MATCH
Communications in Mathematical
and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **84** (2020) 177-215

ISSN 0340 - 6253

Interface Theory of Benzenoids: Basic Applications

Johanna Langner, Henryk A. Witek

Department of Applied Chemistry, Center for Emergent Functional Matter Science,
and Institute of Molecular Science, National Chiao Tung University, Hsinchu, Taiwan

`johanna.langer@arcor.de, hwitek@mail.nctu.edu.tw`

(Received December 20, 2019)

Abstract

We show that the recently introduced interface theory of benzenoids [Langner and Witek, *MATCH Commun. Math. Comput. Chem.* (2020)] can be readily applied to characterize various properties of benzenoids and their Clar covers. A carefully selected collection of examples demonstrates how to use interface theory for detecting non-Kekuléan or essentially disconnected character of benzenoids, computing their Clar numbers, constructing and enumerating their Kekulé structures and Clar covers, and determining their Zhang-Zhang polynomials. The exposition has rather pedagogical character and is supposed to familiarize the reader with the basic toolkit of the interface theory of benzenoids.

1 Introduction

The main purpose of the current paper is to give a practical guide for using *interface theory of benzenoids* for problem solving in chemical graph theory. The interface theory, developed in a prequel to this paper [41], uses the concepts of *fragments* and *interfaces* between fragments to represent uniquely each Clar cover of a given benzenoid [38–40]. We have demonstrated in the previous paper [41] that each Clar cover of a given benzenoid can be completely encoded by the covering orders of the interface bonds. On the other hand, theorems given in [41] provide us with the necessary and sufficient conditions for a set of interface bond coverings to define a valid Clar cover of a given benzenoid. The scope of applications of the interface theory to a given benzenoid is amazingly broad: from demonstration of its Kekuléan (or non-Kekuléan) character, via detecting the regions of fixed bonds, computing its Clar number, construction of a Clar cover with a prespecified number of aromatic sextets, construction of a Clar structure or a Kekulé structure, construction of all its conceivable Clar covers or all Kekulé structures, to computing its Clar covering polynomial (*aka* Zhang-Zhang polynomial or ZZ polynomial). Since it is the first account of using interface theory for practical purposes, and since the introduced concepts may seem somewhat unfamiliar to the reader, we have decided to resort to an elementary level of exposition in the current article to guarantee clear and transparent demonstration of the introduced techniques. We hope that the presented examples convince the chemical graph theory community that the interface theory of benzenoids is a useful and powerful novel tool for solving practical problems [2, 3, 14, 44, 45, 52, 59]. In the forthcoming papers, we are planning to apply the interface theory of benzenoids for finding Clar numbers of various benzenoid classes and for computing closed form of ZZ polynomials for n-tier regular strips. Moreover, a rather straightforward extension of the interface theory to nanotubes and other non-planar structures [1, 7, 19–23, 31–33, 42, 46, 47, 49, 50, 56] is also planned.

2 Preliminaries

A *benzenoid* $\boldsymbol{B}$ is defined as a finite plane graph embedded in a hexagonal lattice [26]. 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 [34] and a *Clar cover* $\boldsymbol{C}$ is a spanning subgraph of $\boldsymbol{B}$ whose components are either K_2 or C_6 [15]. Not every benzenoid has Clar covers. A benzenoid for which at least one Clar cover exists is called *Kekuléan*; otherwise we say it is *non-Kekuléan* [16, 18, 28, 48]. The maximum number Cl of aromatic rings C_6 that can be accommodated in $\boldsymbol{B}$ is called the *Clar number* [15, 27]. A Clar cover with exactly Cl aromatic rings is called a *Clar structure* [15, 27] and a Clar cover with no aromatic rings is called a *Kekulé structure* [6, 17, 26, 34, 43]. We say that a benzenoid $\boldsymbol{B}$ has a *fixed bond* if this bond has the same bond order in every Clar cover of $\boldsymbol{B}$. We say that a benzenoid is *essentially disconnected* if a region of fixed bonds separates $\boldsymbol{B}$ into at least two regions of non-fixed bonds, for which the Clar covers can be constructed independently [9, 10, 35, 37, 54]. The number of conceivable Clar covers of a benzenoid $\boldsymbol{B}$ for a Kekuléan benzenoid is usually quite large. It is convenient to enumerate them using the *Clar covering polynomial* (*aka Zhang-Zhang polynomial* or *ZZ polynomial*) [53, 55, 57, 58]

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

where the coefficient c_k indicates the number of Clar covers containing exactly k aromatic rings C_6, and x is a dummy variable keeping track of these coefficients. The ZZ polynomial conspicuously encodes various quantities characterizing a given benzenoid: the Clar number Cl of $\boldsymbol{B}$ is given by the order of 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. The new terminology used in this paper and pertaining to the interface theory of benzenoids is briefly introduced in the next section.

3 Brief outline of the interface theory of benzenoids

In the following, we summarize the basic concepts and central theorems of the interface theory of benzenoids, which have been introduced and derived formally in the prequel to this manuscript [41]. These concepts, originally tailored only for single zigzag chains, were introduced in a rudimentary form in [38–40]. In the current paper, we follow a practical course for exposition of the definitions and theorems given originally in a formal mathematical language in [41].

Take an arbitrary benzenoid $\boldsymbol{B}$, and orient it in such a way that some of its bonds are aligned vertically. Of course, there are six possible ways of doing so, but for the sake of utilizing the interface theory optimally, it is most convenient to choose an orientation in which the benzenoid is wide rather than tall. The bonds in $\boldsymbol{B}$ that are aligned vertically are called *interface bonds*, and the remaining bonds in $\boldsymbol{B}$ are called *spine bonds.* In the next step, we divide the benzenoid $\boldsymbol{B}$ into horizontal stripes called *fragments.* In practice, it is easiest to perform this step by drawing a set of $K+1$ horizontal partition lines P_0, P_1, …, P_K as shown on the left side of Fig. 1. The portion of the benzenoid $\boldsymbol{B}$ located between the lines P_{k-1} and P_k is called the *fragment* f_k. The set of interface bonds crossed by the line P_k is called the *interface* i_k. Each fragment f_k clearly has two interfaces: i_{k-1} as its *upper interface* and i_k as its *lower interface.* Note that the upper interface i_0 of the first fragment f_1 and the lower interface i_K of the last fragment f_K of $\boldsymbol{B}$ are manifestly empty. The benzenoid shown in Fig. 1 is divided into five fragments f_1, …, f_5 by six partition lines P_0, …, P_5. There exist six interfaces i_0, …, i_5; the terminal interfaces i_0 and i_5 are empty.

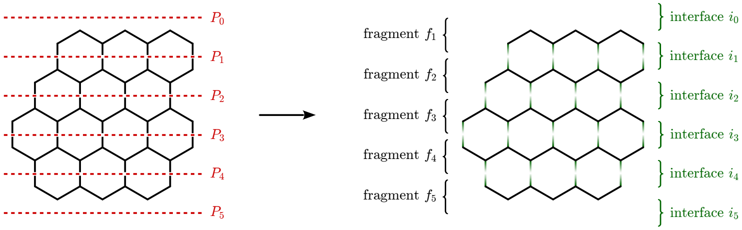


Figure 1. Dividing a benzenoid $\boldsymbol{B}$ into *fragments*. The set of vertical bonds crossed by the partition line P_k forms the *interface* i_k. Note that the first and last interfaces, i_0 and i_5, are empty.

If a fragment f_k is connected, we refer to is as an *elementary fragment*. It may happen that the fragment f_k consists of multiple disconnected pieces; consider for example the fragment f_3 of the benzenoid depicted in panel (a) of Fig. 2, which consists of two components. In this case, each of these pieces is referred to as an *elementary fragment*. A (composite) fragment consisting of multiple elementary fragments is called a *combined*

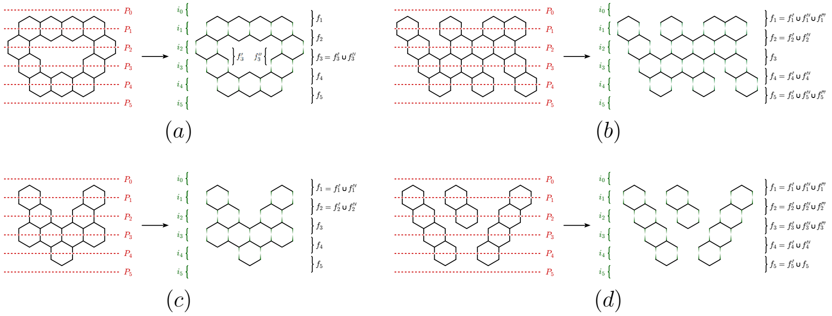


Figure 2. Partition of benzenoids using lines P_0, …, P_K results in a collection of fragments f_1, …, f_K and interfaces i_0, …, i_K. Each fragment consists of one or more connected components, referred to as *elementary fragments*. A fragment consisting of more than one elementary fragments is referred to as a *combined fragment*. The benzenoid in panel (a) has a combined fragment f_3, which consists of two elementary fragments f'_3 and f''_3; the other fragments f_1, f_2, f_4 and f_5 are elementary. The remaining examples demonstrate how to partition various benzenoids into elementary fragments.

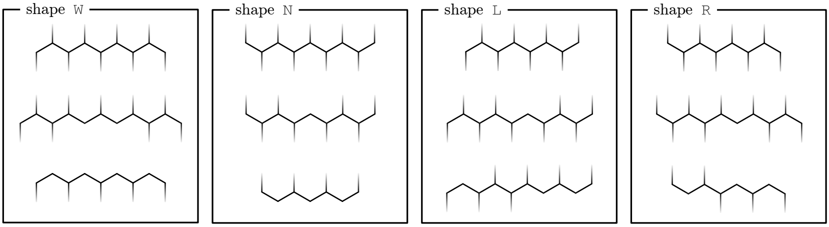


Figure 3. Each elementary fragment can easily be assigned a definite *shape* [`W` (wide), `N` (narrow), `R` (right), or `L` (left)] by inspecting the character (*lower* or *upper*) of its first atom C_1 and its last atom C_m. Note that, for the shape assignment, it is entirely irrelevant whether the interface bonds are present or not.

fragment. In this way, any benzenoid can be cut into a collection of elementary fragments, as illustrated by the examples (a)–(d) in Fig. 2. The notion of elementary fragments is naturally accompanied by the notion of interfaces of elementary fragments. Assume that $f \equiv f_k$ is a fragment containing an elementary fragment $f' \subset f$. Assume further that f has i_u as its upper interface and i_l as its lower interface. Then, the upper interface i'_u and the lower interface i'_l of the elementary fragment f' are simply defined as $i'_u = i_u \cap f'$ and $i'_l = i_l \cap f'$, respectively.

The next step in any practical application of the interface theory is to determine the shape of any elementary fragment obtained from the partition above. This is done very easily simply by looking at the character of the first and the last atom in each elementary fragment. We say that an atom C is an *upper atom* if its position in the fragment can be depicted by one of the following seven symbols: ⋏, ⌊, ⌋, ⌃, ˏ, ˎ, ╵. Similarly, we say that an atom C is an *lower atom* if its position in the fragment can be depicted by one of the following seven symbols: ⋎, ⌈, ⌉, ⌄, ˋ, ˊ, ╷. Based on this classification, the *shape* of an elementary fragment f with the first atom v_1 and the last atom v_m is defined as:

`W`	(wide)	if v_1 is a lower atom,	and v_m is a lower atom.
`N`	(narrow)	if v_1 is an upper atom,	and v_m is an upper atom.
`R`	(right)	if v_1 is an upper atom,	and v_m is a lower atom.
`L`	(left)	if v_1 is a lower atom,	and v_m is an upper atom.

