An upper bound on the independence number of benzenoid systems

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Abstract

Recently, the graph theoretic independence number has been linked to fullerene stability [S. Fajtlowicz, C. Larson, Graph-theoretic independence as a predictor of fullerene stability, Chem. Phys. Lett. 377 (2003) 485–490; S. Fajtlowicz, Fullere
Expanders, A list of Conjectures of Minuteman, Available from S. Fajtlowicz: math0@bayou.uh.edu]. In particular, stable fullerenes seem to minimize their independence numbers. A large piece of evidence for this hypothesis comes from the fact that stable benzenoids—close relatives of fullerenes—do minimize their independence numbers [S. Fajtlowicz, “Pony Express”—Graffiti’s conjectures about carcinogenic and stable benzenoids, ⟨http://www.math.uh.edu/~siemion/pony.html⟩]. In this paper, an upper bound on the independence number of benzenoids is introduced and proven—giving a limit on how large the independence ratio for benzenoids can be. In conclusion, this bound on independence is correlated to an upper bound on the number of unpaired sites a benzenoid system has with respect to a maximum matching, which is precisely the number of zero eigenvalues in the spectrum of the adjacency matrix (due to a conjecture of Graffiti and its proof by Sachs [S. Fajtlowicz, “Pony Express”—Graffiti’s conjectures about carcinogenic and stable benzenoids, ⟨http://www.math.uh.edu/~siemion/pony.html⟩]; H. Sachs, P. John, S. Fajtlowicz, On Maximum Matchings and Eigenvalues of Benzenoid Graphs, preprint—MATCH]). Thus, since zero eigenvalues and unpaired sites are indicative of instability (reactivity), we get a simple but intuitive bound on how reactive a benzenoid molecule can be.

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1. Introduction

1.1. Key definitions

Given a simple graph \( G \), an independent set of vertices is one in which no two members of the set share an edge—a set of mutually non-adjacent vertices. An independent set of edges is one in which no two members of the set share a vertex—a set of mutually non-incident edges. Independent sets of edges are called matchings. The independence number is the cardinality of a largest independent set of vertices and is denoted \( \alpha = \alpha(G) \). The matching number is the cardinality of a largest matching and is denoted \( \mu = \mu(G) \). A perfect matching is one which contains all of the \( n = n(G) \)

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vertices of the graph. Clearly then,

$$\mu(G) \leq \frac{n(G)}{2}$$

and equality holds if and only if $G$ has a perfect matching.

The remainder of this paper will be spent considering the graphs which represent benzenoid hydrocarbon molecules. In such graphs, each vertex represents a carbon atom and each edge is a carbon–carbon sigma bond. The hydrogen atoms are suppressed. It is now necessary to formally define what is meant by benzenoid in this paper, as there is not currently a uniformly accepted definition [13].

A benzenoid is a connected planar graph having only regular congruent hexagons as finite faces such that every pair of hexagons is either disjoint or shares exactly one edge [20]. Equivalently, given a hexagonal tiling of the plane or hexagonal lattice, a benzenoid is the collection of vertices and edges lying on and in the interior of a cycle on the lattice [13]. Benzenoids divide the plane into one external unbounded region and some finite number of internal hexagonal regions. A multi-coronoid is a benzenoid with some internal hexagons removed, such that every pair of hexagons remaining is still disjoint or shares exactly one edge. Both definitions of benzenoid given above exclude multi-coronoids from consideration. (see [7] for more on coronoids)

For any basic graph theory terms not defined in this paper, the reader is referred to [2], or any other introductory graph theory text.

1.2. Motivation and history

Valence bond theory, developed in the early years of quantum chemistry, was one of two competing ideas capable of describing the electronic structure of conjugated organic molecules. Its opponent, molecular orbital theory, emerged victorious, in large part due to the computational difficulties of valence bond theory. These difficulties arise from the vast number of chemical structures to be taken into account. A major, and perhaps crude, simplification of valence bond theory began to flourish in the 1940s and 1950s. This was called resonance theory and dropped all but the kekulé structures from consideration in valence bond theory. (summarized from [13])

A kekulé structure in a conjugated hydrocarbon is simply a perfect matching of the underlying simple graph, and is commonly considered the most important bond structure of the molecule—thus justifying the choice of emphasis for resonance theory. It can be thought of as a collection of disjoint double bonds between the carbon atoms, such that each carbon is incident to precisely one of them.

Herndon gave a quantitative revision of resonance theory, in 1973, which allowed for the prediction of many properties of conjugated hydrocarbons using kekulé structures alone [14]. These predictions rivaled those of some of the best from molecular orbital theory. In short, a simple formula could be derived from Herndon’s resonance theory which inversely related the number of kekulé structures to the resonance energy. (summarized from [13])

Thus, lower energy could be predicted by a greater number of kekulé structures, and vice versa. Since molecules with higher energies should be less kinetically stable, this established a link between perfect matchings of conjugated hydrocarbons and kinetic stability.

