Characterization of distribution of pi-electrons amongst benzenoid rings for Randić's "algebraic" Kekulé structures

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For benzenoid hydrocarbons the distribution of pi-electrons amongst rings is characterized in the context of Randić's mode of assignment attending to the different Kekulé structures. In particular, the mean and mean deviation from the mean are considered, and the benzenoids which achieve maximum deviation are identified.

KEY WORDS: benzenoid, Kekulé structure, deviation, mean deviation

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1. Introduction

Benzenoid hydrocarbons are here considered to correspond to a planar network of fused hexagons, such that there are no other rings of other sizes. See, e.g., Cyvin and Gutman [1], who moreover, focus on Kekulé structures (or perfect matchings) of "benzenoids". For any benzenoid system B, let us denote the number of hexagons (of B) by h, the number of vertices (in B) by n, by e the number of edges (of B) and by n_{in} the the number of the inetranl vertices in B (i.e. vertices that belong to three hexagons).

Let B have a Kekulé structure κ. In a recent paper, Randic [2] has considered a manipulation and representation of Kekulé structures, especially of benzenoids. He terms a conventional Kekulé structure "geometric", and a novel structure called an "algebraic Kekulé structured" is assigned to each geometric Kekulé structure. An algebraic Kekulé structure is a function that assigns to each hexagon of B one of the numbers $0, 1, \ldots, 6$ (a Randić electron count) in special way: Each double bond that belongs to only one hexagon contributes two
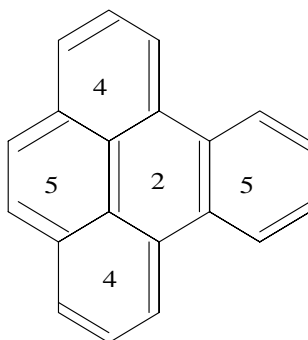
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Figure 1.

electrons to that hexagon and each double bond that is on the border of two hexagons contributes one electron to each hexagon. A self-explanatory example is shown in (figure 1) above:

Such an assignment of electrons to rings has been argued [2] to be chemically meaningful. Thence the characterization of such distributions should also be of interest. We denote by $|\kappa|_\xi$ the Randic electron count for κ in ring ξ of B, by $M(\kappa)$ the mean value of the $|\kappa|_\xi$ averaged over rings ξ of B, by $MD(\kappa)$ the ring-averaged deviation of $|\kappa|_\xi$ for κ of B, and by $SD(\kappa)$ the standard derivation of $|\kappa|_\xi$ over rings of B. e.g., $MD(\kappa) = h^{-1} \sum_{\xi}^{B} \big||\kappa|_\xi - M(\kappa)\big|$.

Here attention is directed to the expected values for $M(\kappa)$, along with upper bounds for associated deviations from the mean. The benzenoids with deviations achieving our upper bounds are identified.

2.   Mathematical results

We start with some useful auxiliary results:

Lemma 1. Let B be a benzenoid with h hexagons and n_{in} internal vertices. Then

(1) $n = 4h + 2 - n_{\text{in}}$

(2) $e = 5h + 1 - n_{\text{in}}$

(3) B is Kekulean $\Rightarrow n_{\text{in}}$ is even and $M(\kappa) = 4 + (2 - n_{\text{in}})/h$ is independent of κ

Proof. (1) and (2) are given in [3,4] and also in [1]. Let us prove (3). Obviously, if B is Kekuléan, then n is even, hence, from (1), it follows that n_{in} is even, too. Note that the sum of Randic electron counts of all hexagons is equal to n. Therefore, $M(\kappa) = n/h = 4 + (2 - n_{\text{in}})/h$.   □

Hereafter $M(\kappa)$ is abbreviated to just M.

Lemma 2. Let B be a Kekuléan benzenoid with h hexagons and n_{in} internal vertices. Then for each Kekulé structure there are at least $2 \cdot n_{in}$ single-electron contributions to some Randic electron-count for the different rings of B.

