $\mathrm{ord}(i_2) = \mathrm{ord}(i_1) + 1 = 2$. This signifies that interface i_2 contains either two double bonds, or two aromatic rings, or exactly one of each.

- The fragment f_3 has shape $\mathtt{N}$, therefore $\mathrm{ord}(i_3) = \mathrm{ord}(i_2) - 1 = 1$.

- The fragment f_4 has shape $\mathtt{R}$, therefore $\mathrm{ord}(i_4) = \mathrm{ord}(i_3) = 1$.

- The fragment f_5 has shape $\mathtt{N}$, therefore $\mathrm{ord}(i_5) = \mathrm{ord}(i_4) - 1 = 0$, which agrees with the fact that the interface i_5 is empty.

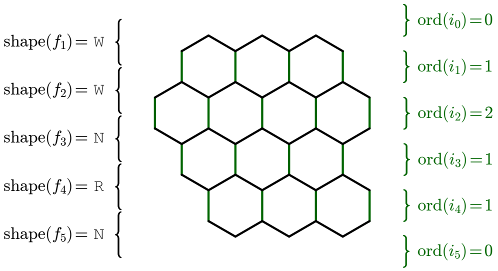


Figure 7. Interface orders of the benzenoid $\boldsymbol{B}$ from Fig. 1, as computed in Example 14.

Example 15. Another immediate result following from Theorem 11 is an upper bound for the Clar number of $\boldsymbol{B}$. The maximum number of aromatic rings that can be placed in each row of $\boldsymbol{B}$ is given by the interface order, therefore summation over all interface orders shows that

$$Cl(\boldsymbol{B}) \leq \sum_k \mathrm{ord}(i_k) = 5.$$

For the structure in Fig. 7, the upper bound is achieved, as can be seen from Fig. 1 (c) as well as from the ZZ polynomial of this structure

$$\mathrm{ZZ}(\boldsymbol{B}, x) = x^5 + 19x^4 + 112x^3 + 280x^2 + 310x + 125. \tag{10}$$

However, it is not difficult to find a benzenoid for which the upper bound is not realized. More examples based on the application of Theorem 11, concerning upper limits for the Clar number, identification of certain non-Kekuléan and essentially disconnected benzenoids, and the form of ZZ polynomials for some special benzenoid structures is given in the sequel to this paper [64].

3.3 Second rule of interface theory

While the interface order criterion (Theorem 11) serves as a convenient tool for a number of purposes, it is not yet sufficient for providing answers to all the relevant questions. For example, it would be useful to have a method of finding the exact value of the Clar number instead of an upper bound, or to prove definitively whether or not a benzenoid is Kekuléan. For such tasks, a more detailed understanding of fragments and interfaces is necessary, which is provided by the following theorem specifying relative positions of covered interface bonds (i.e., interface bonds e_i for which $\mathrm{ord}(e_i) > 0$) within each interface of some Clar cover $\boldsymbol{C}$.

Theorem 16. (Second rule of interface theory: Relative location of covered bonds) *Consider a benzenoid* $\boldsymbol{B}$ *and its Clar cover* $\boldsymbol{C}$*. Further, consider a fragment* f_k *of* $\boldsymbol{B}$ *with* m *atoms. The covered interface bonds of* $\boldsymbol{C}$ *belonging to* f_k *are distributed as follows.*

(*a*) *The first covered interface bond* e_j *occurs for odd* j*.*

(*b*) *The last covered interface bond* e_j *occurs for even* $m-j$*.*

(*c*) *If* e_j *and* $e_{j'}$ $(j' > j)$ *are two consecutive covered interface bonds, then either*

  (c') $j'-j$ *is odd (which signifies that one of the pair* $(e_j, e_{j'})$ *belongs to the upper interface, and the other one to the lower interface), or*

  (c'') $j'-j=2$ *and* e_j *and* $e_{j'}$ *are part of the same aromatic ring* $(e_j, e_{j'} \in E\,(C_6))$ *located in the same—upper or lower—interface.*

Proof. Since by assumption the interface bonds in question correspond to some Clar cover $\boldsymbol{C}$, the necessary condition given by Eq. (4) must be satisfied. For such a set of interface bonds, the orders of the spine bonds are given by Eq. (6). We show below that violating any of the rules (a)–(c) results in a spine bond being assigned an order other than 0, 1/2 or 1, which cannot happen in a well-defined Clar cover.

(a) Assume e_j is the first covered interface bond. If $j = 1$, the statement (a) is obviously true. Assume therefore that $j > 1$, which gives $\operatorname{ord}(e_j) > 0$ and $\operatorname{ord}(e_i) = 0$ for all $i < j$. Using Eq. (6) to compute the order of the spine bond s_{j-1} results in

$$\operatorname{ord}(s_{j-1}) = \begin{cases} 0 & \text{if } j \text{ is odd,} \\ 1 & \text{if } j \text{ is even.} \end{cases} \tag{11}$$

Consequently, applying Lemma 5 to the atom v_j gives the order of the spine bond s_j

$$\operatorname{ord}(s_j) = 1 - \operatorname{ord}(s_{j-1}) - \operatorname{ord}(e_j) < \begin{cases} 1 & \text{if } j \text{ is odd,} \\ 0 & \text{if } j \text{ is even.} \end{cases}$$

If condition (a) is violated, meaning that j is even, then the bond order $\operatorname{ord}(s_j)$ is smaller than 0, which is ill-defined.

