Pairwise Disagreements of Kekule, Clar, and Fries Numbers for Benzenoids: A Mathematical and Computational Investigation

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PAIRWISE DISAGREEMENTS OF KEKULÉ, CLAR, AND FRIES NUMBERS FOR BENZENOIDS: A MATHEMATICAL AND COMPUTATIONAL INVESTIGATION

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Abstract. The Kekulé count, Fries number, and Clar number of a benzenoid are three measurements that are positively correlated with the stability of a benzenoid hydrocarbon. In this paper, we show that these parameters can disagree for benzenoids. That is, there exist pairs of benzenoids of the same size (same number of hexagons and vertices) such that one benzenoid is more stable according one measurement, while the other benzenoid is more stable according to another. We give smallest examples of pairs of benzenoids that have Kekulé-Fries, Kekulé-Clar, and Fries-Clar pairwise disagreements and show that the gaps between these disagreeing measurements can be arbitrarily large for each of the three pairs of parameters. We then initiate a computational investigation of all benzenoids of the same size on up to 13 hexagons. Among the billions of pairs of such benzenoids, we find that the proportion of those with a Kekulé-Fries, Kekulé-Clar, or Fries-Clar pairwise disagreement is relatively small. However, the proportions seem to rise steadily with the size of the benzenoid, and each proportion surpasses 3% in our largest test cases.

1. Introduction

A *benzenoid*, or *benzenoid hydrocarbon*, B, is a 2-connected plane graph which can be embedded in the hexagonal lattice. All faces are hexagons except for one outside face, all vertices are of degree 2 or 3 and degree-2 vertices can only occur on the boundary of the outside face. Three classic measurements that have been used to predict the stability of a particular benzenoid are the Kekulé count, the Fries number, and the Clar number. These three measurements form a natural progression both historically and in conceptual depth.

- Marckwald wrote the first paper on enumerating Kekulé structures for benzenoids in 1894 [11]. A *Kekulé structure* is a perfect matching of the edges of the graph, and corresponds to a double bond structure of the molecule. The *Kekulé count* is the number of perfect matchings in the associated graph, and we denote it by $K(B)$.

- The *Fries number* was introduced in 1927 by Karl Fries and is the maximum number of conjugated hexagons, or benzene rings (hexagons with 3 of their edges in the Kekulé structure), over all possible Kekulé structures in a benzenoid, denoted $F(B)$ [5].
- The *Clar number* was introduced by Erich Clar in 1972 and is the maximum number of independent benzene rings over all possible Kekulé structures, and we denote it by $C(B)$ [2].

In all cases a higher value is associated with a higher stability for the molecule. For example, Figure 1 illustrates two benzenoids with 7 hexagonal faces and 30 vertices. The benzenoid on the right scores higher in all three measures, and so it is predicted to be more stable. Not all benzenoids have a Kekulé structure (for example, a benzenoid can only have a perfect matching if it has an even number of vertices, and this criteria is not sufficient, see [17]). Benzenoids that have no Kekulé structures have a value of zero for all three parameters, and benzenoids that have at least one Kekulé structure are called *Kekuléan benzenoids*. This paper will only consider Kekuléan benzenoids, and thus we will refer to them simply as benzenoids. For further information on these background concepts we refer the reader to [3], [9], [14], [19].

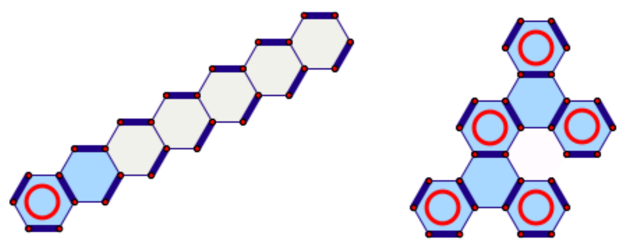

Figure 1. A pair of benzenoids in KFC agreement. The benzenoid on the left is the only (Kekuléan) benzenoid of this size that has: 8 or fewer Kekulé structures, a Fries number of 2 (or less) and a Clar number of 1 (or less), so it is the least stable of its size in all three measurements. The benzenoid B_2 on the right attains the largest possible values for its size in all three measurements as the only example with a highest Kekulé count of 41, as one of 23 benzenoids with a largest Fries number of 7 and one of 2 examples with a largest Clar number of 5. Blue faces show benzene rings contributing to the Fries number, circles show independent benzene rings contributing to the Clar number. One Kekulé structure is shown for each graph with thick edges.

All three of the KFC values are non-negative integers which generally grow as the number of hexagonal faces and vertices in the associated graph grows. For this reason, we define two benzenoids as having the same *size* if the have an equal number of vertices **and** an equal number of faces. We restrict our comparisons to benzenoids with the same size, as is the case in Figures 1-3.

