Clar Theory for Molecular Benzenoids

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Eric Clar's ideas concerning "aromatic sextets" are extended to a quantitative format in terms of a polynomial called the "Clar 2-nomial", along with related derivative quantities. The quantification is successfully tested to make correlations with a selection of numerical data, including resonance energies, bond lengths, and NICS ring-aromaticity values.

Introduction

About 70 years ago, Pauling and Wheland started a fundamental development of resonance theory with a quantitative formulation that entailed diagonalization of ever larger matrices. Still, especially Pauling managed to cast the theory in a more convenient, more chemically manifest, less computational qualitative form as summarized in his masterwork[1] on *The Nature of the Chemical Bond*. Then also in a modestly more quantitative more purely organic focus, Wheland[2] wrote his *Resonance in Organic Chemistry*. However, starting about 60 years ago, there built up a shift to focus ever more toward molecular-orbital theory especially if quantitative conclusions were to be drawn. Still, almost 50 years ago Eric Clar began what may be viewed as a refinement of the simplified qualitative resonance theory, to focus on the efficacy of considering "aromatic sextets", the accompanying notation, and its use to qualitatively correlate a wide range of molecular properties. In 1970, Clar brought this work to a conclusion with the publication of his short charming book[3] *The Aromatic Sextet*, where his ideas were illustrated for the range of benzenoids then available. Since then there have been dramatic developments of related novel conjugated species: benzenoid polymers (such as poly-*para*-phenylene), carbon nanotubes, fullerenes, and miscellaneous other nanostructures (nanocones, nanotori, and hypothetical "negatively-curved" structures); and at the same time more focus on decorated (or defected) graphite has emerged, along with synthetic work on ever larger benzenoids, especially with Müllen's group.[4] It has become not uncommon to note correlations of Clar's formulations with various properties − but almost solely in a purely qualitative manner. Notably, Randic's extensive review[5] of "aromaticity" emphasizes Clar's qualitative ideas, where the author calls attention to the fact that Clar's theory is an easy model that allows understanding and predicting many properties of benzenoid species without the need of complicated calculations.

Here, then a quantitative formulation of Clar theory is sought, to apply not only to benzenoids considered by Clar but also to these various more recent novel conjugated nanostructures. Rather strangely over the decades since Clar's, book surprisingly little quantitative work deriving from his ideas has been reported. Part of the reason for this may be found in Clar's style of exposition − by example, with qualitative rationalizations, and without formal definitions or formal statements of principles. Thence to more plausibly discern Clar's overall idea and intent, one needs to carefully look at his book as a whole. One type of approach to quantification is to seek to parallel Pauling and Wheland's early work in setting up Hamiltonian matrices on a basis of the structures Clar used (rather than the Kekule structures of Pauling−Wheland resonance theory). Indeed this has been nicely done by Herndon and Hosoya,[6] to find quite favorable quantitative correlations with resonance energies otherwise elaborately computed via quantum chemical packages. Moreover, it has been emphasized[7] how Clar's ideas can be seen to directly motivate the (quantitative) "conjugated-circuits" resonance-energy formalism, which however is based on Kekule structures. But in fact such quantum-theoretic rationalization seems to be fairly foreign to Clar's style. Nevertheless, one would surmise that a more direct quantification of Clar's ideas should certainly be successful because of this thoroughly founded empirical basis of Clar's development.

Here, we seek to use "Clar structures," and a few invariants derived directly therefrom to correlate to molecular properties, without any explicit intervention of Hamiltonian matrices or Kekule structures. Moreover, beyond resonance energies we look at bond lengths as well as local aromaticity indices as given from the nuclear independent chemical shift (NICS) values. Indeed, a favorable comparison of NICS aromaticities with Clar's ideas has been recently noted by Ruiz-Morales[8] and Gutman and Ruiz-Morales[9] in terms of their Y-rule. The focus here on conventional benzenoids is to lay the appropriate quantitative groundwork for next dealing with the great variety of related novel nanostructures.

A conjugated polyhex or benzenoid network B is viewed as a graph, consisting of its sites and edges between the pairs of (σ-bonded) sites. A Clar structure C of B may be viewed as a condensation of Kekule structures into aromatic sextets insofar as possible. More formally one considers C to be a substructure of B such that every site is included in C such as to be either paired to exactly one other site or else included in an aromatic sextet (a 6-cycle of B). The set of pairings (or double bonds) and aromatic sextets are all to be disjointed from one another, and done so as to saturate all sites such that among the pairings no triple occurs around a hexagon of B, this rather being recast

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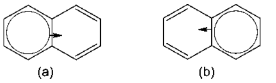

Figure 1. Clar structures of naphthalene.

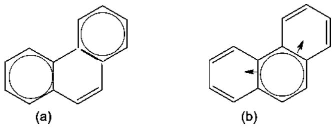

Figure 2. Clar structures of phenanthrene.

as an aromatic sextet. Thus, for naphthalene there are 2 such Clar structures, each with a sextet of 1 ring with 2 pairings remaining in the neighboring ring, as seen in parts a and b of Figure 1, where following Clar the ring associated to a sextet is indicated with a circle inscribed within the (hexagonal) ring. One benzenoid may have Clar structures with different numbers of sextets, with Clar emphasizing[3] that those Clar structures having a maximal number of sextets are preferred. These so-favored Clar structures are here termed sextet-maximum. Thus, for phenanthrene in Figure 2, there are two Clar structures with the first (the sextet-maximum one in part a of Figure 2) with 2 sextets favored over the other (in part b of Figure 2) with but a single sextet. But Clar indicates (on page 15 of his book[3]) that there is some slight degree of "aromaticity" for the center ring (and speaks of its "induced sextet"). He then uses a notation (his structure XI) for this to evidently avoid writing down the second of these structures, though we do not use this summarizing notation involving two (joint) arrows, inasmuch as Clar identifies a second meaning for arrows added into Clar structures. Basically, he also indicates that if a single sextet can "migrate", this adds stability, and also uses an arrow to indicate the mode of "migration". Here, noting the simplest migration is from one ring to a neighbor one that (before migration) has two isolated pairings, we choose to have an *arrow* indicate this possibility. Thus, we can so decorate each of the Clar structures of naphthalene with an arrow from the Clar circle to the adjacent ring. Apparently, Clar draws more arrows even to the nonadjacent rings, here we consider arrows to the adjacent rings first to move the sextets, then again the migration of that sextet to the next adjacent ring, and so on, hence covering all the possibilities considered by Clar. For phenanthrene, the first 2-sextet Clar structure would then have no arrows, whereas the second would have two, from the central sextet to each of the terminal rings. Larger benznoids can have more Clar structures (with more arrows), for example there being eight Clar structures for the three-fold annelated triphenylene of Figure 3. This molecule is particularly noteworthy as Clar relatively clearly enunciates (on page 39 of his book[3]) the relevance of Clar structures that are not sextet-maximum. Particularly in light of resonance theory, when there are many more such sextet-near-maximum Clar structures than the sextet-maximum Clar structures, these nonmaximum Clar structures can be anticipated to manifest some relevance − especially one might imagine for quantitative purposes, as is the goal here. This point may also seen in the earlier mentioned Clar-theoretic works[6,7] involving quantitative chemical application. In this work, we construct Clar 2-nomials with all the Kekule structures in case of essentially Kekulean molecular benzenoids. This also emphasizes the fact that appropriate importance should be given to all the Kekule structures and not only to the sextet-maximum structure as normally done. A final point is that the so-called *Kekulean* benzenoids B considered here are to have at least one Clar structure as defined above − the non-Kekulean benzenoids being radicaloid and addressed in a separate article. It also needs to be mentioned that the general expression for the Clar 2-nomials for linear polyacene series are relatively easier to figure out. However, the same for a higher analogue of zigzag polyacene is rather difficult. Nevertheless, following graph theoretical arguments, algorithms can be developed to get Clar 2-nomials for such systems.