Practical application of this classification is illustrated in Fig. 3 for a series of elementary fragments, many of which appear in Fig. 2. Note that even the most complicated fragments can be easily assigned a definite shape (`W`, `N`, `R`, or `L`) using these simple rules.

In the next step, we can focus on the analysis of the Clar covers of $\boldsymbol{B}$ using the information about its fragments $f_1, \ldots, f_K$ and interfaces $i_0, \ldots, i_K$. The most important tools that will be used for this analysis are the covering orders of the bonds and the covering orders of the interfaces. The *(covering) order* of the bond b in a Clar cover of $\boldsymbol{B}$ is given by

$$\mathrm{ord}(b) = \begin{cases} 0 & \text{if } b \text{ is a single bond,} \\ {}^1\!/\!_2 & \text{if } b \text{ is an aromatic bond,} \\ 1 & \text{if } b \text{ is a double bond.} \end{cases}$$

A bond b is said to be *covered* if $\mathrm{ord}(b) > 0$. Similarly, the *(covering) order* of the interface i consisting of the bonds $b_1, \ldots, b_n$ is given by $\mathrm{ord}(i) = \mathrm{ord}(b_1) + \ldots + \mathrm{ord}(b_n)$. It turns out that the orders of bonds and the orders of interfaces satisfy a number of interesting and useful relationships that can be used for characterizing various topological properties of benzenoids. Let us review briefly the most important of these properties. For proofs and detailed formulation of the forthcoming facts, see Lemma 8, Remark 9, and Theorems 11, 16, and 21 of [41], respectively, together with the discussion about the elementary fragments in Section 3.5 of [41].

Consider a benzenoid $\boldsymbol{B}$. Let f be an elementary fragment of $\boldsymbol{B}$ with i_u as its upper interface and i_l as its lower interface. Denote by v_1 and v_m the first and last atom of f, respectively. Further, if $\boldsymbol{B}$ is Kekuléan, denote by $\boldsymbol{C}$ one of its Clar covers. Then the following facts are true.

Lemma 1. *The orders of the spine bonds in* $\boldsymbol{C}$ *are uniquely determined by the orders of the interface bonds in* $\boldsymbol{C}$*.*

Lemma 2. *The Clar cover* $\boldsymbol{C}$ *is uniquely and fully determined by the orders of its interface bonds.*

Theorem 3 (First Rule of Interface Theory). *The order of the lower interface is fully determined by the order of the upper interface and the shape of the elementary fragment*:

(*a*) *If* f *has the shape* `W`, *then* $\mathit{ord}(i_l) = \mathit{ord}(i_u) + 1$.

(*b*) *If* f *has the shape* `N`, *then* $\mathit{ord}(i_l) = \mathit{ord}(i_u) - 1$.

(*c*) *If* f *has the shape* `R` *or* `L`, *then* $\mathit{ord}(i_l) = \mathit{ord}(i_u)$.

Theorem 4 (Second Rule of Interface Theory). *The covered interface bonds of* $\boldsymbol{C}$ *in* f *are distributed as follows.*

(*a*) *The first covered interface bond in* f *belongs to the* $\genfrac{}{}{0pt}{}{\textit{upper}}{\textit{lower}}$ *interface if* v_1 *is an* $\genfrac{}{}{0pt}{}{\textit{upper}}{\textit{lower}}$ *atom.*

(*b*) *The last covered interface bond in* f *belongs to the* $\genfrac{}{}{0pt}{}{\textit{upper}}{\textit{lower}}$ *interface if* v_m *is an* $\genfrac{}{}{0pt}{}{\textit{upper}}{\textit{lower}}$ *atom.*

(*c*) *Each of the other covered interface bonds (i.e., a double bond or a pair of aromatic bonds) located in the* $\genfrac{}{}{0pt}{}{\textit{upper}}{\textit{lower}}$ *interface is flanked by a pair of covered interface bonds (i.e., double bonds and/or pairs of aromatic bonds) both located in the* $\genfrac{}{}{0pt}{}{\textit{lower}}{\textit{upper}}$ *interface.*

Theorem 5 (Third Rule of Interface Theory). *Assume that covering orders for all interface bonds in* $\boldsymbol{B}$ *have been assigned in such a way that for every elementary fragment* f *of* $\boldsymbol{B}$, *the following three conditions are satisfied:*

(*a*) *The set of aromatic interface bonds can be written as a union of disjoint pairs* (e, e'), *where* e *and* e' *are the left and right interface bonds of some hexagon of* $\boldsymbol{B}$. *Furthermore, the interface bonds connected to this hexagon from above and below are not covered.*

(*b*) *The orders of the upper and lower interface of* f *satisfy the conditions* (*a*), (*b*), *and* (*c*) *of Theorem 3.*

(*c*) *The orders of the upper and lower interface of* f *satisfy the conditions* (*a*), (*b*), *and* (*c*) *of Theorem 4.*

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

4 Introductory examples

The concepts and theorems given in the previous section provide us with valuable information about the graph-theoretical structure of benzenoids. In this section, we demonstrate how to use these tools for predicting the distribution of double bonds and aromatic rings in a given benzenoid, determining an upper bond for its Clar number, and constructing its Clar covers. More advanced applications are given in the next section.

Example 6. Consider the benzenoid  introduced originally in Fig. 1. The First Rule (Theorem 3) provides an easy tool for predicting the number of double bonds or aromatic rings in the interfaces of this structure. The resulting interface orders are given in Fig. 4. The detailed considerations leading to these conclusions can be summarized as follows:

- The interfaces i_0 and i_5 do not contain any bonds, and thus must have order $\mathrm{ord}(i_0) = \mathrm{ord}(i_5) = 0$.
- The fragment f_1 has shape `W`, therefore $\mathrm{ord}(i_1) = \mathrm{ord}(i_0) + 1 = 1$. This signifies that the interface i_1 contains either one double bond or one aromatic ring.
- The fragment f_2 has shape `L`, therefore $\mathrm{ord}(i_2) = \mathrm{ord}(i_1) = 1$. This signifies that the interface i_2 contains either one double bond or one aromatic ring.
- The fragment f_3 has shape `W`, therefore $\mathrm{ord}(i_3) = \mathrm{ord}(i_2) + 1 = 2$. This signifies that the interface i_3 contains either two double bonds, or two aromatic rings, or exactly one of each.
- The fragment f_4 has shape `N`, therefore $\mathrm{ord}(i_4) = \mathrm{ord}(i_3) - 1 = 1$.
- The fragment f_5 has shape `N`, therefore $\mathrm{ord}(i_5) = \mathrm{ord}(i_4) - 1 = 0$, in agreement with earlier observation.

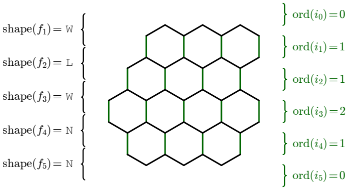


Figure 4. Interface orders of the benzenoid $\boldsymbol{B}$ from Fig. 1 as deduced from Theorem 3.

Example 7. Consider again the benzenoid $\boldsymbol{B}$ = . Example 6 provides us with the order of each interface i_k of $\boldsymbol{B}$, which can be interpreted as the maximal number of aromatic rings allowed in i_k. Therefore, the upper limit for the total number of aromatic rings in $\boldsymbol{B}$ (i.e., for the Clar number of $\boldsymbol{B}$) can be simply computed by summing over all the interface orders determined in Example 6:

$$Cl(\boldsymbol{B}) \le \sum_k \mathrm{ord}(i_k) = 5. \tag{2}$$

Following the information about the interface orders determined in Example 6, it is straightforward to construct a Clar cover in which this upper bound is achieved.

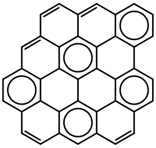


Figure 5. A Clar cover of $\boldsymbol{B}$ from Fig. 1 with five aromatic sextets distributed as suggested by Example 6 shows that its Clar number is at least 5. This fact, together with Eq. (2), which shows that the Clar number is at most 5, establishes that $Cl(\boldsymbol{B}) = 5$.

Since $Cl(\boldsymbol{B}) = 5$, the Clar cover shown in Fig. 5 is actually a Clar structure of $\boldsymbol{B}$. Moreover, as can be seen from the ZZ polynomial of $\boldsymbol{B}$, which is readily calculated using the ZZDecomposer [13],

$$\mathrm{ZZ}(\boldsymbol{B}) = x^5 + 19x^4 + 112x^3 + 280x^2 + 310x + 125847, \tag{3}$$

there is only one Clar cover with five aromatic sextets (because the coefficient of x^5 is 1), which signifies that the Clar cover shown in Fig. 5 is actually *the* Clar structure of $\boldsymbol{B}$.

Subsection 5.3 explores the determination of Clar numbers using interface theory in more detail, including cases in which the upper limit estimated according to Eq. (2) is not achieved.

Example 8. Using Theorem 5, it is easy to construct a Clar cover of the benzenoid $\boldsymbol{B}$ =  with some special characteristics. Here, we show how to construct a Clar cover of $\boldsymbol{B}$ with exactly two aromatic rings. According to Eq. (3), there exist 280 distinct Clar covers with the required property, out of which $\binom{5}{3} \cdot 2^3 = 80$ descent from the Clar structure of $\boldsymbol{B}$ shown in Fig. 5. Let us construct here a Clar cover of order 2 that does not belong to this set.

- Considering the first fragment f_1, we see from Theorem 3 that $\mathrm{ord}(i_1) = 1$, signifying that this interface contains exactly one double bond or one aromatic ring. Theorem 4 imposes no restriction on the placement of the covered bond(s). In other words, we may place one double bond or one aromatic ring anywhere in the first interface. Let us choose a double bond and place it in the third position of i_1.

- Considering the fragment f_2, we see from Theorem 3 that $\mathrm{ord}(i_2) = 1$, signifying that this interface again contains exactly one double bond or one aromatic ring. Theorem 4 applied to the fragment f_2 implies that the first covered bond is located in the lower interface, and that the last covered bond is located in the upper interface. These two facts signify that the covered bond(s) in the lower interface are located *to the left* of the covered bond in the upper interface. Taking into account the actual position of the double bond in the interface i_1, we are left with the possibility of placing a double bond in the first, second, or third position of the interface i_2 or with the possibility of placing an aromatic ring inside the first or second hexagon of the interface i_2. Let us choose an aromatic ring and place it in the first hexagon of i_2. This location of the aromatic ring is *different* from the location of aromatic rings in the Clar structure of $\boldsymbol{B}$, signifying that the Clar cover we construct here does not descent from the Clar structure of $\boldsymbol{B}$ shown in Fig. 5.

- Considering the fragment f_3, we see from Theorem 3 that $\mathrm{ord}(i_3) = 2$. Theorem 4 forces us to place the covered bonds on both sides of the covered bonds of the interface i_2. This signifies that the first covered bond of the interface i_3 *must be placed* in the first position of i_3 and that it *must be* a double bond, as there is not enough space to place an aromatic ring there. For the remaining covered bond(s) of i_3, we are left with the possibility of placing a double bond in the third, fourth, or fifth position of the interface i_3 or with the possibility of placing an aromatic ring inside the third or fourth hexagon of the interface i_3. Let us choose an aromatic ring and place it in the fourth hexagon of i_3.