This progression of KFC values has been accompanied by the implicit assumption that each subsequent measure has refined the previous. For example, two benzenoids may have the same Kekulé count, but one has a higher Fries number than the other, so it is more stable. In other words, the Fries number can be used as a tiebreaker between two benzenoids with the same Kekulé count, and similarly, the Clar number serves as a tiebreaker between two benzenoids with the same Fries number.

In this picture of reality the latter measurements enhance the earlier measurements, and the three measurements coexist in harmony. However, this picture overlooks the fact that the measurements can disagree or contradict each other. For example, consider the two benzenoids in Figure 2 each with 7 hexagonal faces and 30 vertices. The molecule on the left is more stable according to the Fries number, while the molecule on the right is more stable according to the Clar number.

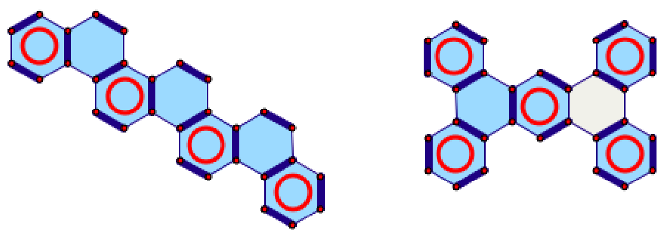

FIGURE 2. A Fries-Clar disagreement. The benzenoid on the left has 7 and 4 for its Fries and Clar numbers, respectively. The benzenoid on the right has 6 and 5 for its Fries and Clar numbers, respectively.

We refer to the situation given in Figure 2 as a *Fries-Clar disagreement* and we similarly define a *Kekulé-Fries disagreement* and a *Kekulé-Clar disagreement*. Collectively, these three types of disagreements are called *pairwise disagreements*. The *gap* of a pairwise disagreement is the minimum difference between the two measurements. In particular, the pair in Figure 2 has a gap of 1 because $\min\{|7-6|, |4-5|\} = \min\{1, 1\} = 1$. If two benzenoids do not form a pairwise disagreement, then we say they are in *KFC agreement*.

A researcher working in this field will likely be surprised that benzenoid pairs of the same size are not always in KFC agreement, and the authors of this article are unaware of any prior publication acknowledging this issue. However, once this reality is presented to a researcher he or she may be able to construct a suitable example by hand. For example, the pair shown in Figure 2 was constructed by Ivan Gutman shortly after learning that such disagreements can exist [8].

The authors' own investigation of this subject began with a computer search for the smallest benzenoids with pairwise disagreements. The outcome of this search is shown in Figure 3 for all three pairs of measurements. We note that the Fries-Clar disagreement in Figure 3 involves smaller benzenoids, but it is somewhat easier to understand the Fries-Clar disagreement in Figure 2.

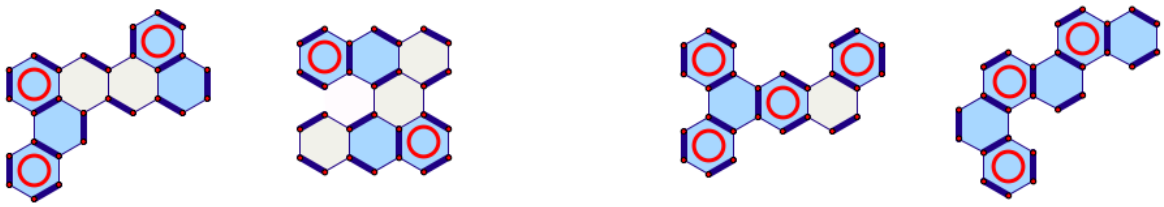

FIGURE 3. Smallest benzenoids with pairwise disagreements. Left: a smallest Fries-Clar disagreement and smallest Kekulé-Fries disagreement on 6 hexagons and 26 vertices with $F(B_1) = 5$, $C(B_1) = 4$, $K(B_1) = 22$ and $F(B_2) = 6$, $C(B_2) = 3$, $K(B_2) = 21$. Right: a smallest Kekulé-Clar disagreement on 7 hexagons and 28 vertices with $F(B_3) = 5$, $C(B_3) = 3$, $K(B_3) = 13$ and $F(B_4) = 4$, $C(B_2) = 2$, $K(B_4) = 16$. This is also a Fries-Kekulé disagreement.

For each of the disagreements in Figure 3, the gap is 1. Observe also that both of these pairs disagree on two parameters. More generally, if there is a disagreement between one pair of parameters, say a Fries-Clar disagreement, there also must either be a Kekulé-Fries disagreement or a Kekulé-Clar disagreement unless the Kekulé count for the two benzenoids is equal.