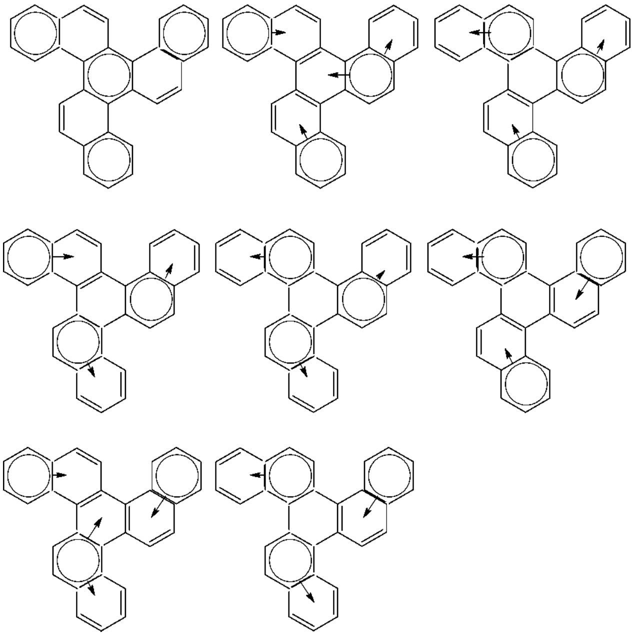

Figure 3. Clar structures of tri annelated triphenylene.

This preceding paragraph constitutes our framework for dealing with Clar structures and their quantifications, though as an aside it may be noted that there are other definitions of Clar structures, as presumably occurred because of Clar's informal style of presentation (without formal definitions or statements of principle, but with a multitude of examples, focusing on rationalizing one or another property, and then in naught but a qualitative manner). Thence, the definition here (and also by several other authors, starting with ref [6]) attends to Clar's "overall usage", and also, as argued in the next sections, it and subsequent quantifications relate to Pauling−Wheland resonance theory. Other definitions of Clar structures are briefly mentioned in the Appendix.

Quantification: Global Invariants. In a zero-order Pauling−Wheland resonance-theoretic picture, each Kekule structure can be approximated as of the same importance in describing a molecule's ground state (and determining molecular properties). Thus, the number $K(B)$ of Kekule structures of B is a chemically meaningful invariant, and in their book[10] Cyvin and Gutman list many formulas for $K(B)$ for different special classes of benzenoids. Clar structures on the other hand even in a zero-order picture are typically of different weights. It is natural to weight them in terms of the number $s_B(C)$ of aromatic sextets occurring in Clar structure C of polyhex B, and perhaps also of relevance is the number $a_B(C)$ of arrows (corresponding to naphthalene subgraphs H of B such that H contains 1 Clar sextet and 2 isolated edges of C). Moreover, $s_B(C)$ and $a_B(C)$ are "additive" (e.g., for disjoint fragmental B), whereas C having each different part of C indicating pairing-resonance occurrences in each corresponding part of the molecule, is a "global" quantity, being like independent "multiplicative" probabilities for each occurrence (especially in the simplifying case of disjoint fragmental B). Thence the *weight* associated to C naturally is

$x^{s_B(C)}y^{a_B(C)}$ with x (and y) indicating a contribution of a sextet (and arrow) to the overall probability of occurrence in the description of B. In as much as one can think of each aromatic sextet comprised from 2 local resonance patterns (with edges alternating around the hexagon in two different ways), and recall the Pauling–Wheland zero-order approximation for Kekule structures, one can surmise that a reasonable (unnormalized) weight for x might be ≈ 2, whereas $y \approx 1$. Nevertheless, at least initially, we leave x and y as variables.

The different weights of the different Clar structures may be added together to give an overall molecular sum, here termed the Clar 2-nomial

$$C_B(x, y) \equiv \sum_C^B x^{s_B(C)} y^{a_B(C)} \tag{1}$$

Clearly, this concisely and elegantly encodes aspects of the Clar structures identified as important by Clar: first, the number of Clar sextets; and second, the sextets' "mobility". Thus, the Clar 2-nomial for naphthalene is $2xy$, and for phenanthrene is $x^2 + xy^2$. Especially with an assignment of numerical values for x and y, $C_B(x,y)$ may be viewed as the analogue of the Kekule structure count $K(B)$ used in conjunction with ordinary resonance theory.

In a more "additive" way, these two aspects (of sextetness and sextet-mobility) are given by

$$\langle s \rangle_B \equiv \frac{\partial \ln C_B(x, y)}{\partial \ln x} = \sum_C^B s_B(C) x^{s_B(C)} y^{a_B(C)} / C_B(x, y) \tag{2a}$$

$$\langle a \rangle_B \equiv \frac{\partial \ln C_B(x, y)}{\partial \ln y} = \sum_C^B a_B(C) x^{s_B(C)} y^{a_B(C)} / C_B(x, y) \tag{2b}$$

Here, the weight $x^{s_B(C)}y^{a_B(C)}/C_B(x,y)$ is essentially a probability for the occurrence of a Clar structure C with s_B sextets and a_B arrows. Thence, eq 2a is an average number of aromatic sextets, and so is called the (average) *sextetness*. Also, eq 2b being an average number of mobility-indicating arrows, is called the (average) *Clar mobility*. For example, for phenanthrene, one has $\langle s \rangle = (2x^2 + xy^2)/(x^2 + xy^2)$ and $\langle a \rangle = (0 + 2xy^2)/(x^2 + xy^2)$, or a little more simply just $\langle s \rangle = (2x + y^2)/(x + y^2)$ and $\langle a \rangle = 2y^2/(x + y^2)$.