Proof. For each peri-vertex i there is one double bond ε in a Kekulé structure κ incident at i, and as such a ε is shared between two rings, each of which makes a single-electron contribution to their Randić numbers as shown in figure 2 below. This proves the claim. $\qquad\square$

Lemma 3. Let B be a benzenoid with h hexagons, $n_{in} = 0$, and Kekulé structure κ. Then

$$MD(\kappa) \leqslant \frac{8}{3} - \frac{4}{3h} - \frac{4}{3h^2}.$$

Proof. Recall that $h \cdot MD(\kappa) = \sum_{\xi}^{hex} \big| |\kappa|_\xi - M \big|$ where the summation is over rings of B, and M is fixed (from lemma **1**) at $4 + (2 - 0)/h$. The plus and minus argument gives that maximum deviations $\big| |\kappa|_\xi - M \big|$ occur when $|\kappa|_\xi$ takes values extreme values (i.e. 6 and 0), respectively. Now the maximum numbers of these maximal ring deviations can be no greater than numbers h_6 and h_0 such that $h_6 + h_0 = h$ and $M = (0 \cdot h_0 + 6 \cdot h_6)/h$. Then

$$h_6 = \frac{Mh}{6} = (4 + \frac{2}{h})\frac{h}{6} = \frac{2h + 1}{3}.$$

If this maximum were achieved for h_6 while $h_0 = h - h_6 = (h - 1)/3$, then the associated value that $MD(6)$ would achieve is

$$MD_{0-bound} = \frac{1}{h}\{h_0 \cdot M + h_6 \cdot (6 - M)\} = \frac{8}{3} - \frac{4(h + 1)}{3h^2}$$
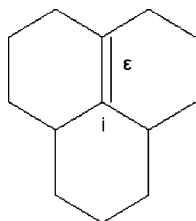
and the lemma is proved. $\qquad\square$

Figure 2.

A benzenoid with $n_{in} = 0$ is called a *cata-hex*. A cata-condensed benzenoid containing no subgraph isomorphic to anthracene is termed an *all-kink* cata-hex. The *inner dual* G* for a planar embedding of a planar graph G such that no two internal cycles share more than a single edge is the graph whose vertices correspond to internal rings of the embedding and whose edges correspond to pairs of these rings (of G) having a common edge (of G). Let us illustrate this with the following example (see figure 3 as shown below).

Theorem 4. The upper bound of Lemma 3 for $MD(6)$ is achieved for a Kekuléan benzenoid B with $n_{in} = 0$ if and only if: first, B is an all-kink cata-hex; and second, all degree-1 and degree-2 vertices are starred in a bipartitioning of the inner dual of B.

Proof.   First for such a cata-hex it may be shown that the bound is achievable. One assigns the rings ξ of B identified with the starred and unstarred vertices of the inner dual B* respective values $|\kappa|_\xi = 6$ and 0. This potential algebraic Kekulé structure may be seen in fact to identify a geometric Kekulé structure: a ring of B corresponding to an end vertex of B* is assigned double bonds as in figure 4a, while a ring of B corresponding to a starred degree-2 or degree-3 vertex of B* is assigned double bonds as in figure 4b or 4c.
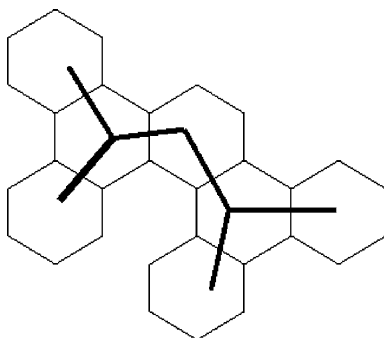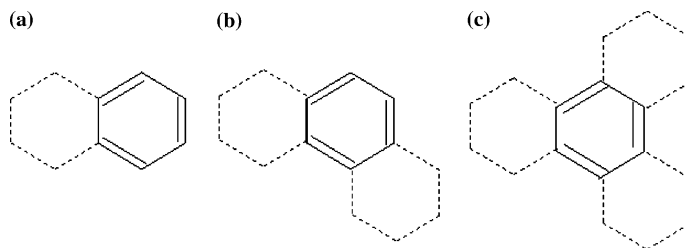

Figure 3.

Figure 4.

Having done this one sees that all the sites in the remaining rings of *B* are double bonded with double bonds in adjacent rings, as in figure 5.