This, however, may not be the whole story. Molecules having no kekulé structures at all are called non-kekuléan. They are generally considered as unstable, reactive, or perhaps transient specimens. In fact, until recently, only a few have ever been synthesized, and these with difficulty (see [1] for example). According to D. Klein, from private correspondence, there is reason to believe that the stability may be more accurately measured or predicted as a function of the size of a maximum matching in the graph and the number of maximum matchings (see also [15]). This is opposed to the traditional view, which hastily discards those molecules with no perfect matchings as unstable—although there is perhaps good evidence for doing this as well. Thus, it may be possible for some theoretical molecule with no perfect matching at all, but lots of large maximum matchings, to be very stable. In any case, this possibility warrants the investigation of just how small a maximum matching in arbitrary hydrocarbons can be.

It is the aim of this paper to study the inverse problem of determining how large a maximum independent set in such a molecule can be. The problem of minimizing the matching number or maximizing the independence number in benzenoids, proposed by Fajtlowicz [9] as a possible measure of “instability”, is considered open and difficult by Klein, a leading researcher in the field [11]. Since all the molecules we will be considering here are bipartite—called
alternate in the chemistry literature—these two problems are equivalent. Namely, due to an early result in graph theory of König (1931), if $G$ is a bipartite graph, then the following equation is satisfied: (see [2] for instance)

$$\alpha(G) + \mu(G) = n(G).$$

Thus, minimizing $\mu(G)$ is equivalent to maximizing $\alpha(G)$ for a fixed $n(G)$. Furthermore, all bipartite graphs satisfy the inequality,

$$\alpha(G) \geq \frac{n}{2},$$

since both parts of a bipartition are independent sets and at least one of them has at least half of the vertices. What this indicates—as first noted in [9]—is that, since the more stable benzenoids have perfect matchings ($\mu = n/2$), they tend to minimize their independence numbers. In fact, this corroborates the independence-stability hypothesis for fullerenes, emerging from conjectures of Minuteman [10], a version of Graffiti, and presented by Fajtlowicz and Larson [12]. This hypothesis states that more stable fullerenes tend to minimize their independence numbers, based on the fact that the most stable observed fullerenes do so. It was actually this hypothesis that led Fajtlowicz to the similar question about stability in benzenoids. Statistically, the independence number can be used to pick out the known stable fullerenes more efficiently than any of several other traditional measures (see [12]). Being very close relatives of benzenoid hydrocarbons—which, as previously stated, do satisfy this hypothesis—the fact that stable fullerenes tend to minimize their independence numbers may not be coincidence. Incidentally, the two most frequently observed fullerenes, the buckminster fullerene $C_{60}$ (truncated dual of the icosahedron) and the stable $C_{70}$ fullerene, are unique among the thousands of fullerene isomers of 60 and 70 atoms, respectively, which minimize their independence numbers. There are even more examples than this [12].

With the intention that it will be a measure on how unstable, or reactive, a benzenoid molecule can be, the rest of this paper will be devoted to proving that every benzenoid satisfies the inequality

$$\alpha(G) \leq \frac{11n(G) - 2}{20}, \quad (1)$$

which is a tight bound with a characterization of equality given. The independence ratio of a graph is the ratio $\alpha/n$. Inequality 1 implies the independence ratio of benzenoids is less than eleven-twentieths.

Given a maximum matching of a benzenoid, an unpaired site is a vertex that is a member of no edge in the matching. Two interesting corollaries to Inequality 1, which we will elucidate later, are that less than a tenth of the carbon atoms of a benzenoid molecule are unpaired sites in any maximum matching, and also that less than a tenth of the eigenvalues of the adjacency matrix of a benzenoid are zeros.

2. Triangulenes

A family of benzenoids of particular interest to us is the family of regular triangulenes, whose first few members are shown in Fig. 1. Let $k \geq 1$ be an integer. The triangulene $T_k$ is a benzenoid with the $k$th triangular number of hexagons, $k(k + 1)/2$. These regular hexagons are arranged in the shape of an equilateral triangle, with each side having the same

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1 A fullerene is a new form of carbon which, graph theoretically, can be described as a planar cubic graph whose every face is pentagonal or hexagonal. The regular dodecahedron is the smallest fullerene.
number of hexagons. This family is not new, and it was essentially pointed out by Clar [5], that the $n$th triangulene has $n - 1$ unpaired sites. It has also been noted by Gutman that this family shows the color excess—that is, the absolute difference between the frequencies of the two colors used in a two-coloring—of a benzenoid can be arbitrarily large [13]. The color excess of $T_n$ is $n - 1$. Incidentally, the triangulenes also show that the difference between the independence number and the matching number, $\alpha(G) - \mu(G)$, can be arbitrarily large; $\alpha(T_n) - \mu(T_n) = n - 1$.