It may be remarked that H. Hosoya and co-workers[11,12] have defined an (a_B-independent) "Clar polynomial" in terms of an alternative definition of Clar structures, and this has been formally studied, even in some subsequent papers by other authors.[13] El-Basil[14] introduces a polynomial the same as $C_B(x,1)$ for the special case that B is a cata-condensed all-kink chain, and he extends[15] this polynomial to all benzenoids, finally calling[16] it the "Clar polynomial", which then also especially Zhang and Zhang[17,18] have dealt with in a formal manner. But neither of these polynomials seems to have been correlated to experimental data – nor have refined "derivative" invariants been studied, or even introduced. The naturalness of the current 2-nomial in encoding relevant information about the whole set of Clar structures recommends them for study.

Table 1 lists the Clar 2-nomials for a selection of benzenoids, as identified in Figure 4. These results are utilized in the fittings of the subsequent sections.

Resonance-Energy Correlations. The resonance energy of a benzenoid compound is a standard measure of the extra stability of the aromatic system compared to the corresponding number of localized double bonds.[1,2,4,7] (and somewhat similar to isolated double bonds, as in separate ethylenes). There are at least two natural Clar-theory-based ways to seek correlations to resonance energies, for example such as those computed by Dewar and de Llano.[19] Our first scheme parallels conjugated-circuits theory,[20,21] and takes the *Clar resonance energy* to be a linear combination of the sextetness and Clar mobility,

$$\mathrm{CRE}(B) \equiv A_1 \langle s \rangle_B + A_2 \langle a \rangle_B \tag{3}$$

where A_1 and A_2 are numerical constants. If the parallels[7] to conjugated-circuits theory are preserved, then A_1 and A_2 should have values respectively slightly less than 1 eV and 1/2 eV.

TABLE 1: Clar Binomial for the Benzenoids Given in Figure 4.

molecule	clar binomial $C_B(x,y)$	CRE(B)
I.	x	0.942
II.	$2xy$	1.447
III.	$2xy + xy^2$	1.616
IV.	$x^2 + xy^2$	1.907
V.	$2x^3 + 3x^2y^4 + 2xy^3$	3.185
VI.	$x^3 + xy^3$	2.753
VII.	$x^2 + 2xy^2$	1.918
VIII.	$2x^2y + xy^2$	2.302
IX.	$x^2y^2 + 2x^2y$	2.558
X.	$4x^2y^2$	2.894
XI.	$2xy^2 + 2xy$	1.700
XII.	$3xy^2 + 2xy$	1.750
XIII.	$2x^3y + xy^3$	3.157
XIV.	$x^3 + 2x^2y^2$	2.861
XV.	$x^3 + 2x^2y^3 + xy^3 + x^2y^2$	3.014
XVI.	$x^3y^3 + 3x^3y^2 + x^3y + 2x^2y^4 + 2x^2y^3 + xy^3$	3.738
XVII.	$x^4 + 2x^3y^2$	
XVIII.	$x^4 + 6x^3y^3 + 2x^2y^5 + 2x^2y^4 + 2x^3y$	4.042
XIX.	$16x^4y^4$	5.783
XX.	$x^7 + 6x^5y^3 + 6x^4y^4 + 2x^3y^6$	
XXI.	$x^6y^6 + 6x^6y^4 + 8x^6y^3 + 3x^6y^2 + 2x^4y^3$	
XXII.	$x^7 + 2x^6 + 6x^6y^2 + 24x^5y^5 + 15x^5y^4 +$ $8x^4y^9 + 6x^4y^4 + 6x^4y^3 + 6x^3y^5 + 2xy^3$	
XXIII.	$x^{13} + 12x^{11}y^3 + 18x^{10}y^5 + 6x^{10}y^3 + 2x^9y^9 +$ $6x^9y^8 + 30x^9y^7 + 15x^9y^6 + 6x^9y^{5+}2x^9y^3 +$ $18\,x^8y^8 + 6x^8y^7 + 6x^8y^6 + 6x^8y^3 + 6x^7y^9 +$ $6x^7y^7 + 2x^7y^{12} + 24x^7y^6 + 12\,x^6y^6 + 6x^6y^5 +$ $2x^6y^3 + 2x^4y^3$	

The Clar resonance energy for 18 benzenoids of different topological patterns (I–XVI, XVIII and XIX in Figure 4) have been treated, with $x = 2$ and $y = 1$. This choice of x and y correlates with Pauling–Wheland resonance-theoretic ideas, if we imagine each aromatic sextet to be made up of 2 local resonant pairing patterns. Though one might imagine modifications to these values, we keep these same simple values for x and y in this article. Parametric quantities in the expression of CRE(B) have been found by a least-squares fit to the resonance energy reported by Dewar and de Llano (DdLRE).[19] The result is

$$A_1 = 0.942\ \mathrm{eV}, A_2 = 0.505\ \mathrm{eV},\ \text{with}\ \sigma = 0.215\ \mathrm{eV}, \quad r = 0.981. \tag{4}$$

The quite reasonable standard deviation (σ) and the high correlation coefficient (r) indicate a quite successful fit, as does the closeness of the parameter values (A_1 and A_2) to those anticipated from the relation[7] to conjugated-circuits theory. The values of CRE(B) estimated for 18 benzenoids are given in Table 1. It is interesting to note that CRE(B) for phenanthrene (IV) is larger that that for anthracene (III), the same has been nicely explained recently by Poater et al.[22] by density functional calculations. Further the agreement is apparent from the plot of CRE(B) vs DdLRE(B) as given by Figure 5. The straight-line nature of the curve with a gradient close to unity supports the argument.