Once the existence of pairwise disagreements is established – by hand or by computer search – it then becomes natural to ask two additional questions:

1) How large of a gap can be created?
2) How often do pairwise disagreements occur?

Regarding the first question, we are able to show that pairwise disagreements can be arbitrarily large. In other words, if you provide a positive value x, then we can produce a pair of benzenoids with an equal number of vertices and an equal number of hexagons which achieve a gap of at least x. Moreover, this can be repeated for any pair of the three measurements. To achieve a result of this type we construct two pairs of infinite classes of benzenoids and calculate their KFC values. The first pair of families $Y_{m,t}$ and Z_n has an arbitrarily large Fries-Clar gap, and these families are discussed in Section 2. The second pair of families W_n and V_m has an arbitrarily large

Kekulé-Fries gap and Kekulé-Clar gap, and these families are discussed in Section 3. All four of these families are *catacondensed benzenoids*, which are benzenoids without internal vertices. A catacondensed benzenoid with h hexagons has $v = 4h+2$ vertices, so pairs that have the same number of hexagons always have the same size.

Regarding the second question, we find that the proportion of Kekulé-Fries, Kekulé-Clar, and Fries-Clar pairwise disagreements is relatively small, but seems to steadily rise with the size of the benzenoid. This comment is the result of a computational investigation which examined all pairs of benzenoids of the same size on up to 13 hexagons. We outline our computational approach in Sections 4 and 5, and then provide results in the form of tables in Sections 6 and 7.

2. Arbitrarily large gap for Fries vs Clar

We achieve an arbitrarily large gap between the Fries and Clar numbers using two classes of benzenoids, "zig-zags" and "zippers." This Fries-Clar gap grows linearly in terms of their numbers of hexagons. The class of zig-zags, Z_n, with n hexagons are well-known, as are their Kekulé count, Fries number and Clar number (see Figure 4).

Remark 1. *For a zig-zag Z_n on n hexagons, the Fries number is n and the Clar number is $\lceil \frac{n}{2} \rceil$.*

Proof. In a zig-zag with n hexagons, a Kekulé structure in which every face is a benzene ring is possible, so the Fries number is n. In this case, every other face is an independent benzene ring, so the Clar number for a zig-zag Z_n is $\lceil \frac{n}{2} \rceil$. □

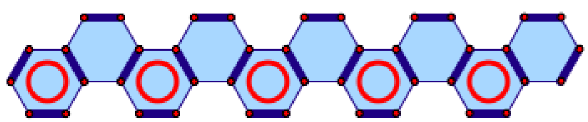

FIGURE 4. Zigzag Z_{10} with a Kekulé structure.

We introduce the class of zippers: The zipper $Y_{m,t}$ has $3m$ faces in a "zipper" pattern and a tail of length t in the direction of the zipper. We can think of a zipper as a zig-zag with an extra hexagon attached to every other face in the zig-zag, followed by a tail of t hexagons. Figure 5 shows $Y_{4,6}$.

Lemma 1. *For a zipper $Y_{m,t}$ on $3m + t$ hexagons, the Fries number is $3m + 2$ and the Clar number is $2m + 1$.*

Proof. For each set of three hexagons before the tail, all three can be benzene rings, and at most two of the three can be independent benzene rings. At most two of the faces in the tail can be benzene rings, and if there are two, they are adjacent. Thus the Fries number of $Y_{m,t}$ is $3m+2$, and the Clar number of $Y_{m,t}$ is $2m+1$. A Kekulé structure that achieves these values is shown on the right in Figure 5, and it is clear that the values hold in the general case. □

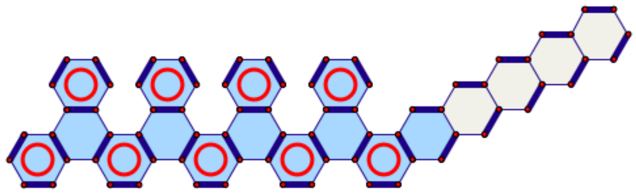

FIGURE 5. Zipper $Y_{4,6}$ with a Kekulé structure.

We will now utilize these results to find arbitrarily large Fries-Clar gaps. We begin with a zig-zag Z_{3m+t} so that the number of hexagons is the same as in the zipper $Y_{m,t}$. Then the zig-zag will have a larger Fries number, and this difference increases as t, the length of the tail on the zipper, increases. The section of the zipper before the tail has a higher proportion of Clar faces than the zig-zag. In order to maximize these two differences simultaneously, we choose the length of the tail of the zipper to be $t = \lceil \frac{m}{3} \rceil$.