In spite of the apparent similarity between color-excess and the value, $\alpha(G) - \mu(G)$, which is the number of unpaired sites in the system, these two values are not, in general, the same. In particular, this is seen from the existence of concealed non-kekuléan benzenoids, starting with 11 hexagons, which have zero color excess and $\alpha(G) > \mu(G)$ (for a review of related topics, see [16]).

Throughout this section, we assume $T_k$ is arranged so that every regular hexagon has two vertical edges, there is a row of $k$ hexagons at the bottom and a single hexagon at the top. Furthermore, we imagine each triangulene $T_k$ is placed on a grid of horizontal lines so that each vertex lies in one of the lines. These lines are labeled 1, 2, ..., $2(k + 1)$, where the first line passes through the vertex at top and the last line passes through the $k$ vertices on bottom. We note in passing that, in this situation, the even and odd rows form a bipartition of the triangulene. Moreover, using the traditional chemistry nomenclature of Coulson and Rushbrooke (1940), the even row set and odd row set divide the vertices into starred and un-starred sets of sites, such that no starred site is adjacent to any other starred site and vice versa. It will be shown that the even rows actually constitute the unique maximum independent set of the triangulene.

Now, to generate $T_k$ from $T_{k-1}$, we simply add a row of $k$ hexagons to the bottom. This addition amounts to adding a path of $2k + 3$ vertices along with some connecting edges (Fig. 2). This generates the following simple recurrence relation for $n$:

$$n(T_k) = n(T_{k-1}) + 2k + 3.$$  

From this we see readily that $n(T_k) = k^2 + 4k + 1$. Moreover, this new row of $k$ hexagons adds precisely $k + 2$ vertices to the sets of vertices in even rows (counting rows from the top proceeding down), and $k + 1$ vertices to the odd-row set. Thus, by letting $n_e(T_k)$ denote the number of vertices on even rows:

$$n_e(T_k) = n_e(T_{k-1}) + k + 2.$$  

This shows that $n_e(T_k) = (k^2 + 5k)/2$ and the independence number of $T_k$ is at least this large.

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2 The benzenoid we are calling $T_3$ here is often referred to as “triangulene” in the chemistry literature. Here, $T_3$ is simply a representative of a specific family of benzenoids—the triangulenes—including benzene itself (though in a trivial way).
Theorem 2.2. Every triangulene $T_n$ has a unique maximum independent set consisting of the $(k^2 + 5k)/2$ vertices lying on even rows in the labeling scheme described above.

Proof. We have begun with $k \geq 2$ since benzene, or $T_1$, is a trivial exception to this theorem (in regard to the uniqueness, not the formula). First, we note by inspection that the theorem is true for $T_2$. Now assume the theorem is true for $T_n$, where $n \geq 3$. Consider $T_{n+1}$. Let $P$ represent the odd path of $2(n + 1) + 3$ vertices which must be added to $T_n$ to generate $T_{n+1}$. Let $E$ represent the $n + 2$ edges needed to attach $P$ to $T_n$ and form $T_{n+1}$. Thus $T_{n+1} = T_n \cup P \cup E$. By inductive assumption, the even row vertices of $T_n$ form a unique maximum independent set of this graph. Also, $P$ has a unique maximum independent set consisting of the bipartition which includes its two pendants, since it is an odd path. Furthermore, in constructing $T_{n+1}$, the two pendant vertices of $P$ are placed in the last row of vertices of $T_n$, which is an even row, and the other vertices in the partition, including these pendants, are placed in the bottom row of $T_{n+1}$, also an even row. The rest of $P$ is placed in an odd row. Since every edge in $E$, which joins these two graphs together, has one vertex in an even row and the other in an odd row, we know that none of the vertices in the unique maximum independent set of $T_n$ are joined to any of the vertices of the unique maximum independent set of $P$ by the edges in $E$. Therefore, by Lemma 2.1, $T_{n+1}$ has a unique maximum independent set which is the union of the unique maximum independent sets of $T_n$ and $P$. This set is exactly the set of vertices on even rows of $T_{n+1}$. Thus we also get the formula for the independence number of triangulenes; $\alpha(T_k) = (k^2 + 5k)/2$ (Fig. 3). 

2.1. Fused triangulenes

An edge-fusion is the amalgamation of two benzenoids at an edge, both of whose endpoints are degree two in both benzenoids. Edge-fused benzenoids are disjoint except for the one edge and two vertices of the edge-fusion. A graph
G is a fused triangulene if and only if: first, G is a benzenoid; second, G is obtained by edge-fusions of a set of regular triangulenes; and third, each of any $T_1$ triangulenes involved are edge-fused to exactly two other triangulenes so that the remaining two vertices of the $T_1$ triangulene are non-adjacent. Fig. 4 shows the four possible structures that exterior hexagons from fused triangulenes may have. Fig. 5 shows a typical example of a fused triangulene.

3. Main result

To prove the theorem, that for all benzenoids $G$, $\pi(G) \leq (11n(G) - 2)/20$, we need two lemmas and the following remark.