(b) The same reasoning applies to the last covered interface bond e_j. If $j = m$, the statement (b) is obviously true. Assume therefore that $j < m$, which gives $\operatorname{ord}(e_j) > 0$ and $\operatorname{ord}(e_i) = 0$ for all $i > j$. Using Eq. (7) to compute the order of the spine bond s_j results in

$$\operatorname{ord}(s_j) = \begin{cases} 1 & \text{if } m - j \text{ is odd,} \\ 0 & \text{if } m - j \text{ is even.} \end{cases} \tag{12}$$

Consequently, applying Lemma 5 to the atom v_j gives he order of the spine bond s_{j-1}

$$\operatorname{ord}(s_{j-1}) = 1 - \operatorname{ord}(e_j) - \operatorname{ord}(s_j) < \begin{cases} 0 & \text{if } m - j \text{ is odd,} \\ 1 & \text{if } m - j \text{ is even.} \end{cases}$$

If condition (b) is violated, meaning that $m - j$ is odd, then the bond order $\operatorname{ord}(s_{j-1})$ is smaller than 0, which is ill-defined.

(c) Let e_j and $e_{j'}$ be two consecutive covered interface bonds. Then, for $j < i < j'$, we have $\operatorname{ord}(e_i) = 0$, and Eq. (8) can be rewritten in the following form.

$$\begin{aligned}
0 &= \sum_{i=1}^{m}(-1)^i\,(1-\operatorname{ord}(e_i)) \\
&= \underbrace{\sum_{i=1}^{j}(-1)^i\,(1-\operatorname{ord}(e_i))}_{(-1)^j\operatorname{ord}(s_j)\text{ by Eq. (6)}} + \sum_{i=j+1}^{j'-1}(-1)^i(1-\underbrace{\operatorname{ord}(e_i)}_{0}) + \underbrace{\sum_{i=j'}^{m}(-1)^i\,(1-\operatorname{ord}(e_i))}_{(-1)^{j'}\operatorname{ord}(s_{j'})\text{ by Eq. (7)}} \\
&= \begin{cases} \operatorname{ord}(s_j) - 0 - \operatorname{ord}(s_{j'-1}) & \text{if } j'-j \text{ is odd,} \\ (-1)^j\left(\operatorname{ord}(s_j) - 1 + \operatorname{ord}(s_{j'-1})\right) & \text{if } j'-j \text{ is even.} \end{cases}
\end{aligned}$$

If $j' - j$ is odd, then e_j and $e_{j'}$ belong to different interfaces, and the claim is demonstrated. Assume now that $j' - j$ is even, i.e.

$$\operatorname{ord}(s_j) + \operatorname{ord}(s_{j'-1}) = 1. \tag{13}$$

Since $\operatorname{ord}(e_j) > 0$ and $\operatorname{ord}(e_{j'}) > 0$, it follows from Lemma 5 that $\operatorname{ord}(s_j) < 1$ and $\operatorname{ord}(s_{j'-1}) < 1$, which leaves only one possible solution of Eq. (13) given by $\operatorname{ord}(s_j) = \operatorname{ord}(s_{j'-1}) = 1/2$. Consecutive application of Lemma 5 for the values $i = j+1, \ldots, j'-1$ shows that also $\operatorname{ord}(s_j) = \operatorname{ord}(s_{j+1}) = \ldots = \operatorname{ord}(s_{j'-2}) = \operatorname{ord}(s_{j'-1}) = 1/2$. (A covering of this type for $j' - j = 10$ is displayed in Fig. 8.) Clearly, for $j' - j \neq 2$, this is a highly unconventional covering which is not considered in the standard theory of Clar covers, which use only K_2 and C_6 as the covering components. Therefore, even $j' - j$ makes sense only when $j' - j = 2$, which proves the claim. ■

Remark 17. Note that other even values of $j' - j$ correspond to generalized Clar covers [70] using covering components such as C_{10}, C_{14}, C_{18}, etc. In particular, the difference $j' - j = 4$, corresponding to C_{10}, was explicitly considered in an interesting paper by Žigert Pleteršek [90]. These possibilities are not further pursued in the current paper.

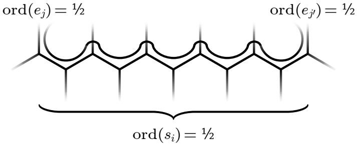


Figure 8. The framework of interface theory technically allows for generalized Clar covers with larger aromatic circuits [70,90], however in the present paper we consider only standard Clar covers with aromatic sextets, where $j' = j + 2$.

In order to simplify formulations, let us introduce a shorthand name for the first covered interface bond before/after a given bond e_j:

Definition 18. Let f_k be a a fragment of a benzenoid $\boldsymbol{B}$ with a Clar cover $\boldsymbol{C}$, and e_j an interface bond of f_k. The *left (right) neighbour (within f_k)* of e_j is the bond $e_{j'} \in f_k$ with $\operatorname{ord}(e_{j'}) > 0$ and $\operatorname{ord}(e_{j''}) = 0$ for all $j' < j'' < j$ (respectively, $j < j'' < j'$) . In the following, the fragment f_k within which the neighbours are determined is not explicitly stated if it is clear from context.