Thus, the "if" part of the theorem is established. For the "only if" part consider that in order to achieve the bound of Lemma 3, it was needed that $n_{in} = 0$ so that a Kekulé structure with only $|\kappa|_\xi = 6$ and 0 could be achieved. Then for such a cata-hex to achieve these extremal values for $|\kappa|_\xi$ it is clear that the terminal rings necessarily having $|\kappa|_\xi > 0$ needs to be chosen as in figure 3a, whence the adjacent rings having $|\kappa|_\xi < 6$ must be chosen with $|\kappa|_\xi = 0$, so that they must be as figure 5. In fact it is seen that alternant rings must have alternate $|\kappa|_\xi$ values (0 and 6), and the overall structure demanded is that indicated in the Theorem. □

Theorem 5. Consider benzenoids in the class of Theorem 4. Then:

(1) such *B* are cata-hexes with $h = 3m + 1$, $m \geqslant 0$;

(2) every such B_+ of $3m + 4$ hexagons, $m \geqslant 1$, can be constructed from one (or more) similar *B* with $3m + 1$ vertices by fusing a phenanthrene to a degree-1 or -2 ring of *B* corresponding to a starred vertex of the inner dual of *B*, as in figure 6; and

(3) every such B_- of $3m + 1$ hexagons, $m \geqslant 0$, can be constructed from one (or more) such benzenoids with $3m + 4$ vertices by the reverse of this fusing procedure.

Proof. First, from Theorem 4 it is clear (with $n_{in} = 0$) that all *B* of the class C of Theorem 4 must be cata-hexes. To see the second of the results of the current theorem, suppose that $B \in$ C, whence it is readily verified that the fusion of figure 6 leads to yet another $B_+ \in$ C: the rings of *B* retain in B_+ the same $|\kappa|_\xi$ values as in *B*, the center ring of the fused phenanthrene has $|\kappa|_\xi = 0$, and the 2 terminal rings of the phenanthrene have $|\kappa|_\xi = 6$. Next for the third of these
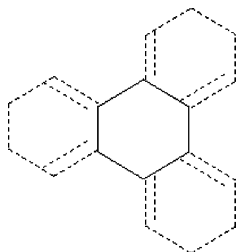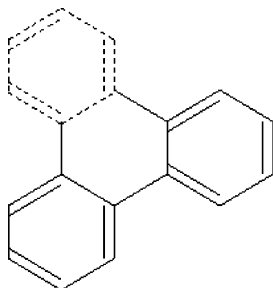

Figure 5.

Figure 6.

results one sees that there is a ring ξ of $B \in \mathtt{C}$ adjacent to two terminal rings; evidently $|\kappa|_\xi = 0$ so that the third neighbor of ξ has corresponding electron counts of 6. Now B_- is obtained by deletion of the ring ξ together with its two terminal neighbors. Then one sees that all finite $B \in \mathtt{C}$ with $h \geqslant 4$ rings can be through repeated such defusions reduced to one of $h \leqslant 3$, whereupon examination of the consequent 4 Kekuléan benzenoids (benzene, naphthalene, anthracene, and phenanthrene) reveals that only benzene entertains a "maximal" Kekulé structure as considered here. Thence finally the first result is established.   □

Consideration of the proofs of the preceding two theorems reveals:

Corollary 6. Of benzenoids in the class of Theorem 4, all have a unique $MD(\kappa)$-maximizing Kekulé structure κ except for benzene (which has 2).

Theorem 7. Amongst Kekuléan benzenoids with arbitrary n_{in} and a number $h = 3m + 1$ of hexagons, the maximum $MD(\kappa)$ is that of Lemma 3 for suitable benzenoids as in Theorem 4.

Proof. To find an upper bound for $MD(\kappa)$ at a given h and n_{in}, start out noting that the number of 1-electron contributions (to the counts $|\kappa|_\xi$) is by lemma 2 equal to 2 n_{in}, so that the number of 2-electron contributions must be $\leqslant (n - n_{\text{in}})/2$. Also $2 < M < 4$ (for $n_{\text{in}} > 0$), so that the maximum conceivable deviation $\big||\kappa|_\xi - M\big|$ for a ring ρ with a 2-electron contribution is >2 (at $|\kappa|_\xi = 6$). Thus an upper bound to $MD(\kappa)$ is obtained if we imagine a prospective maximum number $(n - n_{\text{in}})/6 \equiv h_6$ of rings ρ to make this maximum deviation $6 - M$. That is,

$$MD_{\text{bound}} = \frac{1}{h}\left\{(6 - M)\frac{N - n_{\text{in}}}{6} + \begin{bmatrix} \text{results from} \\ \text{1-electron contributions} \end{bmatrix} + Mh_0\right\},$$

where we shall use h_i to denote the prospective number of rings with $|\kappa|_\xi = i$. Of the imagined rings > with $|\kappa|_\xi \leqslant 5$, there are just $h - h_6 = h - (n - n_{\text{in}})/6$