Remark 3.1. An exterior hexagon of a benzenoid is one which has at least one vertex or at least one edge on the exterior or boundary cycle. If $G$ is a benzenoid with at least two hexagons, then every exterior hexagon of $G$ is one of 11 possible types illustrated as $a$ through $k$ in Figs. 4 and 6. Note that this can also be stated in the following way, which is more useful to us here: either every exterior hexagon of a benzenoid is of type $a$, $b$, $c$, or $d$ (as is the case with the fused triangulenes), or not; in which case, there is at least one exterior hexagon that is of type $e$ through $k$.

Lemma 3.2. If every exterior hexagon of a benzenoid $G$ is of type $a$, $b$, $c$, or $d$, then $G$ is a fused triangulene.

Proof. Let us call hexagons of type $a$, $b$, $c$, and $d$ corners, paths, links, and trivial, respectively. Note that trivial hexagons can only have links or trivial hexagons as neighbors. Moreover, if $x$ is a link, then the isolated hexagon neighbor of $x$ must either be a link or a trivial hexagon. If it is trivial, it has one remaining neighbor which is either a link or trivial. Since benzenoids are finite, we eventually hit another link. Thus, links come in pairs with some finite number—possibly zero—of trivial hexagons between them. This motivates the following definition.

A chain is a sequence—possibly empty—of trivial hexagons terminated on both ends by a link. The length of the chain is the number of trivial hexagons it contains.

Our strategy is induction on the number of chains. For benzenoids satisfying the hypothesis, we call the patches of hexagons lying on either end of a chain, including the link, the components. In this way, the only exterior hexagons
Fig. 6. The other seven types of exterior hexagons a benzenoid with at least two hexagons may have. In addition to those depicted in Fig. 4, these make up all of the eleven exterior hexagons that are possible in benzenoids with at least two hexagons.

in the components are corners and paths, with possibly some links (where the number of links is at most the number of corners). The idea behind the terminology is that the deletion of any link or trivial hexagon—any hexagon in a chain—disconnects the benzenoid, while the deletion of any corner or path does not.

If $G$ is a benzenoid satisfying the hypothesis, then we can create the contracted inner dual of $G$ in the following sense. Replace each component by a vertex and each chain by an edge. This is a tree since it is connected and the existence of a cycle would imply that $G$ was not a benzenoid by our definition. Hence, if there is at least one chain, then there are at least two pendant components in $G$, where a pendant component is just a component with only one chain emanating from it.

Let $j$ be the number of chains in a benzenoid $G$ which satisfies the hypothesis. Suppose $j = 0$. Then every exterior hexagon in $G$ is either a corner or a path. Note that every sequence of paths must begin and end with a corner, in analogy with trivial hexagons being capped by links. Appealing to the geometry of this situation, we see that there must be exactly three corners and an equal number of paths between all three pairs of corners. For otherwise, we are forced to admit hexagons which are not corners or paths along the exterior, which is impossible. Therefore, in this case, $G$ is a regular triangulene $T_k$ with $k \geq 2$. Since regular triangulenes are members of the fused triangulene family, this takes care of the base case.

Now, suppose that all benzenoids satisfying the hypothesis with less than $j \geq 1$ chains are members of the fused triangulene family. Let $G$ be a benzenoid with $j$ chains—including chains of length zero. Let $P$ denote an arbitrary pendant component of $G$. We need two things, that $P$ itself was a triangulene when treating its only link as a corner, and that the removal of $P$ and its chain results in a smaller benzenoid which still satisfies the hypothesis. The first of these matters is settled easily enough by noticing that besides the one link, every exterior hexagon of $P$ is a corner or a path, which we already know implies that $P$ is a triangulene. Now, by removing $P$ and its chain, but leaving the link at the other end of the chain in place, we see that this former link becomes a corner. Since nothing else has changed in this remaining benzenoid, it still satisfies the hypothesis. With fewer than $j$ chains, it is a fused triangulene by inductive assumption. Thus, the addition of $P$ by means of a chain when $P$ itself is a triangulene, implies that $G$ must have been a fused triangulene. $\square$

**Lemma 3.3.** For any fused triangulene, $$\alpha \leq \frac{11n - 2}{20}.$$  

**Proof.** We have already noted that the triangulene $T_k$, with $k \geq 2$, has a unique maximum independent set. There is essentially only two ways to form an edge-fusion between two such triangulenes, both of which leave exactly one vertex of degree two in the link hexagons formed by the fusion. The edge-fusion was proper if these remaining degree two vertices are adjacent to the same vertex of the newly fused edge. Without loss of generality, assume the triangulenes are oriented as before, with an apex pointing upwards. Now, if the edge-fusion was proper, the distance between these
vertices is two and both are in the even-row set of lines—as described above. Hence, proper edge-fusion preserves the unique maximum independent sets of both triangulenes involved.