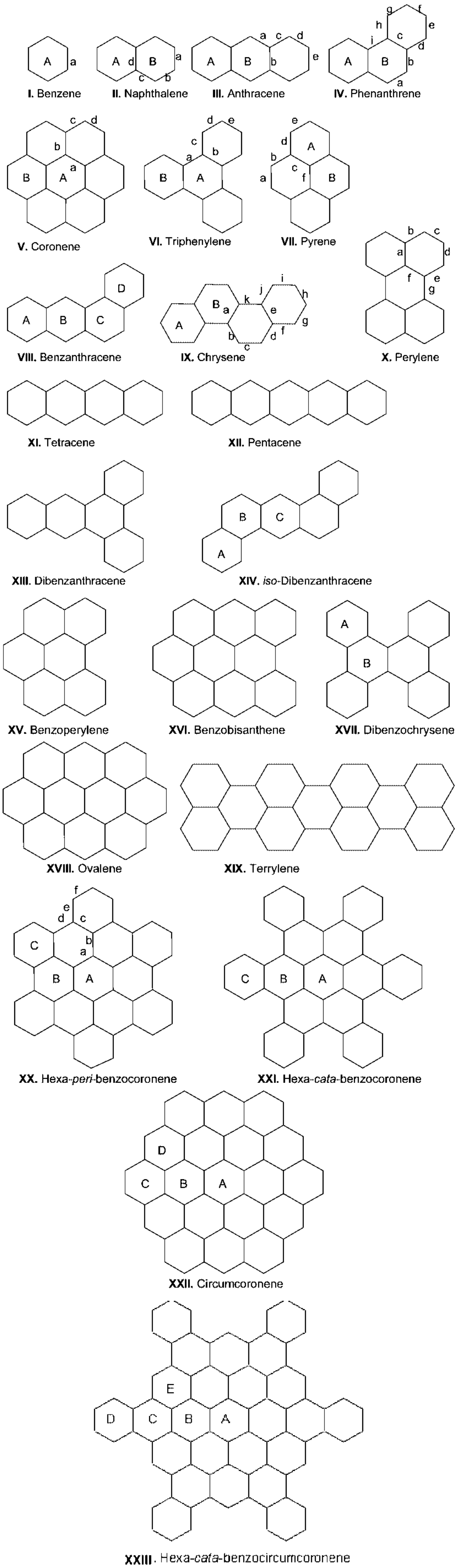

Figure 4. The set of benzenoids I−XXIII; rings of different (local) aromaticity are indicated by A, B, C, etc.; and different bond lengths are indicated by a, b, c, etc. in selected molecules.

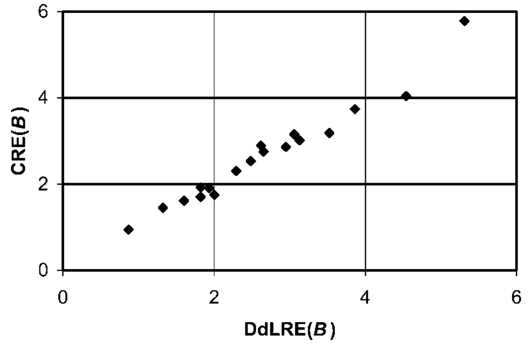

Figure 5. Plot of CRE(*B*) vs DdLRE(*B*).

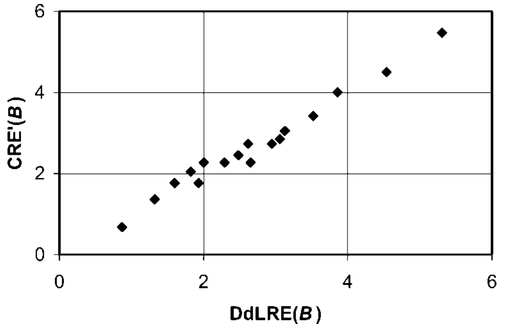

Figure 6. Plot of CRE'(*B*) vs DdLRE(*B*).

A second even simpler scheme parallels the conventional naïve resonance theory, where the resonance energy is expressed purely in terms of the Kekule-structure count $K(B)$. Because $C_B(x,y)$ multiplicatively factors when considering disjoint fragments, it is natural to consider its logarithm as a more nearly additive property − much as in parallel to what has already been done[23] with $K(B)$. That is, this approximation makes a second resonance-energy approximant as

$$\mathrm{CRE}'(B) \equiv A \ln C_B(x, y) \tag{5}$$

where A is a constant. Again we make a least-squares fit to obtain

$$A = 0.987\ \mathrm{eV},\ \text{with}\ \sigma = 0.180\ \mathrm{eV},\ \ r = 0.987 \tag{6}$$

which evidently is a very good fit. We also plot CRE'(*B*) versus DdLRE(*B*) in Figure 6 for the same set of benzenoids as before.

Overall, the prediction of resonance energy of benzenoid systems by either of these simple methods through use of the Clar 2-nomial may prove useful in the study of larger benzenoid systems, where the evaluation of the resonance energy by experiment or by resource-intensive quantum chemical calculations are usually prohibitive.

Local-Invariant Quantification. Besides global invariants (for the molecule as a whole), one desires local invariants for different parts of the molecule. Thus, the *Clar bond order* for the π electrons assigned to an edge e of B is defined as

$$\mathrm{CBO}_B(e) \equiv \sum_C^B \left\{\varepsilon_B(C, e) + \frac{1}{2}\eta_B(C, e)\right\} x^{s_B(C)} y^{a_B(C)} / C_B(x, y) \tag{7}$$

where $\varepsilon_B(C,e)$ is 1 or 0 as e is or is not a double bond in C, and $\eta_B(C,e)$ is 1 or 0 as $e$is or is not in an aromatic sextet of C. That is, for a given edge e of B, its occurrence as a double bond of C fully contributes to a π bond order, whereas its occurrence in an aromatic sextet where bonds are delocalized (being contained in 1 of the component local pairing patterns but not the other) contributes just $^1/_2$ — and otherwise if e does not occur in C it contributes 0. These bond orders CBO_B are typically much easier to compute than the Pauling bond order (or the MO-based Coulson bond order), though they frequently are similar, with the Clar bond order arguably improving a little on the Pauling bond order. That is, the Pauling bond order weights all Kekule structures equally, whereas it is known (e.g., from conjugated-circuits theory, or examples of quantitative Pauling−Wheland VB models) that the Kekule structures admitting more sextets should be weighted more highly (as is done with CBO_B).

Further, there are two related "local aromaticity indices" for a (6-cycle) ring α of a benzenoid B,

$$\mathrm{CAI}_B(\alpha) \equiv \sum_C^B s_B(C,\alpha) x^{s_B(C)} y^{a_B(C)} / C_B(x,y) \qquad (8a)$$

$$\mathrm{CAI}'_B(\alpha) \equiv \sum_C^B a_B(C,\alpha) x^{s_B(C)} y^{a_B(C)} / C_B(x,y) \qquad (8b)$$

where $s_B(C,\alpha)$ is 1 or 0 as α is or not a Clar sextet in C, and $a_B(C,\alpha)$ counts the number of naphthalenes which contain $\alpha \subseteq C$ along with 2 other double bonds of C. Here, then CAI'_B is a secondary aromaticity index indicating Clar's "induced sextets" arising from migration of the sextets. It can be seen that $a_B(C,\alpha)$ is 0, 1.