With this, Theorem 16 can be reformulated in a more geometrical way:

Corollary 19. *Consider a benzenoid $\boldsymbol{B}$ and its Clar cover $\boldsymbol{C}$. Further, consider a fragment f_k of $\boldsymbol{B}$ with m atoms. The covered interface bonds of $\boldsymbol{C}$ belonging to f_k are distributed as follows.*

(*a*) *The first covered interface bond occurs in the upper (lower) interface of f_k exactly if the first atom v_1 is an upper (lower) atom.*

(*b*) *The last covered interface bond occurs in the upper (lower) interface of f_k exactly if the last atom v_m is an upper (lower) atom.*

(c') *If e_j is a double bond in the upper (lower) interface of f_k, then all neighbours of e_j belong to the lower (upper) interface.*

(c'') *If (e_j, e_{j+2}) is a pair of aromatic bonds in the upper (lower) interface of f_k, then the left neighbour of e_j and the right neighbour of e_{j+2} (if any) belong to the lower (upper) interface of f_k.*

Example 20. Let f be a fragment of a benzenoid $\boldsymbol{B}$ with a Kekulé structure $\boldsymbol{K}$. Assume that f has a total of five double interface bonds, and that its first atom v_1 is an upper atom. Then the double interface bonds, from left to right, will belong to the upper, lower, upper, lower, and upper interface, as for example shown in Fig. 9.

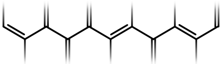


Figure 9. A possible distribution of five double interface bonds on a fragment of shape `N`.

3.4 Third rule of interface theory

In the previous two subsections we have derived two important necessary conditions, given by Theorems 11 and 16, that need to be satisfied by the covering characters of the interface bonds within a Clar cover. Theorem 21 gives a sufficient condition for a collection of interface bond coverings to define a Clar cover. Later, this theorem is reformulated in a more transparent way as a recipe (Algorithm 1 on page 24) for practical construction of Clar covers.

Theorem 21. (Third rule of interface theory: Construction of Clar covers) *Assume that covering orders for all interface bonds in a benzenoid* $\boldsymbol{B}$ *have been assigned in such a way that:*

(a) *The set of aromatic interface bonds can be written as a union of disjoint pairs* (e_j, e_{j+2})*. Moreover, for each pair* (e_j, e_{j+2}) *the condition* $ord(e_{j+1}) = 0$ *needs to be satisfied.*

(b) *The orders of the interfaces satisfy the conditions* (a)*,* (b) *and* (c) *of Theorem 11.*

(c) *The orders of the interface bonds satisfy the conditions* (a) *and* (b) *of Theorem 16.*

(d) *If* e_j *and* $e_{j'}$ $(j' > j)$ *are two consecutive covered interface bonds, then either*

- $j' - j$ *is odd, or*
- $j' - j = 2$ *and* $(e_j, e_{j'})$ *is one of the pairs of aromatic bonds specified in* (a)*.*

Then, there is exactly one Clar cover with the specified interface bonds.

In order to simplify the proof of Theorem 21, we first prove the following technical lemma.

Lemma 22. *Consider a fragment* f_k *of* $\boldsymbol{B}$ *with interface covering orders assigned in agreement with Theorem 21 and one of its interface bonds* e_j*. Then, the quantity*

$$O_j := \sum_{i=1}^{j} (-1)^i \, ord(e_i)$$

takes the following values:

(a) *If* e_j *is a double bond, then* $O_j = \begin{cases} 0 & \textit{if } j \textit{ is even,} \\ -1 & \textit{if } j \textit{ is odd.} \end{cases}$

(b) *If* e_j *is the second bond in a pair of aromatic bonds, then* $O_j = \begin{cases} 0 & \textit{if } j \textit{ is even,} \\ -1 & \textit{if } j \textit{ is odd.} \end{cases}$

(c) *If* e_j *is the first bond in a pair of aromatic bonds, then* $O_j = -1/2$.

(d) *If* e_j *is a single bond which has no left neighbour, then* $O_j = 0$.

(e) *If* e_j *is a single bond with a left neighbour* $e_{j'}$*, then* $O_j = O_{j'}$.

Proof. Note that, according to the condition (a) of Theorem 21, aromatic bonds always appear in distinct pairs, therefore statements (b) and (c) are well-defined. Furthermore, whenever (e_j, e_{j+2}) is a pair of aromatic bonds, condition (a) of Theorem 21 ensures that e_{j+1} is a single bond. This fact will be implicitly used in the following considerations.

Statements (d) and (e) are obvious from Definition 18 of a left neighbour: If e_j is a single bond and has no left neighbour, then all interface bonds e_i with $i \leq j$ are single bonds, meaning that $\mathrm{ord}(e_i) = 0$. Consequently,

$$O_j = \sum_{i=1}^{j} (-1)^i \underbrace{\mathrm{ord}(e_i)}_{0} = 0.$$

If e_j is a single bond with a left neighbour $e_{j'}$, then all interface bonds e_i with $j' < i \leq j$ are single bonds, meaning that $\mathrm{ord}(e_i) = 0$. Consequently,

$$O_j = \underbrace{\sum_{i=1}^{j'} (-1)^i \mathrm{ord}(e_i)}_{O_{j'}} + \sum_{i=j'+1}^{j} (-1)^i \underbrace{\mathrm{ord}(e_i)}_{0} = O_{j'}.$$

The statements (a) and (b) can be shown by induction with respect to the consecutive members of the sequence $(e_{j_1}, e_{j_2}, ..., e_{j_N})$, where $N = \mathrm{ord}(i_{k-1}) + \mathrm{ord}(i_k)$ is the total number of double bonds and aromatic pairs in the interfaces i_{k-1} and i_k of the fragment f_k, and every element e_{j_n} of the sequence denotes either a double interface bond or the second member of a pair of aromatic interface bonds.