- Considering the fragment f_4, we see from Theorem 3 that $\mathrm{ord}(i_4) = 1$. Theorem 4 applied to the fragment f_2 implies that the covered bond(s) in i_4 must be placed between the double bond and the aromatic ring of the interface i_3. Specifically, we are left with a possibility of placing a double bond in the first, second or third position of i_4. Let us place a double bond in the third position of i_4. Note that no aromatic ring can be placed in i_4, as the Clar cover of order 2 we construct already contains two aromatic rings (one in i_2 and one in i_3). This completes the process of assigning covering orders to the interface bonds in ***B***.

- The distribution of the covered bonds in the interfaces of ***B*** satisfies the conditions of Theorem 5, which guarantees that that there exists a unique Clar cover with the selected set of covered interface bonds. The resulting Clar cover is depicted on the right side of Fig. 6.

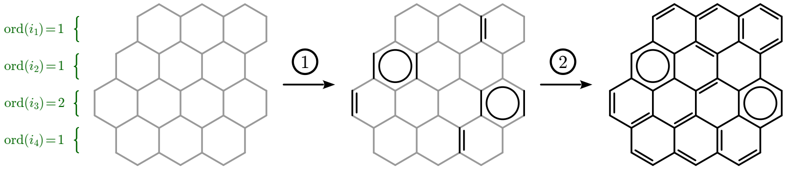
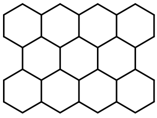


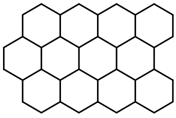
Figure 6. Construction of an arbitrary Clar cover of a benzenoid ***B*** proceeds via ① choosing covered interface bonds in agreement with the conditions of Theorem 5, followed by ② automatic distribution of covered spine bonds in agreement with Lemma 1.

The rules of interface theory may at first appear somewhat complicated; however, with just a little bit of practice, they are easy and straightforward to apply. It might be useful and enlightening for the readers to get involved in the following two exercises.

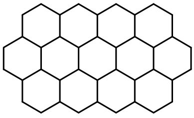
Exercise 9. Which of the following structures can be expected to have the highest Clar number? The solution can be found at the bottom of this page.



Pr(2,4)



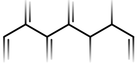
Ch(2,2,4)

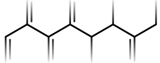


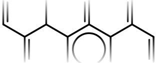
O(2,2,4)

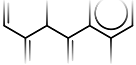
Solution to Exercise 9: According to the First Rule, the orders of the interfaces for $Pr(2,4)$ are: 1, 0, and 1. Similarly, for $Ch(2,2,4)$ and $O(2,2,4)$, we have, respectively, 1, 1, 1, and 1, 2, 1. The resulting upper bounds for the Clar number of these three structures are 2, 3, and 4, respectively. These upper bounds are achieved, because the structures are wide enough to accommodate all the required aromatic rings. Consequently, we find that $O(2,2,4)$ is expected to have the highest Clar number.

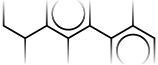
Exercise 10. Are the following distributions of covered interface bonds allowed? If not, which rules are violated?

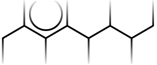
(a)


(b)


(c)


(d)


(e)


(f)


5 Applications

In this section we compile a number of straightforward applications of the interface theory for solving real-life problems in chemical graph theory, including verification of Kekuléan character of benzenoids, identification of essentially disconnected components of benzenoids, determination of their Clar number, as well as computation of their Zhang–Zhang polynomial.

5.1 Kekuléan character

Most non-Kekuléan structures can easily be detected by checking for inconsistencies in the interface orders.

Example 11. In the goblet $X(3,5)$ shown in Fig. 7, the First Rule predicts that the order of the interface i_3 should be -1. Since negative covering orders are not allowed, no Kekulé structure exists for this molecule.

Solutions to Exercise 10:
(a) allowed, **(b)** both the First Rule and condition *(b)* of the Second Rule are violated, **(c)** condition *(c)* of the Third Rule is violated, since a double bond in the upper interface cannot be located between a pair of aromatic bonds in the lower interface, **(d)** the First Rule and condition *(c)* of the Second Rule are both violated, **(e)** allowed, **(f)** the First Rule and condition *(a)* of the Second Rule are both violated.

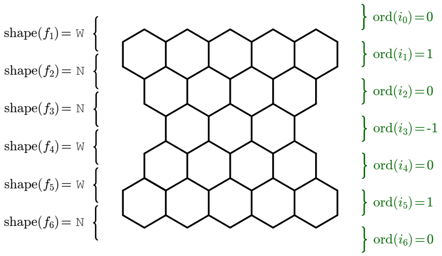


Figure 7. Theorem 3 predicts a negative order for the interface i_3 of the goblet $X(3,5)$. Since this is an absurdity, $X(3,5)$ is non-Kekuléan.

Example 12. Consider the benzenoid shown in Fig. 8. It is clear that for the empty interfaces i_0 and i_4, $\text{ord}(i_0) = \text{ord}(i_4) = 0$. However, a consecutive application of Theorem 3 to the interface sequence $i_0 \to i_1 \to i_2 \to i_3 \to i_4$ predicts that $\text{ord}(i_4) = 1$. This discrepancy proves that no Kekulé structure can be found for this benzenoid.

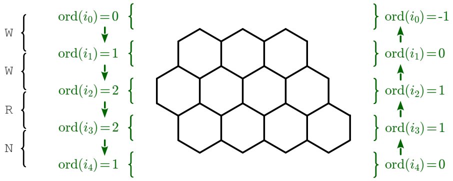


Figure 8. This benzenoid is non-Kekuléan, since it is not possible to find consistent and legitimate interface orders using Theorem 3.

In less obvious cases, where the interface orders behave in agreement with the First Rule, the Kekuléan character of a benzenoid can be verified by attempting to explicitly

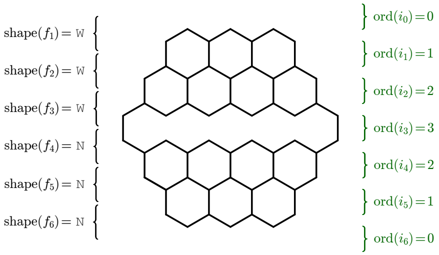


Figure 9. The interface i_3 does not contain sufficiently many locations to accommodate the three double bonds required by $\text{ord}(i_3) = 3$, thus no Kekulé structure is possible.

construct a Kekulé structure using the Third Rule, Theorem 5.

Example 13. Consider the benzenoid shown in Fig. 9. In this case, the interface orders are consistent, but it is not possible to accommodate three double bonds in the interface i_3, because there are only two positions available there. Therefore, no Kekulé structure can be found for this benzenoid.

Example 14. Consider the benzenoid shown in Fig. 10. The interface orders are consistent. The interface i_4, consisting of three interface bonds, has order 3; therefore, all three bonds in i_4 must be double bonds. Consider now the fragment f_4. According to Theorem 4 (c), the double bond in the second position of i_4 must be flanked by two covered interface bonds in i_3. However, the topology of f_4 does not allow this. Therefore, the benzenoid shown in Fig. 10 is non-Kekuléan.

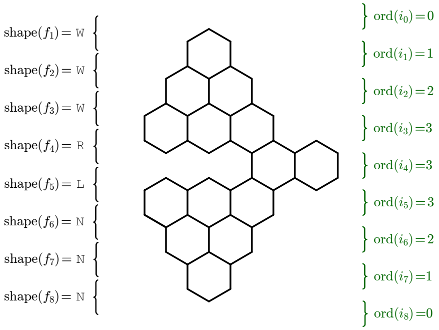


Figure 10. The First Rule requires placing three double bonds in the interface i_4 of the presented benzenoid. However, it is impossible to distribute covered bonds in the interface i_3 in a way that satisfies the Second Rule for the fragment f_4. Consequently, no Kekulé structure can be constructed for this benzenoid.

Example 15. Consider the benzenoid shown in Fig. 11. To demonstrate that this a Kekuléan molecule, it is sufficient to construct a single Kekulé structure for it. This can be easily done by placing double bonds in agreement with the conditions of Theorem 5, as demonstrated for example on the left side of Fig. 11. Note that any of the 41 possible Kekulé structures, which can be constructed in similar way for the studied here molecule, would demonstrate its Kekuléan character .

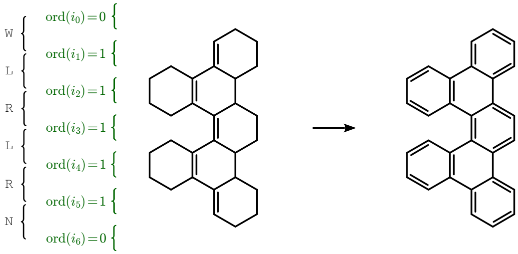


Figure 11. According to the interface theory, a demonstration that a benzenoid is Kekuléan can proceed by placing double interface bonds in agreement with the First Rule and the Second Rule. Then, the Third Rule guarantees that there exists a Kekulé structure with such prespecified covered interface bonds.

5.1.1 Connection to previous results

Gutman and Cyvin [28] introduced a method for identifying Kekuléan structures which is equivalent to the criteria derived here, which relies on the peaks and valleys approach [30]. Their algorithm is based on the concept of monotonous (always going downwards), alternating (passing through single and double bonds alternately), independent (without common atoms) paths from peaks (upper atoms with two spine bonds and no interface bond) to valleys (lower atoms with two spine bonds and no interface bond). According to [24, 28], there is a one-to-one correspondence between Kekulé structures and sets of monotonous alternating independent paths from peaks to valleys that start with a double bond. In the words of the interface theory, each such path is composed of single interface bonds and double spine bonds. The interface bonds that are not involved in any path are exactly the covered interface bonds. This relation is bidirectional: Choosing a set of double interface bonds uniquely determines a set of paths. This one-to-one correspondence is illustrated in Fig. 12. It might be instructive to give here some further discussion of the correspondence mentioned above. Every peak introduces an additional single bond to the following interface, and every valley removes a single bond from the following interface. The fact that one can always find a continuous path between a peak and a valley is closely related to the fact that single interface bonds are always located in adjacent positions in neighbouring interfaces [24], which is a reflection of Theorem 4 applied to Kekulé structures. The algorithm introduced in [28] uses an iterative process to determine the Kekuléan character of a structure, which proceeds as follows. If there is a pendent atom

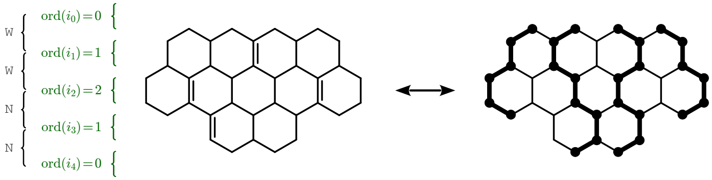


Figure 12. It is equivalent to choose a set of double interface bonds in accordance with Theorem 5 (left) or a set of monotonous alternating independent paths from peaks to valleys (right). The double interface bonds are exactly the interface bonds that do not lie on any path. Either representation determines the same Kekulé structure.

(an atom with only one bond), remove it together with its first neighbor. Otherwise, remove an entire path from the side of a benzenoid. These operations do not change the Kekuléan character of a benzenoid, and are repeated until the remaining structure is clearly Kekuléan or non-Kekuléan. In terms of the interface theory, removing a path does not change the fragment shapes, and is equivalent to assigning single bond character to all interface bonds on the path. Removing a pendent atom that has only a spine bond together with its neighbor does not change the fragment shape, and is equivalent to assigning single bond character to the interface bond of the neighboring atom. Removing a pendent atom that has only an interface bond together with its neighbor does change the fragment shape, and is equivalent to assigning double bond character to that interface bond. In this sense, the algorithm in [28] iteratively selects—whenever possible—a set of covered interface bonds that in the light of the Third Rule corresponds to a unique Kekulé structure.