These various local invariants are intimately related to the earlier considered global invariants. First, $\sum_\alpha^B s_B(C,\alpha) = s_B(C)$ and $\sum_\alpha^B a_B(C,\alpha) = a_B(C)$, so that

$$\langle s \rangle_B = \sum_\alpha^B \mathrm{CAI}_B(\alpha) \text{ and } \langle a \rangle_B = \sum_\alpha^B \mathrm{CAI}'_B(\alpha). \qquad (9)$$

Thus, the expression $A_1\mathrm{CAI}_B(\alpha) + A_2\mathrm{CAI}'_B(\alpha)$ is naturally anticipated to be an overall local aromaticity index for ring α (for example, simulating NICS values). Also, because the net number of π bonds in a Clar structure is just half the number n of sites, one has

$$\frac{n}{2} = \sum_e^B \mathrm{CBO}_B(e). \qquad (10)$$

Being the local indicator of the presence of a bond, $\mathrm{CBO}_B(e)$ should correlate with bond lengths — at least so long as x and y are chosen properly.

Bond-Order Correlations to Bond Lengths. The decrease of bond length from a carbon−carbon single bond and the increase of it from a double bond is a measure of aromaticity in benzenoids. Now, the Clar bond length (CBL) for a bond $e \equiv \{i,j\}$ is presumed to be of the form

$$\mathrm{CBL}(e) = B_1 + B_2\{\mathrm{CBO}_B(e)\} + B_3/\sqrt{d_i d_j} \qquad (11)$$

where B_1, B_2, and B_3 are parametric quantities, and d_i and d_j are the (pi-network) degrees of the two carbons comprising the edge e. This last B_3 term is included because it seems that bond lengths depend on the functionalities of the carbons involved, the functional dependence here being chosen as that involved in the Randic connectivity index,[24] such as has been[25,26] notably successful in making correlations with a wide variety of properties. (An especially clear case manifesting this functionality dependence of the bond lengths is found for the central bond of naphthalene, which is otherwise anomalously long.)

Here, we have chosen ten different benzenoids (I−VII, IX, X, and XX in Figure 4) having a total of 58 different bond lengths which are marked as a, b, c, and so forth in the figure.

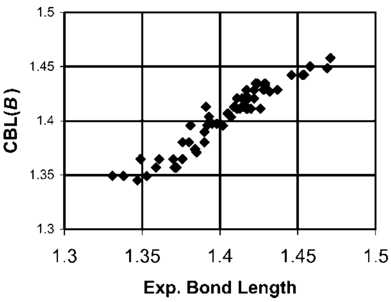

Figure 7. Plot of Clar bond length vs experimental bond length.

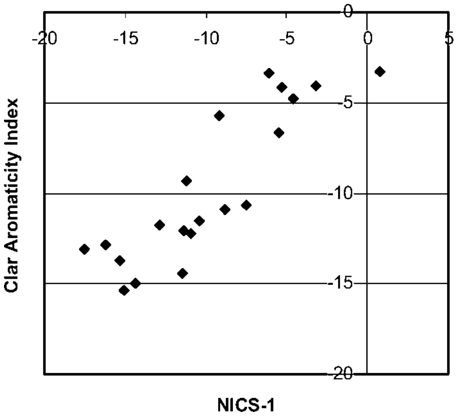

Figure 8. Plot of 1st fit for Clar aromaticity index vs NICS-1.

The experimental bond lengths collected by Kiralj and Ferreira[27] have been least-squares fit to the expression of 11 to give

$$B_1 = 1.520\ \text{Å},\ B_2 = -0.098\ \text{Å},\ B_3 = -0.185\ \text{Å},$$
$$\text{with } \sigma = 0.009\ \text{Å},\ r = 0.957 \qquad (12)$$

which evidently is a decent fit. The set of CBL_B and experimental bond lengths are very much in agreement, as displayed in Figure 7. The numerical values of experimental bond lengths appear in Table 2. The negative values of B_2 and B_3 are expected as these last two factors in eq 11 decrease the bond length from a single-bond length B_1, in a π network. The CBL values also match closely with the theoretically predicted values both by Morikawa et al.[28] and more extensively by Kiralj and Ferreira,[27] who attain a similar r-value, though with more parameters. Not only our Clar bond order but also perhaps more especially our choice for the functionality dependence (in the B_3-term) of the atoms involved in a bond seems a more "economic" choice than Kiralj and Ferreira's triple of parameters associated to their n, l, m indices.

Yet further, the Clar bond order may be correlated with other bond orders computed by other more quantum-chemical procedures, for example for the VB-based bond-order of Li and Jiang,[29] using exact solutions to the nearest-neighbor full covalent-space VB model. They use a bond order linear in the local interaction operator such as to give 1 for a singlet-coupled pair of sites and 0 for a triplet coupled pair of sites. However, the more conventional choice of Penny[30] instead uses the linear operator such as to give 1 for a singlet-coupled pair of sites and 0 for an uncorrelated pair of sites. (It may be deemed that these Penny bond orders have a more reasonable range of values, coming nearer to 0 for neighbor pairs of sites at "essentially single" bonds, and having a sum of bond orders to nearest neighbor sites from a given site that more frequently does not so greatly exceed 1.) This Penny bond order of a bond $e \equiv \{i,j\}$ for a benzenoid B with wave function Ψ is given as

$$\mathrm{PBO}_B(e) \equiv -\frac{4}{3}\langle\Psi|\vec{s}_i\vec{s}_j|\Psi\rangle \qquad (13)$$

where $\vec{s}_k$ is the spin operator for site k. Making a direct comparison of our Clar bond order to the Penny bond orders for the 8 benzenoids of Li and Jiang[29] yields a correlation coefficient of $r = 0.861$. However, the fit may be improved via a least-squares fitting of the same type as used for the experimental bond lengths, whence again for the same 8 benzenoids (and 59 symmetry distinct bonds) as considered by Li and Jiang,[29] we find

$$B_1 = 0.164, B_2 = 0.263, B_3 = 0.643, \text{ with } \sigma = 0.025, \quad r = 0.960 \qquad (14)$$