Theorem 1. *The Fries-Clar disagreement for zig-zags $Z_{3m+\lceil \frac{m}{3} \rceil}$ and zippers $Y_{m,\lceil \frac{m}{3} \rceil}$ grows linearly in terms of their numbers of hexagons, $3m + \lceil \frac{m}{3} \rceil$.*

Proof. The Fries number for the zig-zag $Z_{3m+\lceil \frac{m}{3} \rceil}$ is $3m+\lceil \frac{m}{3} \rceil$ while the Fries number for the zipper is $3m+2$, giving a difference of $\lceil \frac{m}{3} \rceil - 2$ in favor of the zig-zags. The Clar number for the zig-zag $Z_{3m+\frac{m}{3}}$ is $\lceil \frac{3m+\lceil \frac{m}{3} \rceil}{2} \rceil \leq \frac{5m}{3}+2$ and the Clar number for the zipper $Y_{m,t}$ is $2m+1$, giving a difference of at least $\frac{m}{3} - 1$ in favor of the zippers. So the Fries-Clar disagreement gap is at least $\lceil \frac{m}{3} \rceil - 2$. Thus the gap for the Fries-Clar disagreement grows linearly in terms of m (and also linearly in terms of the number of hexagons and the number of vertices for each benzenoid).

□

3. ARBITRARILY LARGE GAP FOR CLAR VS KEKULÉ AND FRIES VS KEKULÉ

We use two classes of graphs, zig-zags with tails, $W_{n,t}$, and chains with one kink, V_m, to find arbitrarily large gaps between the Kekulé count and the Fries number and between the Kekulé count and the Clar number. In these cases, the growth is quadratic in terms of the number of their numbers of hexagons.

Let $W_{n,t}$ be a zig-zag of n hexagons followed by a tail of t hexagons. Figure 6 shows $W_{7,6}$.

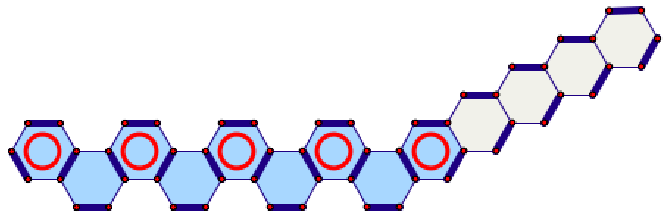

FIGURE 6. Zigzag with tail, $W_{7,6}$, with a Kekulé structure.

Remark 2. *The Fries number of* $W_{n,t}$ *is* $n+2$*, the Clar number is* $\lfloor \frac{n+3}{2} \rfloor$*, and the Kekulé count is* $tF_{n+2} + F_{n+1}$*, where* F_n *denotes the* n^{th} *term in the Fibonacci sequence.*

Proof. Every face of the zig-zag can be a benzene ring while at most two faces of the tail can be, and these faces must be adjacent. Thus the Fries number of $W_{n,t}$ is $n+2$ and the Clar number is $\lfloor \frac{n+3}{2} \rfloor$. Gordon and Davison [6] showed that the Kekulé count of a zig-zag with n hexagons is F_{n+2}, the $(n+2)^{nd}$ term in the Fibonacci sequence (where $F_1 = F_2 = 1$ and $F_{n+2} = F_n + F_{n+1}$). Using their general algorithm for unbranched chains, it can be shown that the Kekulé count of $W_{n,t}$ is $tF_{n+2} + F_{n+1}$. □

Define the class of benzenoids V_m to be a path of m hexagons followed by a path of $m-1$ hexagons after a turn. Figure 7 shows V_7.

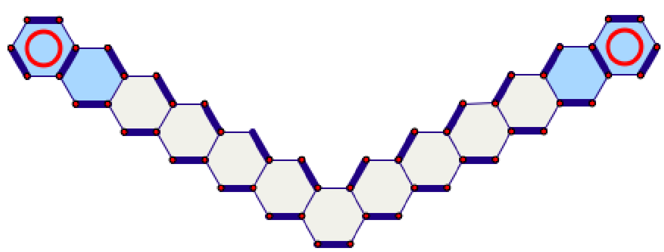

FIGURE 7. V_7 with a Kekulé structure.

Remark 3. *Let* V_m *be a path of* m *hexagons followed by a path of* $m-1$ *hexagons after a turn. Then the number of Kekulé structures is* m^2+1*, the Fries number is 4, and the Clar number is 2.*

Proof. For any linear chain, at most two faces can be benzene rings, and these faces must be adjacent. Thus for a benzenoid V_m, the Fries number is 4 and the Clar number is 2 (see Figure 7). Gordon and Davison's algorithm [6] allows us to calculate the Kekulé count to be m^2+1.