In fact, much more is apparent. Let $F$ be a fused triangulene with at least two components and no trivial $T_1$ components—so that the length of every chain is zero. Supposing that every edge-fusion of $F$ is proper, $F$ also has a unique maximum independent set. Moreover, it is exactly the union of the unique maximum independent sets of the regular triangulenes composing $F$, where, for each pair of regular triangulenes, one vertex is counted twice. If every component is $T_2$, this is clear by inspection. Consider the simple case of fusing $T_k$ with $T_j$, with $j \neq k \geq 3$. Call this graph $T_k + T_j$. It can be described as:

$$T_k + T_j = A \cup B \cup C \cup E,$$

where $A$, $B$, and $C$ are subgraphs whose disjoint union make up the vertex set of $T_k + T_j$, and each has a unique maximum independent set $I_A$, $I_B$, and $I_C$, respectively. Also $E$ is a set of edges satisfying the following properties: (1) each edge in $E$ is incident with two of the three subgraphs and (2) no edge in $E$ joins a vertex from the unique maximum independent set of one to a vertex from the unique maximum independent set of another. This is done as illustrated in Fig. 7.

Now we can appeal to Lemma 2.1 to conclude that $T_k + T_j$ has a unique maximum independent set, which is precisely the union of the unique maximum independent sets of $T_k$ and $T_j$.

Induction on the number of components of $F$ is used to show that $F$ has a unique maximum independent set. Briefly, assume all fused triangulenes satisfying the hypotheses we hold for $F$, but with fewer hexagons than $F$, have unique maximum independent sets comprised of the unique maximum independent sets of their components. Orient a pendant component of $F$ so that the even-row set is the unique maximum independent set of that component, and rotate the rest of $F$ accordingly. Now remove the pendant component and what remains has a unique maximum independent set by the inductive hypothesis. Thus, $F$ has a unique maximum independent set since the removed pendant can be rejoined with a proper edge-fusion (all edge-fusions in $F$ are proper).

It must be noted here that by fusing two triangulenes together the other way, an improper fusion, where the distance between the vertices of degree two on the links is three, the independence number goes down, and uniqueness of a maximum independent set is no longer necessary. It is impossible to get the most\(^3\) out of each triangulene with improper edge-fusions. The reason we excluded the trivial $T_1$ triangulene from these discussions is because its presence in a fused triangulene can only decrease the independence ratio, a quantity we wish to maximize.

Now, we can assume that the fused triangulenes which maximize their independence numbers have only proper edge-fusions and contain no trivial $T_1$ components—all chains have length zero. Under this assumption, we count the total number of vertices and the number of vertices in the unique maximum independent set.

Let $T_k^j$ be the regular $T_k$ triangulene fused together in the prescribed way $j$ times. Now, since the unique maximum independent set of $T_k^j$ is the union of the maximum independent sets of its components, where one vertex in this set is counted twice for each fused edge (chain of length zero);

$$\alpha(T_k^j) = (\alpha(T_k))j - (j - 1) = j \left( \frac{(k^2 + 5k)}{2} \right) - (j - 1).$$

\(^3\) Of course, this is in regard to the number of vertices in a maximum independent set.
Similarly, we can count the number of vertices of $T^j_k$ by noting that its vertex set is the union of the vertex sets of its components, where two vertices are counted twice for each chain (fused edge):

$$n(T^j_k) = (n(T_k))j - 2(j - 1) = j(k^2 + 4k + 1) - 2(j - 1).$$

Now we form the independence ratio of these two quantities and call it $f$. So,

$$f(k, j) = \frac{\lambda(T^j_k)}{n(T^j_k)} = \frac{j((k^2 + 5k)/2) - (j - 1)}{j(k^2 + 4k + 1) - 2(j - 1)} = \frac{(k^2 + 5k - 2)j + 2}{(2k^2 + 8k - 2)j + 4}.$$

Differentiating with respect to $k$, we find that the only positive critical point is

$$k = 1 + \frac{\sqrt{2j(2j + 1)}}{j}.$$

This is a maximum and lies between three and four for any $j \geq 1$. Moreover,

$$\frac{11j + 1}{20j + 2} = f(3, j) \geq f(4, j) = \frac{17j + 1}{31j + 2}$$

for all $j \geq 1$. Therefore, for integers, $f(3, j)$ is the maximum value of this function. This shows that the addition of any triangulene which is not $T_3$ increases the independence ratio by an amount which is less than an addition of $T_3$ would have, since $f$ is decreasing with $k$. In particular, properly edge-fusing $T_3$ to an existing fused triangulene adds 20 vertices to the graph, 11 of which fall in the unique maximum independent set. This ratio of 11/20, cannot be reached or surpassed by the edge-fusion of any other triangulene. We can now say that any fused triangulene with $j$ triangular components has an independence ratio which is at most that of $T_3^j$. This inequality is strict with the exception of $T_4 = T^3_4$, which has an independence ratio equal to that of $T_3 = T^3_3$. Furthermore,

$$\frac{\lambda(T^j_3)}{n(T^j_3)} = f(3, j) = \frac{11j + 1}{20j + 2} = \frac{11}{20} - \frac{1}{10n(T^j_3)}.$$