Base case:

If the first sequence element e_{j_1} is a double bond, it is clear that for $0 < i < j_1$, every interface bond e_i is a single bond, meaning that $\mathrm{ord}(e_i) = 0$. In this case, the value of O_{j_1}

can be determined as

$$O_{j_1} = \sum_{i=1}^{j_1-1} (-1)^i \underbrace{\operatorname{ord}(e_i)}_{0} + (-1)^{j_1} \underbrace{\operatorname{ord}(e_{j_1})}_{1} = (-1)^{j_1}.$$

If the first sequence element e_{j_1} is an aromatic bond, we know from the definition of the sequence that e_{j_1} is the second member of a pair (e_{j_1-2}, e_{j_1}), which implies that $\operatorname{ord}(e_{j_1-2}) = \operatorname{ord}(e_{j_1}) = 1/2$ and $\operatorname{ord}(e_{j_1-1}) = 0$. It is clear that for $0 < i < j_1 - 2$, every interface bond e_i is a single bond, meaning that $\operatorname{ord}(e_i) = 0$. Therefore, in this case, the value of O_{j_1} can be determined as

$$\begin{aligned} O_{j_1} &= \sum_{i=1}^{j_1-3} (-1)^i \underbrace{\operatorname{ord}(e_i)}_{0} + (-1)^{j_1-2} \underbrace{\operatorname{ord}(e_{j_1-2})}_{1/2} + (-1)^{j_1-1} \underbrace{\operatorname{ord}(e_{j_1-1})}_{0} + (-1)^{j_1} \underbrace{\operatorname{ord}(e_{j_1})}_{1/2} \\ &= (-1)^{j_1} \cdot (1/2 + 1/2) = (-1)^{j_1}. \end{aligned}$$

Theorem 21 ensures that condition (a) of Theorem 16 is satisfied, i.e. that j_1 is odd. Therefore, in either case, $O_{j_1} = (-1)^{j_1} = -1$. In other words, statements (a) and (b) hold for e_{j_1}.

Step case:

Consider now a sequence element e_{j_n} with $n > 1$ and assume that statements (a) and (b) hold for $e_{j_{n-1}}$. If e_{j_n} is a double bond, then its left neighbour is $e_{j_{n-1}}$, which means that all interface bonds e_i with $j_{n-1} < i < j_n$ are single bonds, i.e. $\operatorname{ord}(e_i) = 0$. Therefore, in this case, the value of O_{j_n} can be determined as

$$O_{j_n} = \underbrace{\sum_{i=1}^{j_{n-1}} (-1)^i \operatorname{ord}(e_i)}_{O_{j_{n-1}}} + \sum_{i=j_{n-1}+1}^{j_n-1} (-1)^i \underbrace{\operatorname{ord}(e_i)}_{0} + (-1)^{j_n} \underbrace{\operatorname{ord}(e_{j_n})}_{1} = O_{j_{n-1}} + (-1)^{j_n}.$$

If the sequence element e_{j_n} is an aromatic bond, we know from the definition of the sequence that e_{j_n} is the second member of a pair (e_{j_n-2}, e_{j_n}), which implies that $\operatorname{ord}(e_{j_n-2}) = \operatorname{ord}(e_{j_n}) = 1/2$ and $\operatorname{ord}(e_{j_n-1}) = 0$. The left neighbour of e_{j_n-2} is $e_{j_{n-1}}$, which means that all interface bonds e_i with $j_{n-1} < i < j_n - 2$ are single bonds. Therefore, in this case, the value of O_{j_n} can be determined as

$$\begin{aligned} O_{j_n} &= \underbrace{\sum_{i=1}^{j_{n-1}}(-1)^i \mathrm{ord}(e_i)}_{O_{j_{n-1}}} + \sum_{i=j_{n-1}+1}^{j_n-3}(-1)^i \underbrace{\mathrm{ord}(e_i)}_{0} \\ &\quad +(-1)^{j_n-2}\underbrace{\mathrm{ord}(e_{j_n-2})}_{1/2} +(-1)^{j_n-1}\underbrace{\mathrm{ord}(e_{j_n-1})}_{0} +(-1)^{j_n}\underbrace{\mathrm{ord}(e_{j_n})}_{1/2} \\ &= O_{j_{n-1}} + (-1)^{j_n}\cdot(1/2+1/2) = O_{j_{n-1}} + (-1)^{j_n}. \end{aligned}$$

In either case, Theorem 21 ensures that condition (c) of Theorem 16 is satisfied, i.e., that $j_n - j_{n-1}$ is odd.

$$\begin{cases} \text{If } j_{n-1} \text{ is odd, } j_n \text{ is even and } O_{j_{n-1}} = -1. \quad \text{Thus, } O_{j_n} = \underbrace{O_{j_{n-1}}}_{-1} + \underbrace{(-1)^{j_n}}_{1} = 0. \\ \text{If } j_{n-1} \text{ is even, } j_n \text{ is odd and } O_{j_{n-1}} = 0. \quad \text{Thus, } O_{j_n} = \underbrace{O_{j_{n-1}}}_{0} + \underbrace{(-1)^{j_n}}_{-1} = -1. \end{cases}$$

Therefore, statements (a) and (b) hold also for e_{j_n}. By induction, this proves statements (a) and (b) for all relevant interface bonds in f_k.