□

Clearly, as n increases, the Clar and Fries numbers for W_n are arbitrarily larger than the Clar and Fries numbers for V_m. We want to show that for choices of t and m as functions of n, the Kekulé count for V_m is arbitrarily larger than the Kekulé count for $W_{n,t}$.

Theorem 2. *Let n be odd and define $W_n = W_{n,2^n}$. Let $m = \frac{2^n+n+1}{2}$. Then W_n and V_m have both Kekulé-Fries and Kekulé-Clar disagreements, and growth of the gap is quadratic on $h = 2^n + n$, their numbers of hexagons.*

Proof. Define $W_n = W_{n,2^n}$ where n is odd. Then W_n has $2^n + n$ hexagons, and $K(W_n) = 2^n F_{n+2} + F_{n+1}$. Let $m = \dfrac{2^n + n + 1}{2}$. Then V_m also has $2^n + n$ hexagons, and its Kekulé count is $\left(\frac{2^n+n+1}{2}\right)^2 > 2^{2n-2}$.

Consider $K(W_n) = 2^n F_{n+2} + F_{n+1}$

$$= \frac{1}{\sqrt{5}}\left(2^n\left(\left(\frac{1+\sqrt{5}}{2}\right)^{n+2} - \left(\frac{1-\sqrt{5}}{2}\right)^{n+2}\right) + \left(\frac{1+\sqrt{5}}{2}\right)^{n+1} - \left(\frac{1-\sqrt{5}}{2}\right)^{n+1}\right)$$

$$< \frac{1}{\sqrt{5}}\left(\left(2^n\left(2\varphi^{n+2}\right)\right) + \varphi^{n+1}\right)$$

$$< \frac{2}{\sqrt{5}}\left(\left(2^n\left(\varphi^{n+2}\right)\right) + \varphi^{n+1}\right)$$

$< 2^n\varphi^{n+2} + \varphi^{n+2}$, where $\varphi = \frac{1+\sqrt{5}}{2} = 1.618...$, the golden ratio.

Therefore, the difference $K(V_m) - K(W_n) > 2^{2n-2} - 2^n\varphi^{n+2} - \varphi^{n+2}$.

The number of hexagons in each V_m and W_n is $h = 2^n + n \approx 2^n$, so $n \approx \log_2 h$. Substituting gives

$$K(V_m) - K(W_n) > \tfrac{1}{4}2^{2\log_2 h} - 2^{\log_2 h}\varphi^2\varphi^{\log_2 h} - \varphi^2\varphi^{\log_2 h}$$

$$= \frac{1}{4}(2^{\log_2 h})^2 - h\varphi^2\varphi^{\log_2 h} - \varphi^2\varphi^{\log_2 h}$$

$$= \frac{1}{4}h^2 - h\varphi^2\varphi^{\frac{\log_\varphi h}{\log_\varphi 2}} - \varphi^2\varphi^{\frac{\log_\varphi h}{\log_\varphi 2}}$$

$$= \frac{1}{4}h^2 - h\varphi^2 h^{\frac{1}{\log_\varphi 2}} - \varphi^2 h^{\frac{1}{\log_\varphi 2}}$$

$$> \frac{1}{4}h^2 - \varphi^2 h^{1.69424} - \varphi^2 h^{.69424}$$

$$\in O(h^2) = O(v^2)$$

So the growth of this difference is quadratic on the number of hexagons (as well as the number of vertices) of each benzenoid in the pair.

Since $F(V_m) = 4$ and $C(V_m) = 2$ while $F(W_n) = n + 2$ and $C(W_n) = \lfloor \frac{n+3}{2} \rfloor$, the Fries and Clar values are arbitrarily larger for W_n than V_m. Therefore, the gap for the Kekulé-Clar and Kekulé Fries disagreements is quadratic.

□

4. Computational Investigation of Pairwise Disagreements

We now address our second question of how often pairwise disagreements occur. This section outlines the methodology and results of a computer search that considered all 4,047,541 benzenoids with at most 13 hexagonal faces [13]. Results of this type give empirical insight into the validity of these three classic measurements. In particular, if a large percentage of benzenoid pairs are in pairwise disagreement, then it would be impractical for those two measurements to accurately determine relative stability for a given pair benzenoids. On the other hand, if pairwise disagreements are relatively rare, then perhaps they can be safely ignored in the aggregate.

We continue to limit ourselves to pairs of the benzenoids with the same number of vertices and number of hexagons. When referring to our statistics we do not "double count" isomorphic graphs. For example, Figure 8 gives one specific pair with a Fries-Clar disagreement, and rotating one of the benzenoids in the figure would not produce a "different" pair with a Fries-Clar disagreement.