5.2 Essentially disconnected structures

Some Kekuléan benzenoids possess fixed bonds, i.e., bonds that in all Clar covers (naturally including all Kekulé structures) have the same covering order. In some situations, the fixed bonds separate regions with variable bond covering order. Such regions are referred to as disconnected components of the benzenoid and such a benzenoid is referred to as essentially disconnected. In the current section, we show how to use the interface theory to detect fixed bonds in benzenoids and how to discover their essentially disconnected character. The rules are rather simple and straightforward. If an interface has order zero, all its bonds are single bonds. Likewise, if an interface consisting of n bonds has order n, all its bonds must be double bonds. Note that detecting essentially disconnected character of a given benzenoid has far-reaching practical consequences, as the coverings can be constructed independently for each of the disconnected components. Consequently, the ZZ polynomial of an essentially disconnected benzenoid is simply the product of the ZZ polynomials of its disconnected components.

Example 16. In the prolate rectangle $Pr(3,n)$, shown in Fig. 13, the interfaces i_2 and i_4 have order zero, meaning that all bonds in these interfaces are single bonds. Therefore, $Pr(3,n)$ is an essentially disconnected structure, and its ZZ polynomial is simply derived from the ZZ polynomials of the three polyacenes $L(n)$ in the first, third and fifth row:

$$\mathrm{ZZ}(Pr(3,n)) = \mathrm{ZZ}(L(n)) \cdot \mathrm{ZZ}(L(n)) \cdot \mathrm{ZZ}(L(n)).$$

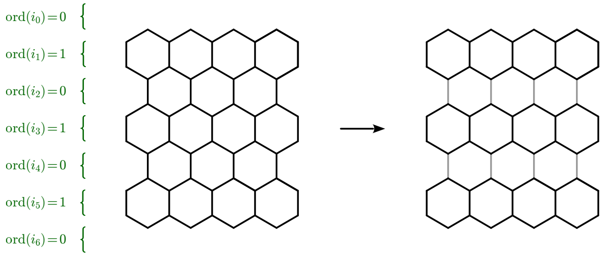


Figure 13. The vanishing interface order for the interfaces i_2 and i_4 of $Pr(3,n)$ naturally implies that i_2 and i_4 consist entirely of single bonds. Therefore, this structure is essentially disconnected and equivalent to three independent polyacenes $L(n)$. This observation is illustrated here for $n=4$.

Example 17. The interface i_3 of the structure $\boldsymbol{B}$ shown in Fig. 14 has order 2, implying that i_3 consists entirely of double bonds. The system of parallel double bonds in i_3 propagates partially to i_2 and i_4, fixing the order of the first bond in each of these interfaces and separating two independent polyacenes $L(2)$, depicted in black in Fig. 14. Therefore, the benzenoid $\boldsymbol{B}$ is essentially disconnected, and its ZZ polynomial is simply the product of the ZZ polynomials of the two disconnected $L(2)$ components

$$\mathrm{ZZ}(\boldsymbol{B}) = \mathrm{ZZ}(L(2)) \cdot \mathrm{ZZ}(L(2)).$$

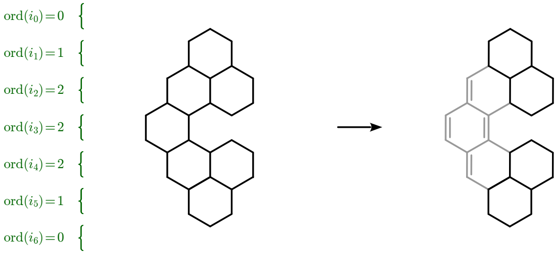


Figure 14. The interface i_3 has order 2, which implies that both bonds in i_3 are double bonds. The Second Rule requires that also the first bonds of the interfaces i_2 and i_4 are double bonds. Consequently, this structure is essentially disconnected.

Example 18. Consider the benzenoid $\boldsymbol{B}$ depicted in Fig. 15. We find that the interface i_4 has order $\mathrm{ord}(i_4) = 2$, which signifies that both bonds in i_4 are double bonds. The double character of these bonds propagates partially to the interfaces i_3 and i_5, fixing the covering order of the first and the last bond in each of these interfaces. As a result, the bonds depicted in gray in Fig. 15 are fixed and the two remaining parallelograms $\boldsymbol{M}(2,2)$ depicted in black can be covered independently. Consequently, the ZZ polynomial of the benzenoid $\boldsymbol{B}$ is computed as the product

$$\mathrm{ZZ}(\boldsymbol{B}) = \mathrm{ZZ}(\boldsymbol{M}(2,2)) \cdot \mathrm{ZZ}(\boldsymbol{M}(2,2)).$$

Example 19. For some benzenoids, the two simple rules exploited in the current section

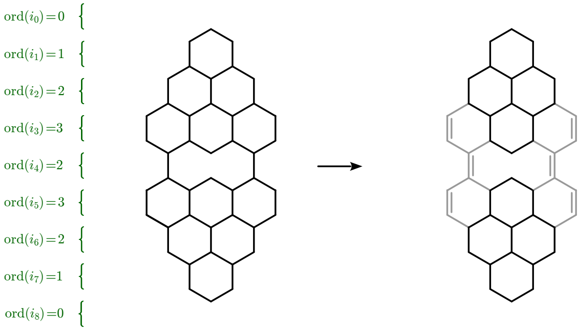


Figure 15. The interface i_4 has order 2, which implies that both bonds in i_4 are double bonds. The Second Rule requires that also the first and the last bonds of the interfaces i_3 and i_5 are double bonds. Consequently, this structure is essentially disconnected.

have indeed far-reaching consequences. Consider the molecule $\boldsymbol{B}$ depicted in Fig. 16. It is not a benzenoid *sensu stricto*, but the interface theory can still be applied to it. The order of the middle interface is $\mathrm{ord}(i_2) = 2$, signifying that both bonds in the interface i_2 are double bonds. Similarly to the Example 18, the system of double bonds in i_2 propagates to i_1 and i_3 and fixes all (!) bonds in this benzenoid. Consequently, there is only one possible Kekulé structure for the molecule $\boldsymbol{B}$, which is depicted in gray in Fig. 16. As a result, the ZZ polynomial of the structure $\boldsymbol{B}$ is

$$\mathrm{ZZ}(\boldsymbol{B}) = 1.$$

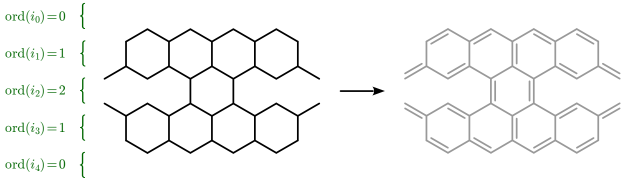


Figure 16. Theorems 3 and 4 show that all bonds in this molecule are fixed. Consequently, there is only one possible Kekulé structure.

5.3 Clar number

The determination of the Clar number $Cl(\boldsymbol{B})$ of some benzenoid $\boldsymbol{B}$ (i.e., the maximal number of aromatic rings that can be accommodated in $\boldsymbol{B}$) using the interface theory proceeds in two steps. The first step involves finding the upper bound for $Cl(\boldsymbol{B})$, which is given by the sum of interface orders determined with the First Rule

$$Cl(\boldsymbol{B}) \leq \sum_k \mathrm{ord}(i_k). \tag{4}$$

The second step involves an attempt to construct a Clar cover with exactly $\sum_k \mathrm{ord}(i_k)$ aromatic rings, where the distribution of the covered aromatic interface bonds is governed by Theorem 5. Example 7 in Section 4 demonstrates a successful application of this strategy. However, it is not always possible to achieve this upper limit, as the following example clearly demonstrates.

Example 20. Consider the benzenoid $\boldsymbol{B}$ = phenanthrene shown in Fig. 17. The interface orders allow one aromatic ring in each row, giving an upper bound for its Clar number

$$Cl(\boldsymbol{B}) \leq \sum_k \mathrm{ord}(i_k) = 3. \tag{5}$$

However, this upper bound cannot be achieved, since placing aromatic rings in three adjacent hexagons of phenanthrene does not produce a valid Clar cover. Consequently, $Cl(\boldsymbol{B}) = 2$, as confirmed by the Clar cover shown in the lower panel of Fig. 17.

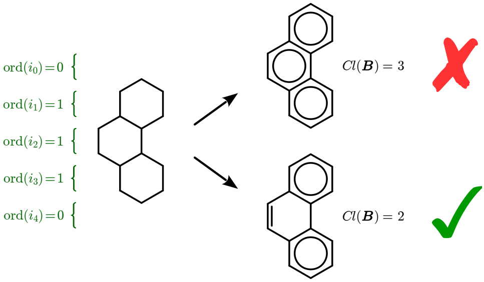


Figure 17. The upper bound $\sum_k \mathrm{ord}(i_k) = 3$ for the Clar number of phenanthrene does not correspond to any valid Clar cover. The only candidate, with three aromatic rings in three consecutive hexagons, is clearly wrong. Consequently, only two aromatic rings may be placed in this benzenoid.

For phenanthrene, the problem of predicting a too large upper bound for the Clar number can be readily resolved, as the following argument suggests. Consider the three possible orientations of the phenanthrene molecule as shown in Fig. 18. For each of these orientations, the interface orders can be determined and used to compute the upper bound using Eq. (4). Clearly, the Clar number of phenanthrene cannot be larger than the smallest of these three values; we have

$$Cl(\boldsymbol{B}) \leq \min(3, 2, 2) = 2.$$

We see that from this point of view, the upper bound is actually achieved.

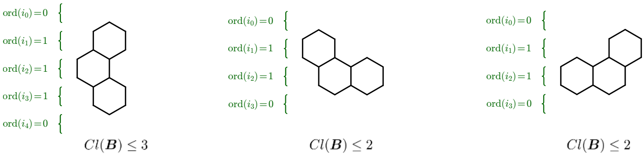
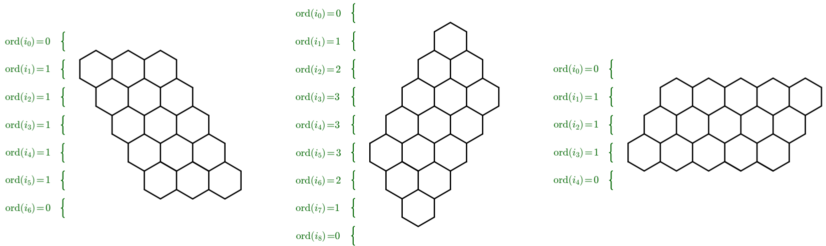


Figure 18. The Clar number of phenanthrene obviously does not depend on its orientation. However, the upper bound for the Clar number determined from the interface orders is clearly orientation dependent. To resolve this apparent obstacle, we take as the upper bound for $Cl(\boldsymbol{B})$ the minimum over the three possible orientations of a given benzenoid $\boldsymbol{B}$.