TABLE 2: Experimental Bond Length and Clar Bond Length of Chosen Bonds in Benzenoids (Figure 4)

molecule and bond	bond	experimental bond length (Å)[24]	CBL(B)/Å
benzene	a	1.390	1.380
naphthalene	a	1.407	1.404
	b	1.371	1.357
	c	1.422	1.421
	d	1.420	1.411
anthracene	a	1.395	1.397
	b	1.432	1.427
	c	1.428	1.429
	d	1.353	1.349
	e	1.418	1.442
phenanthrene	a	1.338	1.349
	b	1.422	1.429
	c	1.413	1.411
	d	1.414	1.413
	e	1.349	1.365
	f	1.381	1.396
	g	1.376	1.365
	h	1.391	1.413
	i	1.454	1.442
coronene	a	1.424	1.435
	b	1.420	1.411
	c	1.414	1.421
	d	1.372	1.357
triphenylene	a	1.469	1.449
	b	1.411	1.411
	c	1.405	1.407
	d	1.385	1.371
	e	1.390	1.390
pyrene	a	1.347	1.345
	b	1.429	1.432
	c	1.417	1.423
	d	1.400	1.397
	e	1.380	1.380
	f	1.423	1.435
chrysene	a	1.402	1.396
	b	1.437	1.429
	c	1.331	1.349
	d	1.417	1.429
	e	1.417	1.411
	f	1.415	1.413
	g	1.361	1.365
	h	1.392	1.396
	i	1.370	1.365
	j	1.409	1.413
	k	1.453	1.442
perylene	a	1.426	1.411
	b	1.411	1.421
	c	1.359	1.357
	d	1.393	1.404
	e	1.384	1.374
	f	1.429	1.435
	g	1.471	1.458
hexa-peri-benzocoronene	a	1.417	1.419
	b	1.446	1.442
	c	1.417	1.419
	d	1.458	1.450
	e	1.398	1.397
	f	1.376	1.380

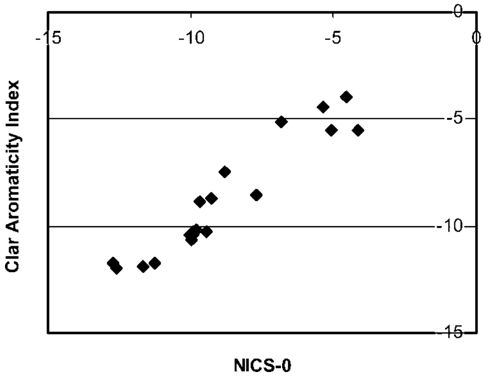

Figure 9. Plot of 2nd fit for Clar aromaticity index vs NICS-0.

The advantage to our Clar bond order is that it is considerably less computationally demanding — the full covalent-space VB bond orders involving wave functions that involve around a million configurations at 26 sites — and with ever increasing numbers thereafter.

Local Aromaticity Correlations to NICS Values. Clar aromaticity is defined in terms of our local aromaticity indices for ring α as

$$CA(\alpha) = C_1 CAI_B(\alpha) + C_2 CAI'_B(\alpha) + C_3\frac{1}{1 + n_\alpha/6} \qquad (15)$$

where C_1, C_2, and C_3 are parameters and n_α is the number of benzene rings which abut to ring α. This third term here can be imagined to be relevant if the aromaticity index to be fitted against has nonlocal contributions (from neighbor rings), such as presumably is the case with nucleus-independent chemical shift (NICS) values, which are a well-advocated measure of local aromaticity in benzenoids[31,32] (and beyond).

First, we chose a set of molecules (I, V, VI, XX-XXII in Figure 4) and compare CA with the NICS-1 values reported by Moran et al.[31] A least-squares fit yields

$$C_1 = -3.345, C_2 = -24.921, C_3 = -5.476, \quad \text{with } \sigma = 2.398 \text{ ppm}, r = 0.860. \qquad (16)$$

This is only a modest fit for such a correlation coefficient, as is also seen from Figure 8. Here, contrary to expectation the second term dominates over the first; that is, the ratio of C_1 and C_2 is inverse to that we anticipated.

As a second comparison, we chose a set of molecules (I−IV, VII−IX, XIV, and XVII in Figure 4) and the NICS-0 data of Portella et al.[32] A least-squares fit yields

$$C_1 = -3.909, C_2 = -9.628, C_3 = -5.426, \quad \text{with } \sigma = 0.831 \text{ ppm}, r = 0.946. \qquad (17)$$

which is a notably better fit as also is seen from Figure 9. Here, also the ratio of C_1 and C_2 is more nearly in concert with our expectations − though even now C_2/C_1 is quite different than $^1/_2$. Further, for both models (of eqs 16 and 17) there is a notable contribution from the third term, such as seems to indicate the fact that NICS indices have noticeable (less local) contributions from the neighboring ring, which has been demonstrated in several examples, in particular, by Poater et al.[33] This comparison between eqs 16 and 17 also indicates that NICS-0 values are better correlated, which is also apparent from Figures 8 and 9.

As a third comparison, we constrain C_1 and C_2 to be in the same ratio as the parameters A_1 and A_2 appearing in the resonance energies. That is, we take $C_1 = CA_1$ and $C_2 = CA_2$ and make a least-squares fit to the NICS-0 data to find

$$C = -8.365, \ C_3 = -4.800, \text{ with } \sigma = 1.609, \ r = 0.784. \tag{18}$$

This evidently works a little worse than the models of eqs 16 and 17, as gauged by σ and r and the plot in Figure 10 in the Supporting Information. However, eq 18 entails notably fewer parameters and has the advantage that the sum of the local aromaticity indices gives (up to scale and the simple C_3 term) the total resonance energy, which is one of the common choices for a numerical value of global aromaticity. This then is a simpler chemically grounded approach.

In ref 32, Poater and co-workers also calculate harmonic oscillator model of aromaticity (HOMA) values for I−IV, VII−IX, XIV, and XVII. It will also be interesting to correlate $CA(\alpha)$ with these HOMA values. Because HOMA values have less influence from the neighboring rings than NICS values, the correlations are likely to improve. In fact, one can make such correlations with many different local and global properties exploiting the properties of Clar 2-nomials.