When restricted to Kekuléan benzenoids of the same size, our study finds that the percentage of pairwise disagreements reaches as high as 3.62%. More specifically, the percentage of Kekuléan benzenoid pairs with 13 hexagons and 46 vertices that have a Kekulé-Fries disagreement is just over 3.62%. Similarly, the largest percentages for Kekulé-Clar and Fries-Clar disagreements are around 3.4%. Full results of this type appear in Tables 5, 6, and 7.

Although the percentage of pairwise disagreements is relatively small, the data does suggest that the percentage grows as the size of the benzenoid increases. In other words, pairwise disagreements seem to be more frequent for larger benzenoids. The number of pairwise disagreements with a gap larger than 1 also appears to be non-trivial. Figure 8 illustrates a pair of benzenoids with a Fries-Clar gap of 2 and a Kekulé-Fries gap of 2. There are 22,083 different pairs of benzenoids over 12 hexagonal faces and 50 vertices in which the first has a Fries number of 10 and a

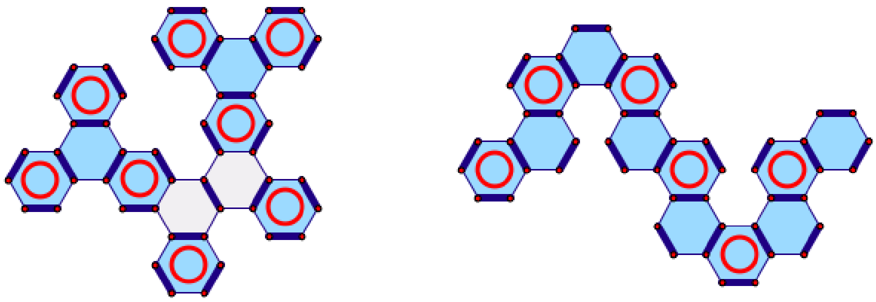

FIGURE 8. Fries-Clar gap of 2 and Kekulé-Fries gap of 2. The benzenoid on the left has a Fries number of 10, a Clar number of 8, and 466 Kekulé structures. The benzenoid on the right has Fries number 12 and Clar number 6 and 377 Kekulé structures.

Clar number of 8 while the second has a Fries number of 12 and a Clar number of 6. Furthermore, the same Fries and Clar numbers are obtained by over 500,000 additional pairs with 13 hexagonal faces. In other words, the pair shown in Figure 8 is not particularly special or strange.

The remainder of this article is organized as follows. In Section 5 we describe our computational approach and the associated computational challenges. Section 6 provides the number of Kekuléan benzenoid pairs based on the number of vertices and hexagonal faces. Section 7 gives our main results in the form of tables containing the percentage of benzenoid pairs that have a pairwise disagreement.

5. Computational Approach

In this section we describe our computational approach including our resources and the computational issues that arose. All programs were written using a combination of C, Python, and awk and are available upon request. All references to time are with respect to a single 2015 Macbook Pro with 16 GB of RAM running an Intel i7 processor at 3.1 GHz.

5.1. **Generating Benzenoid Graphs and Duals.** We began by generating benzenoids using the benzene package from SageMath [18]. More precisely, we separated the `benzene.c` file from the benzene package and ran this program independently for the sake of efficiency. The `benzene.c` file was originally written by Gunnar Brinkmann and Gilles Caporossi and was based on a paper by Brinkmann, Caporossi, and Hansen [1]. The version of the file we accessed had subsequently been adapted for use with Grinvin [7] by Gunnar Brinkmann and Nicolas Van Cleemput. We used this program to generate the *planar codes* for all of the benzenoids with a given number of hexagonal faces. This step was not a bottleneck in our investigation. For example, the command `./benzene 14 p b` could generate 3 gigabytes of data containing all 15,367,577 benzenoids with 14 hexagonal faces in under a minute. For further information on the planar code format refer to the House of Graphs [10].

We then converted each planar code into a dual representation of the graph.[1] For this dual representation we used the labeling of the hexagonal grid in which each face is assigned (x, y) in such a way that y values are incremented by moving vertically, and x values are incremented by moving up and right at a 60 degree angle. For further information on this labeling see the leftmost image in Figure 9 of [15]. For example, a benzenoid with three hexagonal faces in the shape of an 'r' can be represented by labeled faces $(0, 0), (0, 1)$, and $(1, 1)$. Again this step of the computation was not a bottleneck.

5.2. **Computing KFC Values.** Once we had each benzenoid in a suitable representation we computed number of Kekulé structures. We did this in a standard recursive fashion by choosing an edge e, and then recursively generating all perfect matchings that contain e, and all the perfect matchings that do not contain e. For the sake of efficiency we represented each Kekulé structure using an incidence vector of edges that was stored as a bit array. We also stored each face in the same way, and this allowed us to use bitwise operations to determine the benzene rings and hence the Fries numbers. A Python recipe by Mike Sweeney [16] simplified these bitwise tasks. The dual representation also allowed us to compute the Clar numbers more efficiently.