Finally, statement (c) follows from statement (b): Consider a covered interface bond e_j which is the first bond in a pair of aromatic bonds (e_j, e_{j+2}). Noting that

$$O_j = O_{j+2} - (-1)^{j+2}\underbrace{\mathrm{ord}(e_{j+2})}_{1/2} - (-1)^{j+1}\underbrace{\mathrm{ord}(e_{j+1})}_{0} = O_{j+2} - (-1)^j \cdot 1/2,$$

we arrive at the following facts.

$$\begin{cases} \text{If } j \text{ is odd, then by } (b)\ O_{j+2} = -1. \quad \text{Thus, } O_j = \underbrace{O_{j+2}}_{-1} - \underbrace{(-1)^j}_{-1} \cdot 1/2 = -1/2. \\ \text{If } j \text{ is even, then by } (b)\ O_{j+2} = 0. \quad \text{Thus, } O_j = \underbrace{O_{j+2}}_{0} - \underbrace{(-1)^j}_{1} \cdot 1/2 = -1/2. \end{cases}$$

With this, all statements of the Lemma have been demonstrated. ■

Proof. (of Theorem 21) Two points need to be proved here. The first claim to be demonstrated is that a set of covered interface bonds satisfying the conditions (a)–(d) of Theorem 21 define a valid Clar cover. The second claim concerns uniqueness of such a Clar cover.

Existence: All the necessary and sufficient conditions that need to be satisfied in order that an assignment of interface and spine bond orders defines a valid Clar cover can be expressed in a short statement: Such an assignment should define a perfect covering of $\boldsymbol{B}$, i.e., each atom v in $\boldsymbol{B}$ should participate either in exactly one double bond K_2 or in exactly one aromatic ring C_6. In order to demonstrate this, we need to show first that an assignment of covering orders for all interface bonds in $\boldsymbol{B}$ satisfying the conditions of Theorem 21 defines uniquely a valid assignment of covering orders for all spine bonds in $\boldsymbol{B}$. Further, we need to demonstrate that these combined assignments of interface and spine bond orders define a perfect covering of $\boldsymbol{B}$, which in practice signifies that the covering order of every atom v is 1 and that the covering objects are either K_2 or C_6.

Consider any fragment f_k of $\boldsymbol{B}$. Since the interface orders satisfy the conditions (a), (b), and (c) of Theorem 11, according to Corollary 12 the spine bond orders are uniquely determined and given by Eq. (6). This ensures that every atom has order 1 as required by Lemma 5; it remains to be demonstrated that all spine bond orders are well-defined—i.e., have the value 0, $1/2$ or 1—and that aromatic bonds appear only within complete aromatic rings. Eq. (6) may be rewritten as

$$\begin{aligned} \mathrm{ord}(s_j) &= \underbrace{\sum_{i=1}^{j}(-1)^{(i+j)}}_{(1-(-1)^j)/2} - (-1)^j \underbrace{\sum_{i=1}^{j}(-1)^i \mathrm{ord}(e_i)}_{O_j} \\ &= \begin{cases} -O_j & \text{if } j \text{ is even,} \\ 1+O_j & \text{if } j \text{ is odd.} \end{cases} \end{aligned} \tag{14}$$

It was shown in Lemma 22 that O_j can only have the values 0, $-1/2$ or -1. Together with Eq. (14), it follows that the spine bond orders $\mathrm{ord}(s_j)$ can only take the values 0, $1/2$ or 1, and therefore are well-defined.

Let us now show that aromatic spine bonds appear inside a fragment only between a pair of two aromatic interface bonds. Consider an aromatic spine bond s_j. According to Eq. (14) it follows from $\mathrm{ord}(s_j) = 1/2$ that $O_j = -1/2$. Lemma 22 shows that this is possible only in two cases:

- If e_j is a covered interface bond, one of the cases (a), (b) or (c) of Lemma 22 must apply, out of which only case (c) results in $O_j = -1/2$. Thus, in this case, e_j must be the first bond in a pair of aromatic interface bonds (e_j, e_{j+2}).
- If e_j is a single interface bond, one of the cases (d) or (e) of Lemma 22 must apply, out of which only case (e) results in $O_j = -1/2$, provided that the left neighbour $e_{j'}$ of e_j satisfies $O_{j'} = -1/2$, i.e. is the first bond in a pair of aromatic interface bonds $(e_{j'}, e_{j'+2})$. Note now that, if $j = j' + 2$, then e_j would not be a single bond; and if

$j > j' + 2$, its left neighbour would not be $e_{j'}$. It directly follows that $j = j' + 1$, meaning that e_j is the single bond between a pair of aromatic bonds (e_{j-1}, e_{j+1}).

In either case, the spine bond s_j is located between a pair of aromatic bonds, (e_{j-1}, e_{j+1}) or (e_j, e_{j+2}).