From this we will deduce the result, that $\lambda(G) \leq (11n(G) - 2)/20$ for any fused triangulene $G$. It is true when there is one component, as this corresponds to the regular triangulene case. Now, assume for some $j \geq 2$ that every fused triangulene $G$ with less than $j$ components satisfies $\lambda(G) \leq (11n(G) - 2)/20$. Let $F$ be a fused triangulene with $j$ components. Either every component is a $T_3$ or larger regular triangulene or there is at least one component which is $T_2$ (we have already made the assumption that the trivial $T_1$ triangulene is not in $F$ since it can only lower the independence ratio). In the first case we get the following:

$$\frac{\lambda(F)}{n(F)} \leq \frac{\lambda(T^j_3)}{n(T^j_3)} = \frac{11}{20} - \frac{1}{10n(T^j_3)}.$$

From this we see that $\lambda(F) \leq (11n(F) - 2)/20$ since $n(T^j_3) \leq n(F)$. Suppose now that at least one component is $T_2$. Let $R$ be a $T_2$ triangulene in $F$. One of the following must be true; (1) $R$ is a pendant component with one link, (2) $R$ has two links, or (3) $R$ has three links. Now we remove $R$ from $F$ by deleting all vertices exclusive to component $R$ and all edges incident to them. Let $F'$ be the resulting graph. Recall that the components are fused in such a way so as to preserve their unique maximum independent sets. So, in the first case, $\lambda(F') = \lambda(F') + 6, n(F') = n(F') + 11,$ and $\lambda(F') \leq (11n(F') - 2)/20$ since $F'$ has fewer components than $F$. Putting all this together, we find that $\lambda(F) \leq (11n(F) - 2)/20$.

In the second case, $F'$ is actually two disconnected fused triangulenes $A$ and $B$. So, $\lambda(F) = \lambda(A) + \lambda(B) + 5, n(F) = n(A) + n(B) + 9$, and since both $A$ and $B$ are fused triangulenes with fewer components than $F$, $\lambda(A) + \lambda(B) \leq (11n(A) + n(B) - 4)/20$. Together this shows that $\lambda(F) \leq (11n(F) - 2)/20$. 


Theorem 3.4. Every benzenoid has an independence ratio less than eleven-twentieths. More precisely, if $G$ is a benzenoid, then

$$\alpha(G) \leq \frac{(11n(G) - 2)}{20} < \frac{11n(G)}{20}.$$ 

**Proof.** Proceeding by contradiction, suppose $G$ is a minimum counter-example. In particular, let $G$ be a counter-example such that any benzenoid with fewer vertices or with the same number of vertices but fewer edges satisfies the inequality of the theorem.

Note that if all of the exterior hexagons in $G$ are of the first four types—$a$, $b$, $c$, or $d$—then $G$ could not have been a counter-example by Lemmas 3.2 and 3.3.

Thus, we may assume without loss of generality that at least one of the exterior hexagons in $G$ is not of any of the first four types. Let $H$ be such a hexagon of $G$.

**Case 1:** Suppose $H$ is of type $e$. Let $G'$ be the benzenoid remaining after removing from $G$ the vertices and edges of $H$ which are not shared by any other hexagon of $G$. Let $I$ be a maximum independent set in $G$ and $I'$ the remaining vertices of $I$ after removing $H$ in the sense stated above. Now we have $\alpha(G) \leq \alpha(G') + 2$. This is because the cardinality of $I$, which is $\alpha(G)$, is at most two more than the cardinality of $I'$, which is itself at most $\alpha(G')$ since $I'$ is an independent set in $G'$. Furthermore, $\alpha(G') + 2 \leq (11/20)n(G') - 1/10 + 2$ since $G'$ is not a counter-example to the theorem. Together with the fact that $n(G') = n(G) - 4$, this implies that $\alpha(G) \leq (11/20)n(G) - 1/10$, which contradicts the fact that $G$ is a counter-example to the theorem.

**Case 2:** Suppose $H$ is of type $f$. Let $G'_1$ and $G'_2$ be the two benzenoids remaining after removing from $G$ the vertices and edges of $H$ which are not shared by any other hexagon of $G$. Let $I$ be a maximum independent set in $G$ and let $I'_1$ and $I'_2$ be the remaining vertices of $I$ in $G'_1$ and $G'_2$, respectively, after removing $H$ from $G$ in the sense stated above. Now, $\alpha(G) \leq \alpha(G'_1) + \alpha(G'_2) + 1$. This follows since the cardinality of $I$, which is $\alpha(G)$, is at most one more than $|I'_1| + |I'_2|$, and this sum is at most $\alpha(G'_1)$ since $I'_1$ is an independent set in $G'_1$. Furthermore, $\alpha(G'_1) \leq (11/20)n(G'_1) - 1/10$ and $\alpha(G'_2) \leq (11/20)n(G'_2) - 1/10$ since neither $G'_1$ nor $G'_2$ are counter-examples to the theorem. Now, together with the fact that $\alpha(G) = 2 = n(G'_1) + n(G'_2)$, this implies that $\alpha(G) \leq (11/20)n(G) - 1/10$, which contradicts the fact that $G$ is a counter-example to the theorem.