The comparatively less-impressive fits for aromaticity indices might not necessarily be so unsurprising because there are a variety of ways to define numerical aromaticity indexes, either local or global. Really, one can imagine that this variety is a manifestation that aromaticity is properly a "partial ordering" rather than a strict numerical ordering. This has implications for deviations of different properties X from those expected for nonaromatic (bond-localized) species − with different choices for X being: an energy, a geometry (as encoded in terms of bond lengths), various magnetic properties, certain electric properties (e.g., polarizabilities), various reactivities (with different selected reactants), or perhaps UV−optical spectral positions. Indeed, each of such property deviations has been proposed as a measure of "aromaticity", though an ordering of two molecular species under consideration of one property might not agree with that under another property. That is, the true *aromaticity* may be viewed[7,34] generally to satisfy[35] just the general conditions of a partial ordering: $\alpha \pm \beta$ and $\beta \pm \alpha$. and also $\alpha \pm \beta$ and $\beta \pm \gamma$ $\alpha \pm \gamma$ (for species α, β, γ). A related way to say this is that aromaticity generally needs to be represented not by a single number but by a sequence of numbers, the minimum number needed for such a sequence to faithfully represent the partial ordering being termed[36] the "dimensionality" of a partial ordering. If further the different aromaticity indices advocated are simply different linear combinations of the functions determining the different members of the sequence, then this dimensionality devolves to that of a linear space and one obtains the multidimensional aromaticity idea of Katrizky et al.[37] − as has been much studied.[38−41] Thence, we can imagine that the two different NICS-k indices with $k = 0$ or 1 are naught but two different (local) aromaticity indices, with that of eq 18 being a third, such that each of them agrees with the underlying partially ordered aromaticity. That is, the degree of slight but noticeable disagreement between the NICS-0, NICS-1, and CA local aromaticities might well be naught but a manifestation of a partial ordering, as contrasted to a simple linear (or total) ordering. The multidimensional nature of aromaticity as discussed by many authors[42] also points to the fact that aromaticity is difficult to be quantified by a single descriptor, which is also the genesis of the problem discussed here.

Conclusion and Prospects. In conclusion it is seen that Clar's qualitatively illustrated[3] ideas, though harking back to classical chemical bonding ideas, evidently extend in a fairly straightforward way to quantitatively treat several different molecular properties for a range of benzenoid molecules of the type addressed by Clar. These fittings are comparable to some earlier fits, though often a little better, occasionally with slightly higher accuracy, perhaps with fewer parameters, and also often involving comparably simpler computations, with a clearer simple chemical interpretation. Moreover, the variety of different fits are made from one unified "Clar-theoretic" viewpoint. Thence, these results are quite favorable, though it should perhaps not be unsurprising because Clar had such great qualitative success with his ideas. Indeed the real surprise might be that there has been so little previous quantitative application of Clar's ideas.

Overall, our results recommend our interpretation and quantification of Clar's ideas. In particular, the present definition of Clar structures is supported, along with our form of Clar 2-nomial, incorporating "sextetness" and "mobility" ideas in a natural way, in consonance with Pauling−Wheland resonance-theoretic ideas. The values of $x = 2$ and $y = 1$ in particular are suggested from Pauling−Wheland resonance theory, and are supported in that some trial variations of x and y away from these values, indicate that optimal values for x and y are very near these chosen values. We surmise that such quantifications should apply for several of the other properties (molecular reactivities, UV−vis spectra, and chemical shifts) considered by Clar. But of more interest for us is the prospect for the application of Clar's ideas, as embodied in the new ideas and invariants introduced here, to treat related novel conjugated nanostructures, along with further relevant magnetic and electric properties. The success registered here bodes well for this enterprise.

Appendix on Formalizations of Clar's Ideas. In the decades following Clar's book,[3] a number of different definitions of Clar structures have been made and investigated in some fashion. One early definition is that of Hosoya and co-workers[11,12] wherein triples of double bonds alternating around a 6-cycle are allowed, though only with certain relative orientation-dependent arrangements of the bonds − this leads to a final mathematical result that the number of these "Hosoyan" Clar structures equals the number of Kekule structures for the case of cata-condensed benzenoids. He and He[13] and also Guo and Zhang[43] follow Hosoya while allowing even selected larger rings, apparently for the sake of a more general form of this mathematical theorem beyond the cata-condensed case. El-Basil and Randic[44] and others[45,46] also allow larger rings, but do not otherwise follow Hosoya. Sometimes El-Basil follows[47] Hosoya, and sometimes makes yet other choices.[15] Herndon and Hosoya,[6] Randic and El-Basil,[16] El-Basil,[14,48] and Shiu et al.[49] use the definition given here. Zhang and Zhang[17,18] refer to Clar structures as here under the title of "Clar covers". John et al.[50] simply forego the exclusion of cyclic triples of double bonds. However, Randic,[51,52] and often also Gutman,[53,54] as well as Dias[55] and others[56,57] often strengthen this condition with the requirement that the number of aromatic sextets be a maximum for the given benzenoid. Different Clar-related polynomials have also been defined (as associated with alternative definitions of Clar structures), again starting with Hosoya and co-workers[11,12] (and as discussed earlier in our section introducing the Clar

2-nomial). Most of these articles give some formal results or construction, without reference to property data. Again Clar[3] is quite different than the bulk of these later authors, eschewing formalism, and proceeding by a multitude of examples (with focus on explicating diverse experimental data). Somewhat in Clar's tradition, Randic's substantial review[5] of aromaticity champions qualitative chemical understandings from the point of view based on sextet-maximum Clar structures. Ruiz-Morales and Gutman[8,9] focus on Clar structures where a maximum of sextets is only the second rule of selection, with the first dominating rule selecting the collection of sextets in a structure to cover as many internal vertices as possible – and the observed qualitative correspondences to quantum-chemical NICS values speaks to the relevance of this choice. Another type of paper over the last decades has focused on benzenoids in which there is a special Clar structure where no isolated edges occur. Indeed, Clar discussed such "sextet resonant" benzenoids, which he called "fully benzenoid"; and during the past few years there have been several articles that note coincidences beyond classical benzenoids of different special chemical behaviors that correlate with "sextet resonance", but such "sextet resonance" is not the focus in our current article. Again, Herndon and Hosoya[6] who use the present definition also connect to concrete data, while further this idea connects nicely with Pauling–Wheland resonance theory. Thus, there is good (even a priori) reason to entertain the definition given here.

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Supporting Information Available: Plot of 3rd fit for Clar aromaticity index versus NICS-0. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Pauling, L. *The Nature of the Chemical Bond*; Cornell U. Press: Ithaca, NY, 1939.

(2) Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley: New York, 1955.

(3) Clar, E. *The Aromatic Sextet*; John Wiley & Sons: New York, 1970.

(4) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747.

(5) Randic, M. *Chem. Rev.* **2003**, *103*, 3449.

(6) Herndon, W. C.; Hosoya, H. *Tetrahedron* **1984**, *40*, 3987.