Consider now on the other hand a pair of aromatic interface bonds (e_j, e_{j+2}) and the spine bonds s_j and s_{j+1} between e_j and e_{j+2}. It follows directly from Lemma 22 that $O_j = O_{j+1} = -1/2$ and consequently (because of Eq. (14)) that $\mathrm{ord}(s_j) = \mathrm{ord}(s_{j+1}) = 1/2$, i.e. the spine bonds between a pair of aromatic interface bonds must be aromatic. Note that this statement is true for spine bonds in both fragments flanking the interface in which the aromatic interface bonds (e_j, e_{j+2}) are located. The pair of aromatic spine bonds between e_j and e_{j+2} in each of these fragments together with the pair of the aromatic interface bonds (e_j, e_{j+2}) form an aromatic ring C_6.

We have shown that every pair of aromatic interface bonds induces an aromatic ring C_6, and that aromatic spine bonds can only appear within these rings. With this, we have completed the demonstration that an assignment of covering orders to all interface bonds satisfying the conditions (a)–(d) of Theorem 21 defines a valid Clar cover.

Uniqueness: By the assumption of Theorem 21, all interface bonds have been assigned a covering order; this assignment is obviously unique. According to Corollary 12, the spine bond orders are uniquely determined by the covering orders of the interface bonds. Thus, the Clar cover defined above is unique. ■

It is easy to see that the conditions of Theorem 21 are not only sufficient, but also necessary.

Corollary 23. *Consider a benzenoid* $\boldsymbol{B}$ *and its Clar cover* $\boldsymbol{C}$. *The interface bond orders of* $\boldsymbol{C}$ *satisfy the conditions of Theorem 21.*

Proof. Conditions (b) and (c) of Theorem 21 are satisfied because of Theorems 11 and 16. Take now an aromatic interface bond e_j, which belongs to some unique aromatic ring C_6 in $\boldsymbol{C}$ together with its partner aromatic interface bond $e_{j''}$ (with $j'' = j \pm 2$). This (equivalence) relation partitions the set of aromatic interface bonds into a union of disjoint pairs $(e_j, e_{j''})$; furthermore, any interface bond $e_{j'}$ (with, respectively, $j' = j \pm 1$) connected from the top or bottom to an aromatic ring must be a single bond in order to preserve the order of the carbon atoms. This shows that condition (a) of Theorem 21 is satisfied.

To demonstrate that condition (*d*) of Theorem 21 is satisfied, note that any Clar cover (including the Clar cover $\boldsymbol{C}$ considered here) must satisfy the condition (*c*) of Theorem 16 and that these two conditions are equivalent, as the (equivalence) relation mentioned above indicates. ■

Corollary 23 can be equivalently stated in the following way.

Corollary 24. *Any conceivable Clar cover of* $\boldsymbol{B}$ *can be constructed by assigning orders to the interface bonds in a way that satisfies the conditions of Theorem 21 and then assigning the spine bond orders using Eq. (14). If, on the other hand, it is not possible to assign interface bond orders in agreement with Theorem 21, then the benzenoid* $\boldsymbol{B}$ *is non-Kekuléan and has no Clar covers.*

Remark 25. It is quite interesting to observe that the covering characters of the spine bonds are governed by simple rules. Clearly, the spine bonds between any pair of aromatic interface bonds must be aromatic. All other spine bonds are single or double. All double spine bonds located between two consecutive covered interface bonds have the same orientation. Double spine bonds located on either side of a double interface bond (or a pair of aromatic interface bonds) have opposite orientations. These sequences of parallel double spine bonds are well visible in the example given in Fig. 10. This fact in simple geometric terms illustrates why double interface bonds (or pairs of aromatic interface bonds) must alternate between the upper and lower interfaces. Note for example that a double upper-interface bond determines the covering characters of all neighbouring spine bonds and forces all upper interface bonds to be single, until a covered interface bond appears in the lower interface.

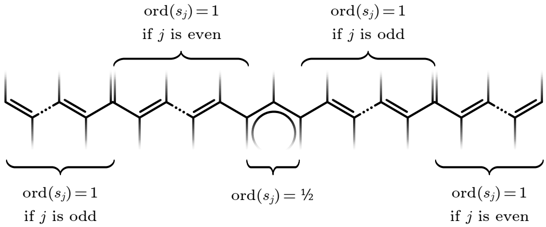


Figure 10. The distribution of the interface bonds in a fragment, which follows Theorem 21, uniquely determines covering orders of the spine bonds as indicated. Note the alternating character of the positions of the covered interface bonds as well as the orientation of the double spine bonds.