At the end of this stage we had a one-line description of each benzenoid that included its number of vertices and hexagonal faces, along with its Kekulé, Fries, and Clar numbers, and a unique index which linked to its dual representation. However, computing the KFC values was the biggest bottleneck in our investigation, and optimizing this step could allow for comparisons well beyond 13 hexagonal faces.

5.3. **Pairwise Comparisons and Buckets.** We next counted and dismissed all those benzenoids with no Kekulé structures since these cannot be involved in a pairwise disagreement. Then we used command-line tools to separate the benzenoids based on the number of faces and the number of vertices.

Restricting the investigation to benzenoids of the same size has the computational advantage of limiting the number of benzenoids that need to be compared. However, the combinatorial explosion associated with pairwise comparisons still must be addressed. For example, there are 589,703 benzenoids that have 13 hexagonal faces and

[1]It is possible that this dual representation could be obtained more directly from `benzene.c`. One issue is that `benzene.c` can also generate a generalization of benzenoids called fusenes, which are not necessarily embeddable in the hexagonal grid and hence do not have such a representation.

	Fries Number										
Clar Number	2	3	4	5	6	7	8	9	10	11	12
1	1										
2		1	13								
3			3	83	301						
4				1	218	1996	2502				
5					1	299	5436	13302	6034		
6							231	6675	20094	11872	1299
7								86	3022	5878	1591
8									17	115	41

Table 1. The size of the Fries-Clar buckets for benzenoids with 12 hexagons and 50 vertices. The $(12, 6)$ and $(10, 8)$ buckets provide $17 \times 1299 = 22,083$ pairs that have a Fries-Clar gap of 2.

52 vertices, and a brute force comparison would involve 173,874,519,253 pairs of benzenoids. To avoid this computational problem we used an approach from computer science called 'bucketing' which is most commonly associated with the well-known bucket sort algorithm.

To employ this approach we put each benzenoid into a 'bucket' based on two of the KFC values. For example, all benzenoids with Fries number 10 and Clar number 8 would be placed into the same bucket. This allows us to find pairwise disagreements by comparing pairs of buckets instead of comparing pairs of benzenoids. In other words, we reduce the cost of making $O(n^2)$ comparisons by changing n from the number of benzenoids to the number of buckets.

To make this description more tangible, Table 1 contains the Fries-Clar buckets for benzenoids with 12 hexagons and 50 vertices. From the table we can see that there are a several different pairs of buckets that can be used to create pairwise disagreements. In particular, there are 17 such benzenoids with Fries number 10 and Clar number 8, and 1299 such benzenoids with Fries value 12 and Clar number 6. Therefore, we obtain a Fries-Clar disagreement with gap 2 by taking any single benzenoid from the $(10, 8)$ bucket and any single benzenoid form the $(12, 6)$ bucket. The product of these two bucket sizes, namely 17 and 1299, gives the total of 22,083 that was previously mentioned in Section 1. Similarly, the 500,000 figure mentioned in Section 1 comes from the sum of 15×8480 (13 hexagons and 52 vertices) and 33×12178 (13 hexagons and 54 vertices).

6. Number of Kekuléan Benzenoid Pairs

This section provides tables containing the number of benzenoids, the number of Kekuléan bezenoids, and the number of pairs of Kekuléan benzenoids. In each case the numbers are computed based on a fixed number of vertices and hexagonal faces. Tables 3 and 4 in this section are restricted to Kekuléan benzenoids since non-Kekuléan benzenoids cannot belong to a pairwise disagreement.

As discussed in Section 2, our data was generated based on the number of hexagonal faces. For this reason we only have complete data on benzenoids with up to 40 vertices.

7. Percentage of Pairwise Disagreements

In this section we provide tables that show the percentage of benzenoid pairs that have are in disagreement. More specifically, Tables 5, 6, and 7 are focused on Kekulé-Fries, Kekulé-Clar, and Fries-Clar disagreements. In each case the table is organized by the number of hexagons and the number of vertices, and each entry shows the percentage of such pairs which are in disagreement.

The data shows that pairwise disagreements are relatively rare with the maximum percentage being 3.62%. However, the data also shows that the proportion of disagreements appears to be increasing with the size of benzenoids. The proportion generally increases as the row values (number of hexagons) and column values (number of vertices) increases. In particular, in all three tables the maximum values along each row steadily increase starting at 7 hexagons. In other words, the greater the number of hexagonal faces, the greater the percentage of disagreements for all pairs of measurements.