**Case 3:** Suppose $H$ is of type $g$. By the same argument as in case 1: $\alpha(G) \leq \alpha(G') + 1 \leq (11/20)n(G') - 1/10 + 1 = (11/20)(n(G) - 2) - 1/10 + 1 < (11/20)n(G) - 1/10$. This contradicts the fact that $G$ was a counter-example.

**Case 4:** Suppose $H$ is of type $h$. Now removing $H$ just involves removing the three edges of $H$ which are not shared by any other hexagons. This breaks $G$ into three pieces $G'_1$, $G'_2$, and $G'_3$. In this case we have the following inequalities; $\alpha(G) \leq \alpha(G'_1) + \alpha(G'_2) + \alpha(G'_3) \leq (11/20)n(G) - 3/10 < (11/20)n(G) - 1/10$. This contradicts the fact that $G$ was a counter-example.

**Case 5:** Suppose $H$ is of type $i$. The removal of $H$ does not reduce the total number of vertices in the two components created $G'_1$ and $G'_2$. In this case, $\alpha(G) \leq \alpha(G'_1) + \alpha(G'_2) \leq (11/20)n(G'_1) + n(G'_2) - 2/10 = (11/20)n(G) - 2/10 < (11/20)n(G) - 1/10$. Thus, this too contradicts the fact that $G$ is a counter-example.

**Case 6:** Suppose $H$ is of type $j$. This case follows exactly the same lines as that of case 5. Namely, $\alpha(G) \leq \alpha(G'_1) + \alpha(G'_2) \leq (11/20)n(G'_1) + n(G'_2) - 2/10 = (11/20)n(G) - 2/10 < (11/20)n(G) - 1/10$. Of course, this too is a contradiction.

**Case 7:** Suppose $H$ is of type $k$. Now, $G'$ has the same number of vertices and one less edge than $G$. Thus, $G'$ is not a counter-example by the minimality of $G$, and $\alpha(G) \leq \alpha(G') \leq (11/20)n(G) - 1/10$. A contradiction of the fact that $G$ was a counter-example.

In conclusion, if there was a minimum counter-example to the theorem, then at least one of its exterior hexagons was of type $e$, $f$, $g$, $h$, $i$, $j$, or $k$, and each of these situations leads to a contradiction. So no minimum counter-example could exist and this proves the theorem. □
Corollary 3.5. If $G$ is a benzenoid, then $\chi(G) = (11n(G) - 2)/20$ if and only if $G = T_3^1$.

Proof. First, $G = T_3^1$ implies that $\chi(G) = (11n(G) - 2)/20$ by Lemma 3.3, so we only need to show the converse. Namely, suppose that for some benzenoid $G$, $\chi(G) = (11n(G) - 2)/20$. We will show that $G = T_3^1$.

Case 1: At least one exterior hexagon of $G$ is of type $e, f, g, h, i,$ or $j$. From the theorem, we see that each of these cases imply that $\chi(G) < (11n(G) - 2)/20$ which contradicts the supposition that $\chi(G) = (11n(G) - 2)/20$. Therefore, this case is not possible.

Case 2: Every exterior hexagon is of type $a, b, c, d,$ or $k$. We can subdivide this case into two subcases; namely, that at least one exterior hexagon of $k$ while all others are of the first four types, or all exterior hexagons are of the first four types.

Case 2a: At least one exterior hexagon is of type $k$ while all others are of the first four types. Since every vertex of a type $k$ hexagon is shared by at least one other hexagon, removing these hexagons from $G$ just amounts to removing the edge that constitutes it. Let $H$ be a type $k$ hexagon in $G$. Remove $H$ from $G$. Note that

$$\frac{(11n(G) - 2)}{20} = \chi(G) \leq \chi(G \setminus H) \leq \frac{(11n(G \setminus H) - 2)}{20} = \frac{(11n(G) - 2)}{20}. $$

Now, one of three situations must be true for $G \setminus H$:

1. At least one exterior hexagon of $G \setminus H$ is of type $e, f, g, h, i,$ or $j$. But this leads to an immediate contradiction. The existence of a hexagon of one of these types implies that the benzenoid has independence number strictly less than $(11n(G) - 2)/20$. So this case is impossible.
2. All exterior hexagons are of type $a, b, c, d,$ or $k$. But then $G \setminus H$ is a fused triangulene and must be $T_3^1$ by Lemmas 3.2 and 3.3. This is a contradiction since there is no way to add one hexagon to $G \setminus H = T_3^1$ without increasing the number of vertices, and yet $G$ is exactly $G \setminus H$ plus an edge. So this case is impossible.
3. At least one hexagon of $G \setminus H$ is of type $k$ while all others are of type $a, b, c, d,$ or $k$. But then we can remove another hexagon of type $k$ and repeat this situation. We see that after iteration, we arrive eventually at a benzenoid which has a hexagon of type $e, f, g, h, i,$ or $j$; or else we arrive at a benzenoid, all of whose hexagons are of the first four types. But we see from above that neither of these two situations is possible. Therefore, this case is also impossible.