Algorithm 1: Construction of an arbitrary Clar cover for a Kekuléan benzenoid $\boldsymbol{B}$ is performed by assigning covering characters to interface bonds located in consecutive fragments. Progressively, for each consecutive fragment, a set of interface bond coverings is selected, which satisfies all the conditions of Theorem 21.

```
Data: Benzenoid $\boldsymbol{B}$ with fragments $f_1, \ldots, f_K$ and interfaces $i_0, \ldots, i_K$ consisting of bonds
        $i_k = \{e_j^k\}_{j=1}^{m_k}$.
Result: A Clar cover expressed via a set of bond covering orders $\mathrm{ord}(e_j^k)$ for all interface bonds.
$\mathrm{ord}(i_0) := 0$;                                  // Start from empty interface
for $k = 1, ..., K$ do                                     // Loop over interfaces
    switch shape($f_k$) do                                 // Determine ord($i_k$)
        case W do $\mathrm{ord}(i_k) := \mathrm{ord}(i_{k-1}) + 1$;
        case N do $\mathrm{ord}(i_k) := \mathrm{ord}(i_{k-1}) - 1$;
        otherwise do $\mathrm{ord}(i_k) := \mathrm{ord}(i_{k-1})$;
    end
    forall $e_j^k \in i_k$ do $\mathrm{ord}(e_j^k) := 0$;       // Initialize bond orders in $i_k$
    $n := 0$;                                              // Count covered interface bonds
    if shape($f_k$) = W or L then                          // First covered interface bond
        $n := n + 1$;
        either select bond $e_{j_1}^k \in i_k$ with no left neighbour;
            $\mathrm{ord}(e_{j_1}^k) := 1$;                       // Assign a double bond
        or select bonds $e_{j_1-2}^k, e_{j_1}^k \in i_k$ with no left neighbour;
            $\mathrm{ord}(e_{j_1-2}^k) := 1/2$;
            $\mathrm{ord}(e_{j_1}^k) := 1/2$;                     // Assign an aromatic pair
        end
    end
    while $n < \mathrm{ord}(i_k)$ do                       // Assign interface bonds
        $n := n + 1$;
        either select bond $e_{j_n}^k \in i_k$ with both neighbours in $i_{k-1}$
                and the neighbours not forming an aromatic pair;
            $\mathrm{ord}(e_{j_n}^k) := 1$;                       // Assign a double bond
        or select bonds $e_{j_n-2}^k, e_{j_n}^k \in i_k$ with both neighbours in $i_{k-1}$
                and $\mathrm{ord}(e_{j_n-1}^k) = 0$;
            $\mathrm{ord}(e_{j_n-2}^k) := 1/2$;
            $\mathrm{ord}(e_{j_n}^k) := 1/2$;                     // Assign an aromatic pair
        end
    end
    if shape($f_k$) = W or R then                          // Last covered interface bond
        $n := n + 1$;
        either select bond $e_{j_n}^k \in i_k$ with no right neighbour;
            $\mathrm{ord}(e_{j_n}^k) := 1$;                       // Assign a double bond
        or select bonds $e_{j_n}^k, e_{j_n+2}^k \in i_k$ with no right neighbour;
            $\mathrm{ord}(e_{j_n}^k) := 1/2$;
            $\mathrm{ord}(e_{j_n+2}^k) := 1/2$;                   // Assign an aromatic pair
        end
    end
end
```

3.5 Structures with holes

As so far, we have restricted our considerations to benzenoids without holes, i.e., to benzenoids without missing spine bonds. With this in mind, Theorems 7, 11 and 16 have been formulated for fragments in which all spine bonds exist. Note that all these theorems remain valid for structures with missing spine bonds, such as fenestrenes (see Example 27 below), only with a slight modification of the definition of a fragment. The modified Theorems 7, 11 and 16, in which the notion of a fragment f_k accompanied by its upper interface i_{k-1} and its lower interface i_k is replaced by a notion of an elementary fragment f'_k accompanied by its upper interface i'_{k-1} and its lower interface i'_k, can be now used to describe also benzenoids with holes.

Definition 26. A connected component f' of a fragment f will be referred to as an *elementary fragment.* The set of upper (lower) interface bonds in f' are referred to as the *upper (lower) interface of the elementary fragment* f'. A fragment consisting of multiple elementary fragments will be referred to as a *combined fragment.*

It is easy to see that a fragment f with m atoms is elementary if and only if it contains all spine bonds $s_1, s_2, \ldots, s_{m-1}$. If one of these spine bonds would be missing, the fragment f would split into two elementary fragments f' and f''.

Example 27. Consider a fenestrene $F(5,5)$ shown in Fig. 11 [23,25]. The fragments f_1, f_2, f_5, and f_6 are elementary fragments. The fragments f_3 and f_4 are combined fragments, each consisting of two elementary fragments: $f_3 = f'_3 \cup f''_3$ and $f_4 = f'_4 \cup f''_4$. The interface orders behave as follows.

- Fragments f_1 and f_2 behave as usual: $\text{shape}(f_1) = \text{shape}(f_2) = \texttt{W}$, and therefore by Theorem 11 $\text{ord}(i_0) = 0$, $\text{ord}(i_1) = 1$, and $\text{ord}(i_2) = 2$.
- Let us denote the upper interfaces of f'_3 and f''_3 by i'_2 and i''_2, respectively. Since $i'_2 \cup i''_2 = i_2$, the total order of the interface i_2, $\text{ord}(i_2) = 2$, can be partitioned into $\text{ord}(i'_2) + \text{ord}(i''_2)$ only in three feasible ways:

  $\text{ord}(i'_2) = 2,\ \text{ord}(i''_2) = 0,$ signifying two double bonds in i'_2,

  $\text{ord}(i'_2) = 0,\ \text{ord}(i''_2) = 2,$ signifying two double bonds in i''_2,

  $\text{ord}(i'_2) = 1,\ \text{ord}(i''_2) = 1,$ signifying one double bond or one aromatic ring in both i'_2 and i''_2.

- Let us denote the lower interfaces of f_3' and f_3'' by i_3' and i_3'', respectively. We find that shape(f_3') $=$ `R` and shape(f_3'') $=$ `L`, and therefore according to Theorem 11 $\mathrm{ord}(i_3') = \mathrm{ord}(i_2')$ and $\mathrm{ord}(i_3'') = \mathrm{ord}(i_2'')$. Since $i_3 = i_3' \cup i_3''$, it follows that $\mathrm{ord}(i_3) = \mathrm{ord}(i_3') + \mathrm{ord}(i_3'') = 2$.