Example 21. To illustrate the point from the previous example on a more complicated pericondensed benzenoid, consider the parallelogram $\boldsymbol{M}(5,3)$. The interface orders and the upper bounds for $Cl(\boldsymbol{M}(5,3))$ determined for the three possible orientations of $\boldsymbol{M}(5,3)$ are given in Fig. 19. The actual, orientation-independent upper bound for $Cl(\boldsymbol{M}(5,3))$ is taken as the minimum of these three values; we have

$$Cl(\boldsymbol{M}(5,3)) \leq \min\,(5,15,3) = 3.$$



$Cl(\boldsymbol{B}) \leq 5$ $Cl(\boldsymbol{B}) \leq 15$ $Cl(\boldsymbol{B}) \leq 3$

Figure 19. The three possible orientations of the parallelogram $\boldsymbol{M}(5,3)$ generate three different sets of interface orders and three different upper bounds for its Clar number $Cl(\boldsymbol{M}(5,3))$. The minimum over these upper bounds usually corresponds to the widest/lowest orientation of the benzenoid.

To show that this upper bound is actually achieved, we need to construct a Clar cover of $\boldsymbol{M}(5,3)$ with three aromatic rings. This can be done independently for each of the three possible orientations of $\boldsymbol{M}(5,3)$. Obviously, choosing any of these orientations would be sufficient here for demonstrating our claim, but we have written before that the interface theory works most efficiently when the benzenoid is oriented in such a way that it is wider than taller, and the current example constitutes a convenient demonstration ground for illustrating this guideline.

For the first orientation shown in the left panel of Fig. 19, the interface orders allow one aromatic ring in each row. However, according to Theorem 4, each aromatic ring has to be located to the right of the previous one. Therefore, three aromatic rings can be accommodated in the first three interfaces of $\boldsymbol{M}(5,3)$, with the covered bonds in the interfaces i_4 and i_5 being necessarily double bonds, as depicted in the left panel of Fig. 20. Very similar reasoning applies to the last orientation shown in the right panel of Fig. 19, for which Theorem 4 requires placing each aromatic ring to the left of the previous ring;

a distribution of covered interface bonds obtained in this way is shown in the right panel of Fig. 20. Constructing an appropriate Clar cover for the tallest orientation, shown in the center of Fig. 19, is most time-consuming, as the number of covered interface bonds is as large as 15. A possible distribution of covered interface bonds resulting from such a construction is depicted in the center of Fig. 20. It is obvious that the construction of an appropriate Clar cover has been most straightforward for the orientation in which $\boldsymbol{M}(5,3)$ is widest and lowest.

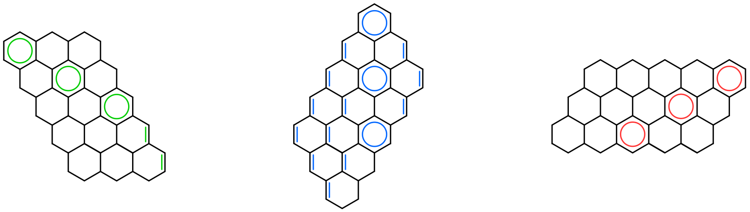
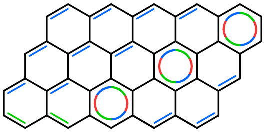


Figure 20. Distribution of covered interface bonds leading to a Clar structure can be performed for any of the three orientations of a benzenoid, but the most straightforward and least time-consuming construction is performed for its widest/lowest orientation shown on the right in red.

Note that the three distributions of the covered interface bonds shown in Fig. 20 for the three possible orientations of $\boldsymbol{M}(5,3)$ correspond exactly to the same Clar cover



which we have depicted using the same color scheme as in Fig. 20 to demonstrate that the covered interface bonds in one orientation correspond to the covered spine bonds in the remaining two orientations.

Example 22. At this point, one may be tempted to claim that

$$Cl(\boldsymbol{B}) = \min\left\{\sum_{i_k\in\rotatebox{60}{\mathbf{B}}}\operatorname{ord}(i_k), \sum_{i_k\in\mathbf{B}}\operatorname{ord}(i_k), \sum_{i_k\in\rotatebox{-60}{\mathbf{B}}}\operatorname{ord}(i_k)\right\}, \tag{6}$$

where $\rotatebox{60}{\mathbf{B}}$, $\mathbf{B}$ and $\rotatebox{-60}{\mathbf{B}}$ denote the three possible orientations of a benzenoid $\boldsymbol{B}$. This idea is disproven by considering the hollow structure $\boldsymbol{B}$ considered originally in Example 17, for which the minimum over the three orientations shown in Fig. 21 yields an upper bound of 3 for $Cl(\boldsymbol{B})$. This upper bound is not achieved due to the region of fixed bonds in $\boldsymbol{B}$ discovered in Example 17 and explicitly shown here again in gray in Fig. 22. Each of the remaining black fragments can accommodate at most one aromatic ring, which results in a Clar number of $Cl(\boldsymbol{B}) = 2$.

Example 23. Let us now identify the Clar numbers of the hexagonal flakes $O(3, 2, 3)$ and $O(3, 2, 4)$ shown in Fig. 23. The interface orders are identical for both structures and predict an upper bound for their Clar number

$$\sum_k \mathrm{ord}(i_k) = 6,$$

with at most one aromatic ring in the first and last interface, and at most two aromatic rings in the second and third interface. However, it turns out that placing two aromatic rings in the second interface of $O(3, 2, 3)$ prevents one from placing two aromatic rings in its third interface (and vice versa), as there is not sufficient space left there for accommodating the other aromatic ring. Consequently, only five aromatic rings can be accommodated in

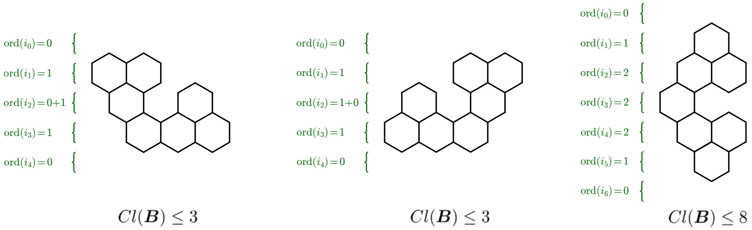


Figure 21. The upper bound for the Clar number of the benzenoid $\boldsymbol{B}$, computed as a minimum of the upper bounds for its three possible orientations, is 3. However, as Fig. 22 clearly demonstrates, this upper bound is not achieved.

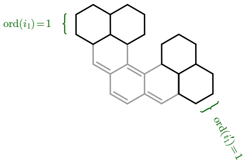


Figure 22. In every Clar cover that can be constructed for the essentially disconnected benzenoid $\boldsymbol{B}$ from Fig. 21 the bonds depicted in gray are fixed, i.e. have constant orders. Consequently, only each of the remaining fragments depicted in black can accommodate one aromatic ring, showing that $Cl(\boldsymbol{B}) = 2$.

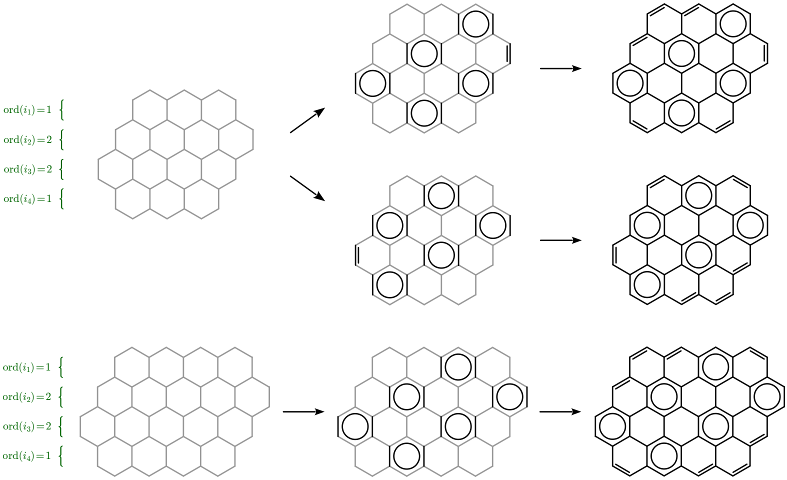


Figure 23. Determination of the Clar number of a benzenoid $\boldsymbol{B}$ by constructing its Clar structure using the rules of interface theory.

$O(3,2,3)$, and such an arrangement can be performed in two possible ways, resulting in two distinct Clar structures, which are depicted in Fig. 23. It follows that $Cl(O(3,2,3)) = 5$. No such difficulty occurs for $O(3,2,4)$, for which the length of the interfaces i_2 and i_3 is sufficient to accommodate two aromatic rings in each of them without collisions. It follows that $Cl(O(3,2,4)) = 6$.

5.3.1 Connection to previous results

It was shown by Klavžar, Žigert, and Gutman [36] that in catacondensed benzenoid hydrocarbons, the Clar number is equal to the minimum number of straight lines (along the centers of rows of hexagons) required to intersect all hexagons. In the language of interface theory, this fact is directly connected to the observation that in a catacondensed benzenoid, all interfaces of elementary fragments have order one, and every line utilized by Klavžar *et al.* lies along one of these interfaces. On the other hand, as noted in [36], the method of intersecting lines does not predict the correct Clar number for most pericondensed benzenoids. For example, for the structures depicted in Fig. 24, the minimum number of lines needed to intersect every hexagon is 3. However, the Clar numbers are 2 and 4, respectively, as anticipated from the analysis of the interface orders using interface theory.

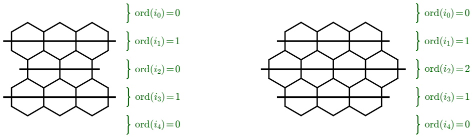


Figure 24. Two benzenoid structures (B_6 and B_7 of [36]) clearly show that in peri-condensed molecules, lines crossing rows of hexagons correspond to interfaces of not necessarily order 1, and therefore cannot be used to count the maximum possible number of Clar sextets.

5.4 Zhang–Zhang polynomials

Our main motivation stimulating the development of the interface theory of benzenoids comes from the need for efficient and robust computation of ZZ polynomials of benzenoids. In the previous Examples 16–19, we have shown how to use the interface theory to compute the ZZ polynomials for essentially disconnected benzenoids. Here, we give a brief account how to apply it to general benzenoids. We start with an obvious example.

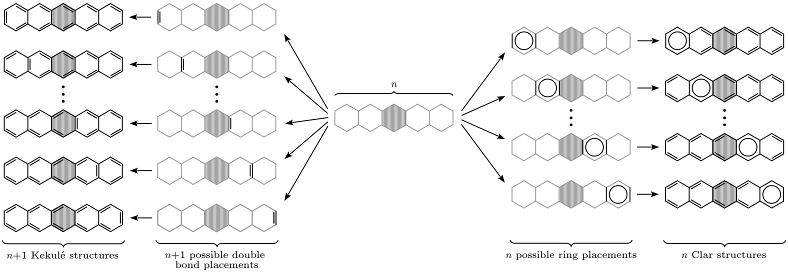


Figure 25. The polyacene $L(n)$ has only one interface, which is fully covered by one aromatic ring or one double interface bond, because $\mathrm{ord}(i_1) = 1$. Various placements of the covered interface bond(s) give rise to all possible Clar covers of $L(n)$. The shaded hexagon schematically represents a segment of width $n - 4$.

Example 24. The order of the only non-empty interface i_1 of a polyacene $L(n)$ is 1. In other words, the entire polyacene chain shown in Fig. 25, no matter how long, contains exactly one aromatic ring or one double interface bond. Combinatorially speaking, there are n available locations for the aromatic ring and $n+1$ available locations for the double interface bond, therefore

$$\mathrm{ZZ}(L(n)) = \underbrace{n \cdot x^1}_{\text{aromatic ring}} + \underbrace{(n+1) \cdot x^0}_{\text{double bond}} = n(x+1)+1.$$

Similar considerations will be used in a forthcoming paper to determine closed–form formulas of the Zhang–Zhang polynomials of regular strips.