(7) Klein, D. J. *J. Chem. Educ.* **1992**, *69*, 691.

(8) Ruiz-Morales, Y. *J. Phys. Chem. A* **2004**, *108*, 10873.

(9) Gutman, I.; Ruiz-Morales, Y. *Polycyc. Arom. Compd.* **2007**, *27*, 41.

(10) Cyvin, S. J.; Gutman, I. *Kekule Structures in Benzenoid Hydrocarbons*; Springer Verlag: New York, 1986.

(11) Hosoya, H.; Yamaguchi, T. *Tetrahedron Lett.* **1975**, *16*, 4659.

(12) (a) Ohakami, N.; Hosoya, H. *Nat. Sci. Rep. Ochanomizu University* **1984**, *35*, 71. (b) Ohakami, N.; Hosoya, H. *Theor. Chim. Acta* **1983**, *64*, 153.

(13) He, W.; He, W. *Theor. Chim. Acta* **1986**, *70*, 43.

(14) El-Basil, S. *Disc. Appl. Math.* **1988**, *19*, 145.

(15) El-Basil, S. *Theor. Chim. Acta* **1986**, *70*, 53.

(16) Randic, M.; El-Basil, S. *J. Mol. Struct. (Theochem)* **1994**, *304*, 233.

(17) Zhang, H.; Zhang, F. *Disc. Appl. Math.* **1996**, *69*, 147.

(18) Zhang, H.; Zhang, F. *Disc. Math.* **2000**, *212*, 261.

(19) Dewar, M. J. S.; deLlano, C. *J. Am. Chem. Soc.* **1968**, *91*, 789.

(20) Herndon, W. C. *Thermochim. Acta* **1974**, *8*, 225.

(21) (a) Randic, M. *Tetrahedron* **1975**, *33*, 1905. (b) Randic, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.

(22) Poater, J.; Visser, R.; Sol, M.; Bickelhaupt, F. M. *J. Org. Chem.* **2007**, *72*, 1134.

(23) (a) Carter, P. G. *Trans Faraday Soc.* **1949**, *45*, 597. (b) Swinborne-Sheldrake, R.; Herndon, W. C.; Gutman, I. *Tetrahedron Lett.* **1975**, *16*, 755. (c) Seitz, W. A.; Klein, D. J.; Schmalz, T. G.; Garcia-Bach, M. A. *Chem. Phys. Lett.* **1985**, *115*, 139.

(24) Randić, M. *J. Am. Chem. Soc.* **1975**, *97*, 6609.

(25) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Chemistry and Drug Research*; Academic Press: New York, 1976.

(26) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Structure-Activity Analysis*; Research Studies Press: Letchworth, 1986.

(27) Kiralj, R.; Ferreira, M. M. C. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 508.

(28) Morikawa, T.; Narita, S.; Shubuya, T. I. *J. Mol. Struct. (Theochem)* **1999**, *466*, 137.

(29) Li, S.; Jiang, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8401.

(30) Penny, W. G. *Proc. R. Soc. London, Ser. A* **1937**, *158*, 306.

(31) Moran, D.; Stahl, F.; Bettinger, H. F.; Schaefer, H. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 6746.

(32) Portella, G.; Poater, J.; Sola, M. *J. Phys. Org. Chem.* **2005**, *18*, 785.

(33) Poater, J.; Sol, M.; Vigione, R. G.; Zanasi, R. *J. Org. Chem.* **2004**, *69*, 7537.

(34) Klein, D. J.; Babic, D. *J. Chem. Inf. Comp. Sci.* **1997**, *37*, 656.

(35) See, for example, the classic Birkhoff, G. *Lattice Theory*; AMS: Providence, RI, 1948.

(36) (a) Or a more recent presentation of, Neggers, I.; Kim, H. S. *Basic Posets*; World Scientific: Singapore, 1998. (b) Dushnik, B.; Miller, E. W. *Am. J. Math.* **1941**, *63*, 600.

(37) Katrizky, A. R.; Barczynkki, P.; Musumurrra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.

(38) Cyranski, M.; Krygowski, T. M. *Pol. J. Chem.* **1995**, *69*, 1088.

(39) Schleyer, P. v. R.; Freeman, P. K.; Hiao, H.; Goldfuss, B. *Angew. Chem., Intl. Ed. Engl.* **1995**, *34*, 337.

(40) Krygowski, T. M.; Czarnocki, M. K.; Czarnocki, Z.; Hafelinger, G.; Katrizky, A. R. *Tetrahedron* **2000**, *56*, 1783.

(41) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333.

(42) (a) Schleyer, P. V. R.; Jiao, H.; Goldfuss, B.; Freeman, P. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337. (b) Bultinck, P. *Faraday Discuss.* **2007**, *135*, 347. (c) Feixas, F.; Matito, E.; Poater, J.; Sola, M. *J. Comput. Chem.* **2008**, *29*, 1543.

(43) Guo, X.; Zhang, F. *J. Math. Chem.* **1992**, *9*, 279.

(44) El-Basil, S.; Randic, M. *J. Math. Chem.* **1987**, *1*, 281.

(45) Fowler, P.; Zheng, M. *DIMACS Series in Discrete Mathematics & Theoretical Computer Science 51*: Am. Math. Soc.: Providence, RI, 2000.

(46) Salem, K. *MatCh* **2005**, *53*, 427.

(47) El-Basil, S. *Croat. Chim. Acta* **1984**, *57*, 47.

(48) El-Basil, S. *J. Mol. Struct. (Theochem)* **2000**, *531*, 9–21.

(49) Shiu, W. C.; Lam, P. C. B.; Zhang, H. *J. Mol. Struct. (Theochem)* **2003**, *622*, 239.

(50) John, P. E.; Sachs, H.; Zheng, M. *J. Chem. Inf. Comp. Sci.* **1995**, *35*, 1019.

(51) El-Basil, S.; Randic, M. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1875.

(52) Randic, M. *J. Mol. Struc. (Theochem)* **1991**, *229*, 139.

(53) Gutman, I. *Naturforsch.* **1981**, *36*, 69.

(54) El-Basil, S.; Gutman, I. *Chem. Phys. Lett.* **1983**, *94*, 188.

(55) Dias, J. R. *J. Mol. Struct. (Theochem)* **2002**, *581*, 59.

(56) Klavzar, S.; Zigert, P.; Gutman, I. *J. Mol. Strut (Theochem)* **2002**, *586*, 235.

(57) Balaban, A. T.; Schmalz, T. G. *J. Chem. Inf. Modelling* **2006**, *46*, 1563.

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