- Let us denote the lower interfaces of f_4' and f_4'' by i_4' and i_4''. The upper interfaces of f_4' and f_4'' are i_3' and i_3'', respectively. We have shape(f_4') $=$ `L` and shape(f_4'') $=$ `R`, therefore according to Theorem 11 $\mathrm{ord}(i_4') = \mathrm{ord}(i_3')$ and $\mathrm{ord}(i_4'') = \mathrm{ord}(i_3'')$. Since $i_4 = i_4' \cup i_4''$, we have $\mathrm{ord}(i_4) = \mathrm{ord}(i_4') + \mathrm{ord}(i_4'') = 2$. Note that the actual partition of $\mathrm{ord}(i_4)$ into $\mathrm{ord}(i_4')$ and $\mathrm{ord}(i_4'')$ [as well as the partition of $\mathrm{ord}(i_3)$ into $\mathrm{ord}(i_3')$ and $\mathrm{ord}(i_3'')$] is fully determined by the choice made above for $\mathrm{ord}(i_2')$ and $\mathrm{ord}(i_2'')$.

- The fragment f_5 has i_4 as its upper interface with $\mathrm{ord}(i_4) = 2$. Since shape(f_5) $=$ `N`, we have $\mathrm{ord}(i_5) = 1$.

- The fragment f_6 behaves as usual: since shape(f_6) $=$ `N` and $\mathrm{ord}(i_5) = 1$, we have $\mathrm{ord}(i_6) = 0$, as required by the fact that i_6 is empty.

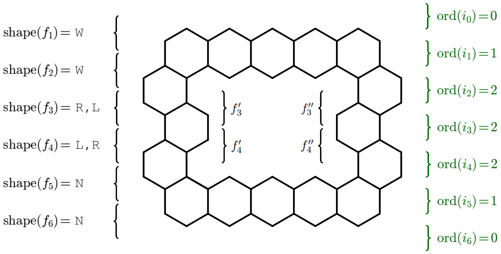


Figure 11. The fenestrene $F(5,5)$ contains two combined fragments: $f_3 = f_3' \cup f_3''$ and $f_4 = f_4' \cup f_4''$. The Theorems 7, 11 and 16 apply to the elementary fragments f_1, f_2, f_3', f_3'', f_4', f_4'', f_5 and f_6.

4 Conclusion

We have developed an *interface theory* of benzenoids that can be used for determining whether a given benzenoid is Kekuléan, for finding its Clar covers and Kekulé structures, for computing its ZZ polynomials, as well as deriving closed forms of ZZ polynomials for whole families of structurally related benzenoids, and for many other interesting applications. The presented here interface theory of benzenoids is based on novel concepts of *fragments* and *interfaces* between the fragments [62, 63]. We derive and demonstrate a number of fundamental theorems pertinent to the interface theory, which show that the theory is internally consistent and in a natural way can be employed for constructing perfect coverings of benzenoid structures using double bonds K_2 and aromatic rings C_6 as the covering components. In particular, we are able to establish necessary and sufficient conditions required for the existence and uniqueness of a Clar cover in terms of interface bond coverings. Lemma 7 states that a Clar cover of a benzenoid is completely determined by just the covering of its interface bonds. Theorem 11 gives a necessary criterion for the total number of double and aromatic bonds in each interface of a Clar cover. Theorem 16 is another necessary criterion describing the distribution of double and/or aromatic interface bonds in each fragment. Finally, Theorem 21 crowns the presented here development by stating a set of conditions that is both necessary and sufficient. As a result, the construction of Clar covers becomes simply an exercise of assigning the interface bond orders in agreement with the theorem, as the presented Algorithm 1 clearly demonstrates. The presented Algorithm 1 is fairly efficient with complexity of $O\left(K \cdot M\right)$, where K denotes the number of fragments in the benzenoid $\boldsymbol{B}$ and M is the maximal interface order of $\boldsymbol{B}$. Every benzenoid $\boldsymbol{B}$ can be analyzed in three distinct orientations, so it is important to select the orientation which gives the minimal value of $K \cdot M$, which in most cases corresponds to the orientation in which $\boldsymbol{B}$ is wider than taller. Note finally, that since K can be bounded by the height of $\boldsymbol{B}$ and M, by the width of $\boldsymbol{B}$, their product is bounded by the area of $\boldsymbol{B}$ proportional to the number of vertices in $\boldsymbol{B}$.

We believe that the presented interface theory of benzenoids is an important new tool for characterization of benzenoid structures and for studying their perfect coverings. We feel that the presented theorems open up new vistas in chemical graph theory and once popularized may constitute an important research methodology in this field. For this reason, we have decided to accompany this theory paper by an application paper [64], where we give numerous examples of some of the most straightforward applications of the interface theory developed here to basic problems in chemical graph theory, including the demonstration of non-Kekuléan character for some non-Kekuléan benzenoids, detection of essentially disconnected components of benzenoid structures, as well as the determination of Clar numbers and the calculation of ZZ polynomials. In the near future, we are planning to demonstrate how to utilize the theorems of interface theory to determine closed-form formulas for the ZZ polynomials of regular benzenoid strips and hexagons, and how to efficiently calculate ZZ polynomials of arbitrary benzenoids. Moreover, a rather straightforward extension of the interface theory to nanotubes and other non-planar structures is planned.

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