Example 25. Consider the fenestrene $F(n,m)$ shown in Fig. 26. The fragments f_1, f_2, f_m and f_{m+1} of $F(n,m)$ are elementary fragments. All fragments in between are combined fragments, each consisting of two elementary fragments: $f_k = f'_k \cup f''_k$ for $k = 3, \ldots, m-1$. The interface i_1 has order 1.

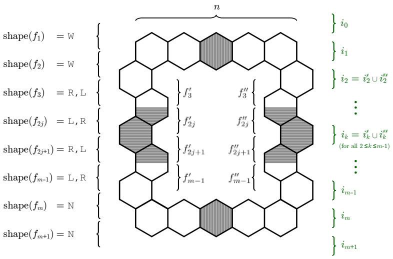


Figure 26. Fenestrene $F(n,m)$. The hatched sections are repeated $n-4$ and $\frac{1}{2}(m-5)$ times, respectively. The fragments f_k with $3 \leq k \leq m-1$ are combined: $f_k = f'_k \cup f''_k$. Theorems 3 and 4 apply to the elementary fragments of $F(n,m)$: f_1, f_2, f'_3, f''_3, …, f'_{m-1}, f''_{m-1}, f_m and f_{m+1}.

Let us denote the upper interface of f'_3 and f''_3 by i'_2 and i''_2, respectively. Likewise, denote the lower interface of each f'_k and f''_k by i'_k and i''_k, respectively. It is clear that $i_k = i'_k \cup i''_k$ and consequently $\mathrm{ord}(i_k) = \mathrm{ord}(i'_k) + \mathrm{ord}(i''_k)$ for all $k = 2, \ldots, m-1$. In the first step, the First Rule is invoked to determine the interface orders. Clearly, the interfaces i_1 and i_2 have the orders $\mathrm{ord}(i_1) = 1$ and $\mathrm{ord}(i_2) = 2$. Considering the situation from the perspective of the fragment f_3, the interface i_2 is naturally split into the upper interfaces i'_2 and i''_2 of f'_3 and f''_3. The interface order can be distributed between i'_2 and i''_2 in three different ways:

1. $\mathrm{ord}(i'_2) + \mathrm{ord}(i''_2) = 2 + 0$, signifying two double bonds in i'_2.
2. $\mathrm{ord}(i'_2) + \mathrm{ord}(i''_2) = 1 + 1$, signifying one double bond or one aromatic ring in each of the interfaces i'_2 and i''_2.

3. $\mathrm{ord}(i'_2) + \mathrm{ord}(i''_2) = 0 + 2$, signifying two double bonds in i''_2.

Note now that all elementary fragments f'_k and f''_k (for $k = 3, \ldots, m-1$) have either the shape `R` or the shape `L`. Therefore, the First Rule shows that

$$\mathrm{ord}(i'_2) = \mathrm{ord}(i'_3) = \ldots = \mathrm{ord}(i'_{m-2}) = \mathrm{ord}(i'_{m-1})) \text{ and}$$

$$\mathrm{ord}(i''_2) = \mathrm{ord}(i''_3) = \ldots = \mathrm{ord}(i''_{m-2}) = \mathrm{ord}(i''_{m-1})).$$

The upper interface i_{m-1} of the fragment f_m is the union of i'_{m-1} and i''_{m-1}, and consequently $\mathrm{ord}(i_{m-1}) = \mathrm{ord}(i'_{m-1}) + \mathrm{ord}(i''_{m-1}) = \mathrm{ord}(i'_2) + \mathrm{ord}(i''{}_2) = 2$. Finally, it is clear that the interfaces i_m and i_{m+1} have the orders $\mathrm{ord}(i_m) = 1$ and $\mathrm{ord}(i_{m+1}) = 0$.

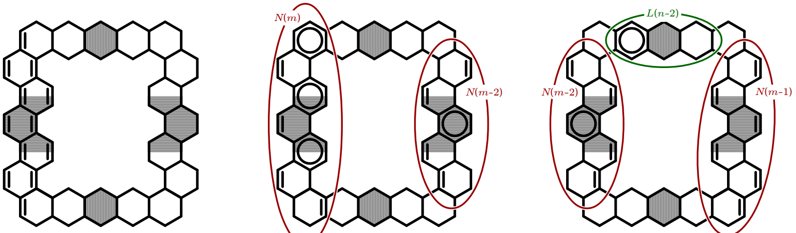
These observations can be used to determine the ZZ polynomial of $F(n, m)$. There are three fundamentally different ways of of distributing the covered interface bonds in i_2 between i'_2 and i''_2, given as cases 1–3 above. Let us consider each case more closely.

1. Assume that both double bonds of i_2 are located in i'_2. We see from the above considerations that $\mathrm{ord}(i'_k) = 2$ and $\mathrm{ord}(i''_k) = 0$ for all $2 \leq k \leq m-1$. Since both bonds in i_2 and i'_{m-1} are double bonds, it follows from the Second Rule given in Theorem 4 that the first interface bond in i_1 and i_m must be a double bond; all other bonds in i_1 and i_m are single bonds due to $\mathrm{ord}(i_1) = \mathrm{ord}(i_m) = 1$. With this, the covering orders of all interface bonds are decided, meaning that case 1 allows only one Clar cover, which is shown in the first part of Fig. 27.

2. Assume that i'_2 and i''_2 each contain one double bond, which implies $\mathrm{ord}(i'_k) = \mathrm{ord}(i''_k) = 1$ for $1 < k < m$, meaning that the vertical parts on the left and right side of the fenestrene act like single zigzag chains $N(l)$ with a length l of at least $m-2$; examples for this behaviour are given in the last two parts of Fig. 27. (It is easy to see that single zigzag chains always have interface order 1, compare also [38].) Each of the interfaces i_1 and i_m contains either one double bond or one pair of aromatic bonds, which can be positioned in three different ways:

    a. The covered interface bond(s) are located within the first two interface bonds, extending the left single zigzag chain by one hexagon.

    b. The covered interface bond(s) are located within the last two interface bonds, extending the right single zigzag chain by one hexagon.



Case 1

Case 3, a in i_1
a in i_m

Case 3, c in i_1
b in i_m

Figure 27. Depending on the position of the covered interface bond(s) in i_2, the Clar cover of the fenestrene $F(n,m)$ is either uniquely defined (cases 1 and 2), or can be interpreted as some combination of Clar covers of single zigzag chains $N(m')$ and/or polyacenes $L(n-2)$ (cases 3 a–c).

c. None of the above. In this case, the interface bonds behave as if they were part of a polyacene $L(n-2)$ in which the first and last interface bond are not allowed to be double bonds (which would count towards case a or b).

3. Assume that both double bonds of i_2 are located in i_2''. Mirrored versions of the considerations from case 1 apply; exactly one such Clar cover is possible.

Considering all possible combinations of these cases leads to the following ZZ polynomial of a fenestrene $F(n,m)$, in agreement with [11,13] (for the sake of brevity, we write N_m instead of ZZ$(N(m))$, etc., and (x,y) for „Case x in interface i_1, Case y in i_m"):

$$F_{n,m} = \underbrace{2}_{\text{Cases 1, 2}} + \underbrace{\underbrace{2\,N_m N_{m-2}}_{\text{(a,a) and (b,b)}} + \underbrace{2\,N_{m-1}^2}_{\text{(a,b) and (b,a)}} + \underbrace{4\,N_{m-1}N_{m-2}(L_{n-2}-2)}_{\text{(a,c), (b,c), (c,a) and (c,b)}} + \underbrace{N_{m-2}^2(L_{n-2}-2)^2}_{\text{(c,c)}}}_{\text{Case3}},$$

Note that, while of course the result of the derivation shown here is the same as that of the derivation in [13], the process is rather different. This new way of determination of ZZ polynomials through combinatorial considerations will, in subsequent publications, be used to derive new results for larger classes of benzenoids, such as regular benzenoid strips.

Example 26. Let us consider now some arbitrary benzenoid $\boldsymbol{B}$ consisting of K fragments. The ZZ polynomial of $\boldsymbol{B}$ can be computed using an algorithm that is a straightforward generalization of the method presented earlier for single zigzag chains [38,39]. The algorithm involves a number of steps. In the first step, one uses the First Rule to determine the orders of the interfaces i_0, i_1, …, i_K. In the second step, for each of the interfaces of

$\boldsymbol{B}$, one creates a complete list of interface bond coverings corresponding to the interface orders determined in step one. The next step involves establishing a connectivity network between coverings of consecutive interfaces; we say that two coverings, one of the interface i_{k-1} and one of i_k, are connected if there exists a covering of the fragment f_k compatible with the interface coverings. In practice, it is never necessary to identify an appropriate covering of the fragment f_k, because it is sufficient to verify that the interface coverings satisfy the conditions of the Third Rule. The connectivity network can be represented in a form of an directed connectivity graph, with vertices corresponding to the interface coverings and edges corresponding to the fragment coverings. The orientation of each edge is such that it points from a covering of i_{k-1} to a covering of i_k. In addition, the (empty) covering of the empty interface i_0 is referred to as Start and the (empty) covering of the empty interface i_K is referred to as End. Finally, in the last step, the connectivity graph can be used to compute the ZZ polynomial of $\boldsymbol{B}$ as the sum of monomials x^a over all possible paths from Start to End, where a stands for the number of aromatic rings along a given path.

The connectivity graph can be utilized also in many other useful ways.

- A path from Start to End represents uniquely some Clar cover of $\boldsymbol{B}$.
- The full set of paths on the connectivity graph from Start to End corresponds to the full set of Clar covers of $\boldsymbol{B}$.
- The total number of Clar covers of $\boldsymbol{B}$ corresponds to the number of possible paths on the connectivity graph from Start to End.
- A path on the connectivity graph from Start to End passing only through interface coverings without aromatic rings represents uniquely some Kekulé structure of $\boldsymbol{B}$.
- The full set of paths on the connectivity graph from Start to End passing only through interface coverings without aromatic rings corresponds to the full set of Kekulé structures of $\boldsymbol{B}$.
- The total number of Kekulé structures of $\boldsymbol{B}$ corresponds to the number of possible paths on the connectivity graph from Start to End passing only through interface coverings without aromatic rings.

- Non-Kekuléan character of $\boldsymbol{B}$ reveals itself by the fact that the vertices Start and End are disconnected.

We feel that it instructive to illustrate these rather abstract ideas with a simple example. Let us consider the benzenoid $\boldsymbol{B} = M(2,2)$ for this purpose. The three examples below demonstrate how to construct the connectivity graph for $M(2,2)$, how to use it for determining the total number of Clar covers in $M(2,2)$, and finally, how to use it for computing the ZZ polynomial of $M(2,2)$.