Since one of these must be true and yet all of them are impossible, we find that case 2a is itself impossible. Thus we are left with only one alternative.

Case 2b: All of the exterior hexagons of $G$ are of type $a, b, c, d,$ or $k$. Again, by appeal to Lemma 3.2, this implies that $G$ is a fused triangulene. The fact that it is a fused triangulene compounded with the assumption that $\chi(G) = (11n(G) - 2)/20$, implies via Lemma 3.3 that $G = T_3^1$ for some $j \geq 1$. □

Things are actually a bit messier than this when the integer part of this upper bound is considered. The general case of equality for the floor of this upper bound is unknown. But, I should remark that there are 115 benzenoids with six or less hexagons and among them, there are 52 for which equality holds. The cata-condensed benzenoids on enough hexagons are examples where equality does not hold.

A benzenoid with some connected set of internal hexagons removed is called a coronoid and the removed hexagons are a coronoid hole or just a hole [7]. A coronoid with more than one hole is sometimes called a multi-coronoid [7]. To see that this upper bound for independence number in benzenoids does not hold for multi-coronoids, consider the following example. It can be thought of in two ways. First, as a $T_6$ triangulene with a central vertex which is not in the unique maximum independent set removed, increasing the independence ratio and producing a multi-coronoid with one hole (Fig. 8). Second, as the mutual edge fusion of three $T_3$ triangulenes at their apices, each fused to the other two.

Fractal benzenoid and coronoid families have been considered before in [16,17], and then later in [20]. Next, we show a family of fractal multi-coronoids which achieve a conjectured maximum independence ratio for this family.

Conjecture 3.6. The independence ratio of a multi-coronoid does not exceed 21/38. Moreover, if correct, this constant is best possible since the independence ratio’s of the family of multi-coronoids depicted in the following figure can be made arbitrarily close to 21/38 (Fig. 9).
Corollaries

Graffiti conjectured that the number of positive eigenvalues of a multi-coronoid was equal to its matching number [9]. This result for cata-condensed benzenoids, due to Gutman, was known for some time (see [4] for instance). Recently, Sachs proved Graffiti’s conjecture for benzenoids [21].

Theorem 4.1 (Sachs, John, Fajtlowicz). If G is a benzenoid with matching number $\mu$ and $p_+$ positive eigenvalues in its adjacency matrix, then $\mu = p_+$. This theorem is equivalent to the following.

Theorem 4.2. The number of unpaired sites in a benzenoid system with respect to any maximum matching is equal to the number of zero eigenvalues of its adjacency matrix.

Proof. Given a maximum matching $M$ of a benzenoid, the number of vertices not in $M$ is the number of unpaired sites in the system with respect to $M$. This is because each such vertex has three single (sigma) bonds but no double

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4 A cata-condensed benzenoid is one whose inner dual has no cycles.
(pi) bond, and as a representation of the 4-valent carbon, has an unpaired electron. By letting $F$ denote the number of unpaired sites and by using the equation, $\alpha + \mu = n$ (since benzenoids are bipartite), we can write these observations as,

$$F = n - 2\mu = 2\alpha - n = \alpha - \mu.$$  

Now, let $p_+, p_-$, and $p_0$ denote the number of positive, negative, and zero eigenvalues of the adjacency matrix. Bipartite graphs have symmetric spectrums so that $p_+ = p_-$. Using Theorem 4.1, we find

$$F = n - 2\mu = n - 2p_+ = n - p_+ - p_- = p_0.$$  

Now we can state an interesting corollary to our main result.

**Corollary 4.3.** Let $G$ be a benzenoid with $p_0$ zero eigenvalues and $F$ unpaired sites with respect to a maximum matching. Then, $G$ satisfies the following:

$$F = p_0 \leq \frac{(n(G) - 2)}{10} < \frac{n(G)}{10}.$$  

**Proof.** Using Theorem 3.4, we get

$$F = p_0 = 2\alpha(G) - n(G) \leq 2\left(\frac{11n(G) - 2}{20}\right) - n(G) = \frac{22n(G) - 4 - 20n(G)}{20} = \frac{2n(G) - 4}{20} = \frac{n(G) - 2}{10} < \frac{n(G)}{10}.$$  

Since zero eigenvalues and unpaired sites are both indicative of instability or reactivity, this theorem gives us a way to know how unstable a given benzenoid can be based only on the number of carbon atoms.

**References**