8. Final Remarks

This paper introduces several open problems. Can one find infinite classes of benzenoids with larger or faster growing gaps? Given that these parameters can disagree, which of the three is a better measure of stability? With improved methods for computing the KFC values we are certain that other researchers would be able to extend these results well beyond benzenoids with 13 hexagonal faces. As the size of benzenoids increases, what proportion of benzenoids have KFC disagreements, and how large do the gaps tend to be? This approach for finding pairwise disagreements could be applied to any number of parameters for benzenoids or other molecules.

9. Acknowledgements

The authors wish to thank Patrick Fowler [4] and Ivan Gutman [8] for interesting discussions on this topic. We would also like to acknowledge help from the operators of MCLA's supercomputer [12].

Number of Benzenoids																	
	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54
6	3	14	36														
7		1	10	68	118												
8				9	67	329	411										
9					4	55	396	1601	1489								
10						1	42	416	2340	7652	5572						
11								26	333	2811	13415	36109	21115				
12									13	279	2713	18306	74985	168318	81121		
13										4	187	2459	20119	114326	408785	776452	314075

TABLE 2. Number of Benzenoids by hexagonal faces (rows) and number of vertices (columns). Only benzenoids with an even number of vertices are considered.

Number of Kekuléan Benzenoids																	
	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54
6	2	13	36														
7		1	9	62	118												
8				8	58	287	411										
9					3	46	333	1352	1489								
10						1	34	337	1907	6256	5572						
11								20	264	2191	10552	28737	21115				
12									10	213	2085	13805	57019	130665	81121		
13										3	139	1836	14896	83376	300833	589703	314075

TABLE 3. Number of Kekuléan Benzenoids by hexagonal faces (rows) and number of vertices (columns).

Number of Pairs of Kekuléan Benzenoids																	
	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54
6	1	78	630														
7		0	36	1891	6903												
8				28	1653	41041	84255										
9					3	1035	55270	913270	1107816								
10						0	561	56616	1817371	19565640	15520806						
11								190	34716	2399145	55667076	412893216	222911055				
12									45	22578	2172570	95282110	1625554671	8536605780	3290267760		
13										3	9591	1684530	110937960	3475737000	45250096528	173874519253	49321395775

TABLE 4. Number of pairs of Kekuléan Benzenoids based on the number of hexagonal faces (rows) and number of vertices (columns).

Percentage of Kekuléan Benzenoid Pairs with a Kekulé-Fries Disagreement																	
	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54
6	0	0	0.7937														
7			0	0.4231	0.7823												
8				0	0.7864	2.2051	1.2510										
9					0	0.2899	1.8018	2.6405	1.7018								
10							0.1783	1.2117	2.0903	2.8834	2.0266						
11								0	1.6793	2.3524	2.7828	3.1496	2.3987				
12									0	1.5502	2.6534	3.0411	3.2546	3.4197	2.7182		
13										0	0.9801	2.1809	2.9869	3.3601	3.5472	3.6221	3.0133

Table 5. Percentage of Kekuléan Benzenoid pairs that have a Kekulé-Fries disagreement. The maximum value for each row (number of hexagons) is shaded.

Percentage of Kekuléan Benzenoid Pairs with a Kekulé-Clar Disagreement																	
	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54
6	0	0	0														
7			0	0.5288	0.6084												
8				0	0.7864	0.9551	0.9697										
9					0	0.8696	1.1198	1.6891	1.7100								
10							0.7130	1.2011	2.0677	2.1438	2.0059						
11								1.0526	1.1753	2.1374	2.4258	02.6834	2.6431				
12									0	1.2800	1.9355	2.6678	1.1954	1.4259	2.9599		
13										0	1.1365	1.8611	2.6344	3.2429	3.4480	3.4565	3.4024

Table 6. Percentage of Kekuléan Benzenoid pairs that have a Kekulé-Clar disagreement. The maximum value for each row (number of hexagons) is shaded.

Percentage of Kekuléan Benzenoid Pairs with a Fries-Clar Disagreement																	
	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54
6	0	0	1.2698														
7			0	0	0.6953												
8				0	0	0	1.5548										
9					0	0.5797	0.7598	1.1212	1.9359								
10							0	0.3886	0.7962	0.9315	2.1281						
11								0	0.1498	0.2573	0.6802	1.1918	2.6567				
12									0	0.5669	0.6682	0.8878	1.1954	1.4259	2.9599		
13										0	0.4379	0.5346	0.8717	1.1252	1.3220	1.6247	3.3702

Table 7. Percentage of Kekuléan Benzenoid pairs that have a Fries-Clar disagreement. The maximum value for each row (number of hexagons) is shaded.

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