Example 27. The parallelogram $M(2,2) =$  has three nonempty interfaces with the orders $\mathrm{ord}(i_1) = \mathrm{ord}(i_3) = 1$ and $\mathrm{ord}(i_2) = 2$. To construct the connectivity graph of $M(2,2)$ shown in Fig. 28, first we generate all the possible coverings of these interfaces with appropriate orders. The interfaces i_1 and i_3 have three coverings each, and the interface i_2 has five coverings. We distribute these coverings in horizontal rows, beginning with the (empty) covering Start of the interface i_0 in the first row, continuing with the

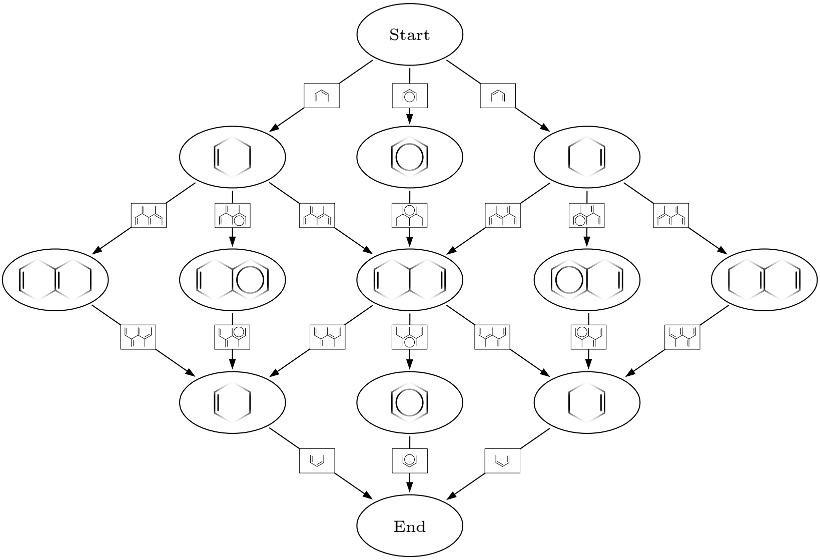


Figure 28. The connectivity graph—here constructed for $M(2,2)$—consists of vertices corresponding to the coverings of the interfaces and edges corresponding to the coverings of the fragments. The coverings of the same interface are distributed in the same horizontal row. The vertices Start and End correspond to the empty interfaces i_0 and i_K.

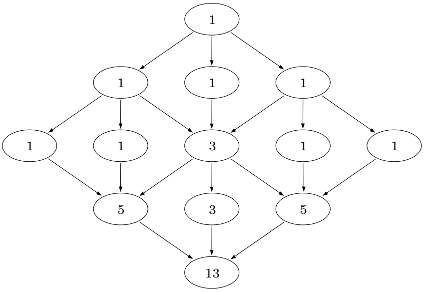
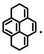


Figure 29. The weight of each vertex in the connectivity graph for $\boldsymbol{B}$ is defined as the number of distinct paths leading to it from the vertex Start. In this way, the weight of the vertex End is identical with the number of Clar covers of $\boldsymbol{B}$. These ideas, applied to the connectivity graph of $M(2,2)$ shown in Fig. 28, lead to the conclusion that $M(2,2)$ has 13 distinct Clar covers.

coverings of the interface i_1 in the second row, coverings of i_2 in the third row, and coverings of i_3 in the fourth row, we finish with the (empty) covering End of the interface i_4 in the last row. The edges of the $M(2,2)$ connectivity graph are generated in agreement with the conditions of the Third Rule. For example, the covering  of the interface i_1 is connected in Fig. 28 to the covering  of the interface i_2, because the covered aromatic bonds in i_1 are flanked on both sides by double bonds in i_2 and because the middle bond in i_2 is not covered as required by the condition (a) of Theorem 5. In this way, the conditions of the Third Rule are satisfied and the edge exists. In fact, it is quite straightforward to identify the valid covering  of the fragment f_2 which incorporates both interface coverings. Each edge is depicted in Fig. 28 with an arrow pointing from a covering of i_{k-1} to a covering of i_k; in addition, to convince the reader that each edge is legitimately placed, a small drawing of the fragment covering compatible with both interface coverings is depicted at the center of each arrow. This completes the construction of the connectivity graph for $M(2,2)$. Now, every path from Start to End corresponds to some Clar cover of $M(2,2)$. For example, the path crossing the rightmost vertices of the connectivity graph in Fig. 28 corresponds to the Clar cover .

Example 28. The connectivity graph shown in Fig. 28 can be readily used for computing the total number of Clar covers of $M(2,2)$. To do this, we assign a weight to each vertex following two easy rules: (i) the Start vertex is initialized with a weight of 1, (ii) the weight of every other vertex is computed as the sum of weights of the predecessor

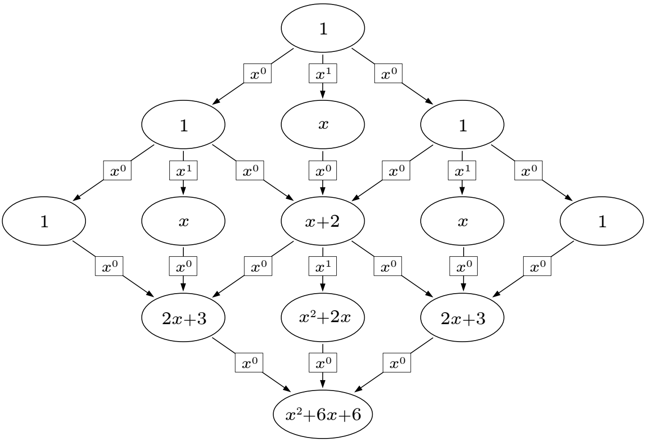


Figure 30. Initializing the weight of the Start vertex with 1 and propagating it all the way down along the connectivity graph of $\boldsymbol{B}$ to the End vertex produces the ZZ polynomial of $\boldsymbol{B}$ if one uses the following propagation rules: (*i*) every edge multiplies the weight of the vertex it originates from by its own weight, (*ii*) every vertex sums over all the incoming edges. The weight x^a of each edge indicates the number a of aromatic rings of the vertex it terminates at. For $M(2,2)$, propagating the weights all the way down through the depicted connectivity graph produces the ZZ polynomial of $M(2,2)$.

vertices. Following these rules, it is straightforward to assign the weights to all vertices of the connectivity graph as it is shown in Fig. 29. The weight of the End vertex is found to be 13, which signifies that $M(2,2)$ has exactly 13 distinct Clar covers.

Example 29. The determination of the ZZ polynomial of $M(2,2)$ using its connectivity graph follows closely the determination of the total number of Clar covers discussed in Example 28. The only difference concerns additional weights assigned to the edges of the connectivity graph. The weight of the edge connecting a covering of i_{k-1} with a covering of i_k is given by the factor x^a, where a is the number of aromatic rings in the covering of i_k. For example, the weight of the edge connecting the covering ⏣ of the interface i_1 with the covering ⬡⬡ of the interface i_2 is x^0, because ⬡⬡ contains 0 aromatic rings. Similarly, the weight of the edge connecting the covering ⬡⬡ of the interface i_2 with the covering ⏣ of the interface i_3 is x^1, because ⏣ contains 1 aromatic ring. Now, as in the previous example, every path on the connectivity graph shown in Fig. 30 corresponds to a Clar cover of $M(2,2)$, and the order of this Clar cover (i.e., the number of aromatic rings in it) can be easily computed by multiplying the factors x^a along this path. Determination of the ZZ polynomial of $M(2,2)$ can be now achieved as follows. The Start vertex is initialized with the weight 1. The weight of every vertex is propagated to the next vertex by multiplying it by the weight of the edge; if a vertex has more than one arrow pointing toward it, then its weight is calculated as a sum over all the incoming arrows. Then, the weight of the End vertex determined in this way is automatically equal to the Zhang-Zhang polynomial $\mathrm{ZZ}\left(M(2,2),x\right) = x^2+6x+6$. Note that substituting $x=1$ automatically assigns all edge weights to 1 and reproduces the total number of Clar covers of $M(2,2)$ as $\mathrm{ZZ}\left(M(2,2),1\right) = 13$, making the previous Example 28 obsolete.

The presented ideas are general and can be applied for determination of ZZ polynomials of arbitrary benzenoids. The efficiency of the underlying algorithm is higher than the efficiency of the previously reported algorithms [12, 13, 29] and we are currently working on its robust implementation to provide the community with an efficient tool for computing ZZ polynomials of large pericondensed benzenoids. In some situations, however, it is preferred to determine the ZZ polynomials not following the general algorithm introduced above, particularly if one aims at discovering a closed-form ZZ polynomial formula applicable to a whole family of structured benzenoids. Two such situations are discussed in the forthcoming papers, where we apply the interface theory of benzenoids for computing closed form ZZ polynomials for n-tier regular strips and analyzing and enumerating the Clar covers of various families of fenestrene benzenoids.

6 Conclusion

We present here a collection of basic applications of the recently introduced interface theory of benzenoids [41]. The selected examples have mainly didactic function and are designed to familiarize the reader with the application of the interface theory framework to practical problems in chemical graph theory. The presented material starts with a brief exposition of the *basic rules* of the interface theory in terms of benzenoid fragments and interfaces mediating neighbouring fragments. The *First Rule* determines interface covering orders and introduces a number of straightforward applications of interface theory, such as detecting a non-Kekuléan or essentially disconnected character of many benzenoids or computing an upper limit for their Clar numbers. The *Second* and *Third Rule* provide us with further tools permitting to discern whether or not *any* given benzenoid $\boldsymbol{B}$ is

Kekuléan and give rise to algorithms allowing to find its Clar number, to construct any possible Clar cover of $\boldsymbol{B}$, to determine the total number of Clar covers for $\boldsymbol{B}$, as well as to compute its ZZ polynomial. The latter tasks are most conveniently performed by constructing the so-called connectivity graph of $\boldsymbol{B}$, for which every oriented path from Start to End encodes a distinct Clar cover of $\boldsymbol{B}$. In this way, the whole set of Clar covers simply corresponds to the totality of paths from Start to End on the connectivity graph. The total number of Clar covers and the ZZ polynomial of $\boldsymbol{B}$ can be readily computed as the weight of the vertex End of the connectivity graph in the way described in Examples 28 and 29, respectively. These ideas lead naturally to a robust implementation of the connectivity graphs in form of an automatized computer program to provide the community with an efficient tool for computing ZZ polynomials; work along this line is in progress. The presented here basic applications of interface theory will be further illustrated by more involved, combinatorial applications leading to a novel way of deriving Zhang–Zhang polynomials for various families of benzenoids and finding closed form formulas of ZZ polynomials for the n-tier regular strips. We hope that the presented here appetizing morsels of applied interface theory will stimulate broader scientific interest in its further applications to various graph theoretical problems [4, 5, 8, 25, 51, 60].

7 Open problems

The Clar theory of basic benzenoids slowly enters into its maturity with closed-form formulas for the ZZ polynomials known for most classes of basic benzenoids. The two important missing components of the general theory are the closed-form formulas for the ZZ polynomials of hexagonal flakes $O(k, m, n)$ and of oblate rectangles $Ob(n, m)$.

Another topic that was just recently initiated is the determination of ZZ polynomials (and generally: classification of Clar covers) for complex benzenoids obtained by merging or overlapping of smaller, regular-shape benzenoids with a well-understood structure of Clar covers. This topic brings about a natural question, that is, whether the John-Sachs theory of Kekulé structures—based on the determination of the total number of Kekulé structures of some benzenoid $\boldsymbol{B}$ by finding all of its monotonic subgraphs $\boldsymbol{b}_{ij}$, computing $K\{\boldsymbol{b}_{ij}\}$, and arranging them in a determinant—can be generalized to the world of Clar covers. We have recently discovered numerous numerical results, which we plan to communicate soon, that suggest that this indeed might be possible.

Another attractive avenue in the development of the Clar theory is writing an efficient computer code related to the communicated here interface theory and possibly based on the Algorithm 1 in [41]. The existing ZZDecomposer algorithm is based on the decomposition scheme, which, for large pericondensed benzenoids, becomes prohibitively slow. We anticipate that the code based on the interface theory—or even better: on the merge of both theories—would perform much better for these large pericondensed benzenoids. We believe that an initial dissection of a large benzenoid into smaller fragments using the interface theory and subsequent recursive decomposition of the smaller fragments might be the optimal strategy for determination of ZZ polynomials.