remaining rings on which to distribute the $2n_{in}$ different 1-electron contributions. Further, since 1-electron contributions cannot occur at adjacent bonds all of these remaining rings (with $|\kappa|_\xi \leqslant 5$ and without 2-electron contributions) must have $|\kappa|_\xi \leqslant 3$, and we obtain an upper bound on $MD(\kappa)$ as

$$MD_{bound} = \frac{1}{h}\left\{(6-M)\frac{N-n_{in}}{6} + |M-3|h_3 + (M-2)h_2 + (M-1)h_1 + Mh_0\right\}$$

$$= \frac{1}{h}\left\{(6-M)\frac{N-n_{in}}{6} + (|M-3|-M)h_3 - 2h_2 - h_1 + M(h-h_6)\right\}$$

with $3 < M < 4$, we have $-3 < (|M-3|-M) < -1$, and one sees that in our expression for MD_{bound} the middle terms involving h_3, h_2, and h_1 make negative contributions of no more than –1 per 1-electron contribution. That is, if this upper bound is imagined to be as low as possible, then these terms involving h_3, h_2, and h_1 may be taken into account by a single term of $-1 \times (2n_{in})$, thusly

$$MD_{bound} = \frac{1}{h}\left\{(6-M)\frac{N-n_{in}}{6} - 2n_{in} + M(h-h_6)\right\}.$$

Substitution of $h_6 = (n - n_{in})/6$, $n = 4h + 2 - n_{in}$, and $M(\kappa) = 4 + (2 - n_{in})/h$, then leads to

$$MD_{bound} = \frac{1}{h}\left\{\frac{8}{3}h - \frac{4}{3} - \frac{4}{3h} - n_{in} + 2\frac{n_{in}}{h} - \frac{2n_{in}^2}{3h}\right\}$$

$$= MD_{0-bound} - \frac{n_{in}}{h}\left\{1 - \frac{2}{h} + \frac{2n_{in}}{h}\right\},$$

where $MD_{0-bound}$ is the ($n_{in} = 0$) bound of Lemma 3. Since $n_{in} \geqslant 2$ and $h \geqslant 4$, we have $MD_{bound} < MD_{0-bound}$, whence the theorem is established. □

Corollary 8. The value 8/3 for $MD(\kappa)$ is approached (from below) arbitrarily closely for finite benzenoids B, and is achieved only for infinite B, such B satisfying the conditions of Theorems 4 and 5.

Parallel results follow for $SD(\kappa)$:

Lemma 3′. For a benzenoid B with h hexagons, $n_{in} = 0$, and a Kekulé structure κ,

$$SD(\kappa) \leqslant \sqrt{8 - \frac{4}{h} - \frac{4}{h^2}}.$$

Theorem 4′–8′. For Kekuléan benzenoids the $SD(\kappa)$ upper bound of lemma 3′ is achieved in exactly the same circumstances as described in Theorems 4 and 5, Corollary 6, Theorem 7, and Corollary 8 for achievement of the $MD(\kappa)$ upper bounds.

3.   Discussion and conclusion

A possible point of interest is that the class of benzenoids with an inner dual which is a tree with all vertices of degree-1 or -3 (somewhat as in Theorem 4) is [5] also that with a maximum number of Kekulé structures per hexagon. Given a maximum number of Kekulé structures it is perhaps not so surprising that one also finds maximal deviations.

The maximizing Kekulé structures of Theorems 4 and 5 look like what might be called "anti-Fries" structures, "Fries structures" being Kekulé structures which have a sort of maximum of sharing of double bonds between rings. In more detail (in honor of Fries early work [6, 7]), a *Fries structure* of a graph G is a Kekulé structure κ such that there is a maximal number of rings of G which are conjugated 6-circuits in κ. The most favorable Fries structures κ occur for benzenoids where every hexagonal ring is a conjugated 6-circuit of. Notably such favorable Fries structures occur [8] precisely for those benzenoids which are all-kink cata-hexes. Moreover, there is a unique fullerene which has such a favorable Fries structure – namely, buckminsterfullerene.

In conclusion, Randić's "algebraic" Kekulé structure representation has been further characterized. The distribution of electrons amongst rings is characterized as to the maximum possible deviation $MD(\kappa)$ from the mean, and the apparently interesting class of benzenoids achieving this maximum have been identified.

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