Finally, we would like to interest the reader in the communicated here connectivity graphs for benzenoid interfaces. The connectivity graphs have been introduced in our previous work [38] in three different forms. It seems to us that the interface connectivity graph is the most interesting and its properties can be used to discover many important properties of benzenoids. One could for example study the adjacency matrix associated with this graph and try to connect it to the number of Kekulé structures, the number of Clar structures, or the ZZ polynomial of a given benzenoid. The connectivity graphs (particularly the reduced ones) produce also completely new recurrence relations that can be used for determination of ZZ polynomials. None of these topics has been elucidated in the literature.

Acknowledgment: This work was financially supported by Ministry of Science and Technology of Taiwan (MOST108-2113-M-009-010-MY3) and the Center for Emergent Functional Matter Science of National Chiao Tung University from the Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE), Taiwan.

References

[1] M. B. Ahmadi, E. Farhadi, V. A. Khorasani, On computing the Clar number of a fullerene using optimization techniques, *MATCH Commun. Math. Comput. Chem.* **75** (2016) 695–701.

[2] M. Antić, B. Furtula, S. Radenković, Aromaticity of nonplanar fully benzenoid hydrocarbons, *J. Phys. Chem. A* **121** (2017) 3616–3626.

[3] A. T. Balaban, Using Clar sextets for two- and three-dimensional aromatic systems, *Phys. Chem. Chem. Phys.* **13** (2011) 20649–20658.

[4] N. Bašić, I. Estélyi, R. Škrekovski, N. Tratnik, On the Clar number of benzenoid graphs, *MATCH Commun. Math. Comput. Chem.* **80** (2018) 173–188.

[5] E. R. Bérczi-Kovács, A. Bernáth, The complexity of the Clar number problem and an exact algorithm, *J. Math. Chem.* **56** (2018) 597–605.

[6] S. Brezovnik, N. Tratnik, P. Žigert Pleteršek, Resonantly equivalent catacondensed even ring systems, *MATCH Commun. Math. Comput. Chem.* **82** (2019) 625–638.

[7] J. A. Carr, X. F. Wang, D. Ye, Packing resonant hexagons in fullerenes, *Discr. Optim.* **13** (2014) 49–54.

[8] J. Chapman, J. Foos, E. J. Hartung, A. Nelson, A. Williams, Pairwise disagreements of Kekulé, Clar, and Fries numbers for benzenoids: A mathematical and computational investigation, *MATCH Commun. Math. Comput. Chem.* **80** (2018) 186–206.

[9] R. S. Chen, S. J. Cyvin, B. N. Cyvin, Recognition of essentially disconnected benzenoids, *MATCH Commun. Math. Comput. Chem.* **25** (1990) 71–81.

[10] R. S. Chen, F. J. Zhang, Coronoid systems with fixed bonds, *J. Mol. Struct.* **403** (1997) 237–243.

[11] C. P. Chou, Y. T. Li, H. A. Witek, Zhang–Zhang polynomials of various classes of benzenoid systems, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 31–64.

[12] C. P. Chou, H. A. Witek, An algorithm and FORTRAN program for automatic computation of the Zhang–Zhang polynomial of benzenoids, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 3–30.

[13] C. P. Chou, H. A. Witek, ZZDecomposer: A graphical toolkit for analyzing the Zhang–Zhang polynomials of benzenoid structures, *MATCH Commun. Math. Comput. Chem.* **71** (2014) 741–764.

[14] A. Ciesielski, T. M. Krygowski, M. K. Cyrański, A. T. Balaban, Defining rules of aromaticity: a unified approach to the Hückel, Clar and Randić concepts, *Phys. Chem. Chem. Phys.* **13** (2011) 3737–3747.

[15] E. Clar, *The Aromatic Sextet*, Wiley, London, 1972.

[16] S. J. Cyvin, J. Brunvoll, B. N. Cyvin, Search for concealed non–Kekuléan benzenoids and coronoids, *J. Chem. Inf. Model.* **29** (1989) 236–244.

[17] S. J. Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer, Berlin, 1988.

[18] S. J. Cyvin, I. Gutman, Topological properties of benzenoid systems. XLIV. Obvious and concealed non–Kekuléan benzenoids, *J. Mol. Struct. (Theochem)* **150** (1987) 157–169.

[19] T. Došlić, Fullerene graphs with exponentially many perfect matchings, *J. Math. Chem.* **41** (2007) 183–192.

[20] T. Došlić, Finding more perfect matchings in leapfrog fullerenes, *J. Math. Chem.* **45** (2009) 1130–1136.

[21] Y. Gao, Q. L. Li, H. P. Zhang, Fullerenes with the maximum Clar number, *Discr. Appl. Math.* **202** (2016) 58–69.

[22] Y. Gao, H. P. Zhang, The Clar number of fullerenes on surfaces, *MATCH Commun. Math. Comput. Chem.* **72** (2014) 411–426.

[23] Y. Gao, H. P. Zhang, Sharp upper bounds on the Clar number of fullerene graphs, *Discuss. Math. Graph Theory* **38** (2018) 155–163.

[24] M. Gordon, W. H. T. Davison, Theory of resonance topology of fully aromatic hydrocarbons. 1, *J. Chem. Phys.* **20** (1952) 428–435.

[25] J. E. Graver, E. J. Hartung, Kekuléan benzenoids, *J. Math. Chem.* **52** (2014) 977–989.

[26] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989.

[27] I. Gutman, Clar formulas and Kekulé structures, *MATCH Commun. Math. Comput. Chem.* **17** (1985) 75–90.

[28] I. Gutman, S. J. Cyvin, Recognizing Kekuléan benzenoid molecules, *J. Mol. Struct. (Theochem)* **138** (1986) 325–331.

[29] I. Gutman, B. Furtula, A. T. Balaban, Algorithm for simultaneous calculation of Kekulé and Clar structure counts, and Clar number of benzenoid molecules, *Polycyc. Aromat. Comp.* **26** (2006) 17–35.

[30] P. Hansen, M. L. Zheng, A linear algorithm for perfect matching in hexagonal systems, *Discr. Math.* **122** (1993) 179–196.

[31] E. Hartung, Fullerenes with complete Clar structure, *Discr. Appl. Math.* **161** (2013) 2952–2957.

[32] E. J. Hartung, Clar chains and a counterexample, *J. Math. Chem.* **52** (2014) 990–1006.

[33] F. Kardoš, D. Král', J. Miškuf, J.-S. Sereni, Fullerene graphs have exponentially many perfect matchings, *J. Math. Chem.* **46** (2009) 443–447.

[34] A. Kekulé, Untersuchungen über aromatische Verbindungen, *Liebigs Ann. Chem.* **137** (1866) 129–196.

[35] L. Kerong, S. J. Cyvin, B. N. Cyvin, R. S. Chen, Recognizing essentially disconnected benzenoids with fixed double bonds, *Appl. Math. J. Chinese Univ.* **9** (1994) 299–305.

[36] S. Klavžar, P. Žigert, I. Gutman, Clar number of catacondensed benzenoid hydrocarbons, *J. Mol. Struct. (Theochem)* **586** (2002) 235–240.

[37] P. C. B. Lam, W. C. Shiu, H. P. Zhang, Elementary blocks of plane bipartite graphs, *MATCH Commun. Math. Comput. Chem.* **49** (2003) 127–137.

[38] J. Langner, H. A. Witek, Connectivity graphs for single zigzag chains and their application for computing ZZ polynomials, *Croat. Chem. Acta* **90** (2017) 391–400.

[39] J. Langner, H. A. Witek, Algorithm for generating generalized resonance structures of single zigzag chains based on interface theory, *J. Math. Chem.* **56** (2018) 1393–1406.

[40] J. Langner, H. A. Witek, Equivalence between Clar covering polynomials of single zigzag chains and tiling polynomials of $2\times n$ rectangles, *Discr. Appl. Math.* **243** (2018) 297–303.

[41] J. Langner, H. A. Witek, Interface theory of benzenoids, *MATCH Commun. Math. Comput. Chem.*, in press.

[42] J. A. Montoya, L. V. Cadavid, Computing the Clar number of nanotubes and other fullerenes, *J. Math. Nanosci.* **8** (2018) 77–89.

[43] O. E. Polansky, I. Gutman, Graph–theoretical treatment of aromatic hydrocarbons V: The number of Kekulé structures in an all–benzenoid aromatic hydrocarbon, *MATCH Commun. Math. Comput. Chem.* **8** (1980) 269–290.

[44] M. Randić, Novel insight into Clar's aromatic π-sextets, *Chem. Phys. Lett.* **601** (2014) 1–5.

[45] M. Randić, A. T. Balaban, Local aromaticity and aromatic sextet theory beyond Clar, *Int. J. Quantum Chem.* **118** (2018) 1–21.

[46] H. Sachs, Kekulé count in tubular hydrocarbons, *MATCH Commun. Math. Comput. Chem.* **33** (1996) 169–241.

[47] J.-S. Sereni, M. Stehlík, On the sextet polynomial of fullerenes, *J. Math. Chem.* **47** (2010) 1121–1128.

[48] R. Q. Sheng, S. J. Cyvin, I. Gutman, Remarks on Kekuléan and non-Kekuléan benzenoid hydrocarbons, *J. Mol. Struct. (Theochem)* **187** (1989) 285–289.

[49] L. J. Shi, H. P. Zhang, Counting Clar structures of (4, 6)-fullerenes, *Appl. Math. and Comput.* **72** (2019) 559–574.

[50] D. Ye, H. P. Zhang, Extremal fullerene graphs with the maximum Clar number, *Discr. Appl. Math.* **157** (2009) 3152–3173.

[51] S. H. Zhai, D. Alrowaili, D. Ye, Clar structures vs Fries structures in hexagonal systems, *Appl. Math. Comput.* **329** (2018) 384–394.

[52] F. J. Zhang, X. F. Guo, H. P. Zhang, Advances of Clar's aromatic sextet theory and Randić's conjugated circuit model, *Open Org. Chem. J.* **5** (2011) 87–111.

[53] F. J. Zhang, H. P. Zhang, Y. T. Liu, The Clar covering polynomial of hexagonal systems II, *Chin. J. Chem.* **14** (1996) 321–325.

[54] F. J. Zhang, X. L. Li, H. P. Zhang, Hexagonal Systems with fixed bonds, *Discr. Appl. Math.* **47** (1993) 285–296.

[55] H. P. Zhang, The Clar covering polynomial of hexagonal systems with an application to chromatic polynomials, *Discr. Math.* **172** (1997) 163–173.

[56] H. P. Zhang, D. Ye, An upper bound for the Clar number of fullerene graphs, *J. Math. Chem.* **41** (2007) 123–133.

[57] H. P. Zhang, F. J. Zhang, The Clar covering polynomial of hexagonal systems I, *Discr. Appl. Math.* **69** (1996) 147–167.

[58] H. P. Zhang, F. J. Zhang, The Clar covering polynomial of hexagonal systems III, *Discr. Math.* **212** (2000) 261–269.

[59] S. Zhou, H. P. Zhang, I. Gutman, Relations between Clar structures, Clar covers, and the sextet-rotation tree of a hexagonal system, *Discr. Appl. Math.* **156** (2008) 1809–1821.

[60] X. Q. Zhou, H. P. Zhang, Clar sets and maximum forcing numbers of hexagonal systems, *MATCH Commun. Math. Comput. Chem.* **74** (2015) 161–174.