

# Numerical Kekulé Structures of Fullerenes and Partitioning of $\pi$ -Electrons to Pentagonal and Hexagonal Rings<sup>†</sup>

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We calculated the partitioning of  $\pi$ -electrons within individual pentagonal and hexagonal rings of fullerenes for a collection of fullerenes from C<sub>20</sub> to C<sub>72</sub> by constructing their Kekulé valence structures and averaging the  $\pi$ -electron content of individual rings over all Kekulé valence structures. The resulting information is collected in Table 2, which when combined with the Schlegel diagram of fullerenes (illustrated in Figure 7) uniquely characterizes each of the 19 fullerenes considered. The results are interpreted as the basic information on the distributions (variation) of the local (ring)  $\pi$ -electron density.

## INTRODUCTION

Buckminsterfullerene, C<sub>60</sub>, has 12 500 Kekulé valence structures.<sup>1–3</sup> Even when one focuses attention on the set of symmetry nonequivalent structures, which is 158 in the case of C<sub>60</sub>,<sup>2,4</sup> this is still a substantial collection of valence structures to be analyzed. The collection of Kekulé valence structures may be of limited use for the practical characterization of fullerenes, including small fullerenes, which may have a large number of Kekulé valence structures. On the other hand, in the case of polycyclic conjugated hydrocarbons the Kekulé valence structures are a source of important chemical information on such systems, which offer insights into some of their properties, like variations in CC bond lengths.<sup>5</sup> For an illustration we have collected in Table 1 a dozen interesting characteristics of polycyclic conjugated hydrocarbons which can be extracted from their Kekulé valence structures. The first, the “classic” such quantity, is the Pauling bond order,<sup>6,7</sup> which indicates how many times an individual CC bond appears as a C=C bond in the totality of Kekulé valence structures. More recent “treasures” that were hidden in Kekulé valence structures for over 100 years include the expressions for the resonance energy, which are based on enumeration of conjugated circuits within individual Kekulé valence structures,<sup>8–11</sup> and the innate degree of freedom of Kekulé valence structures.<sup>12–14</sup> They are given by the smallest number of C=C bonds which determine the location of the entire remaining C=C bonds within a single Kekulé valence structure. One of the major discoveries related to Kekulé valence structures is that a *single* Kekulé valence structure contains information on *all* the remaining Kekulé valence structures, as demonstrated by Gutman and

Randić.<sup>15–18</sup> Close examination of Kekulé valence structures also leads to an index of local aromatic properties, which is given by the count, for each individual benzene ring separately, of how many Kekulé valence structures contain three C=C bonds.<sup>19</sup> Finally, the concept of the resonance graph illustrates the dominant interactions between contributing valence structures. In this graph vertices represent Kekulé valence structures and edges connect Kekulé valence structures which differ only in the distributions of C=C bonds in a single benzene ring.<sup>20–22</sup>

To this impressive list of the “hidden treasures” of Kekulé valence structures we may add the most recent: the discovery of the numerical Kekulé valence structures<sup>5,23</sup> and the partition of the classification of the  $\pi$ -electrons to individual rings of polycyclic conjugated molecule.<sup>24</sup> Numerical Kekulé valence structures are based on the partition of the  $\pi$ -electrons to individual rings of a polycyclic conjugated molecule and assign to each benzene ring of the polycyclic system a single numerical value. In analogy with Pauling bond orders, which show that different CC bonds are associated with different bond lengths, here it follows that different rings in benzenoid systems may involve a different “amount” of  $\pi$ -electrons. In contrast the classification of  $\pi$ -electron ring partitions of the whole set of Kekulé valence structures leads to a universal representation of benzenoid systems by a string of seven entries, each signifying the number of benzene rings having from six to zero  $\pi$ -electrons.<sup>24</sup>

## ON CHARACTERIZATION OF LOCAL PROPERTIES OF CONJUGATED SYSTEMS

An alternative representation of unsaturated molecules to a collection of all its Kekulé valence structures is characterization of local molecular features. A number of such schemes, involving different degrees of complexity, have been considered in the past.<sup>25–35</sup> A simple, elegant, and insightful, though *qualitative*, approach is advocated by Clar, in which characterization of local properties of conjugated hydrocarbons is based on aromatic  $\pi$ -sextets.<sup>36</sup> A alternative, elegant, and insightful *quantitative* characterization of local

<sup>†</sup> Dedicated to Professor Nenad Trinajstić on the occasion of his 70th birthday.

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**Table 1.** List of Interesting Properties of Kekulé Valence Structures<sup>a</sup>

topic	outline
Pauling bond order conjugated circuits	numbers that represent the frequency a particular CC bond appear as C=C circuits within individual Kekulé valence structures which have an alternation of C–C and C=C bonds
aromaticity	based on the relative count of $4n+2$ and $4n$ conjugated circuits
resonance energy	expressions based on the average count of $4n+2$ and $4n$ conjugated circuits
local aromaticity	expressed by the count a benzene ring in polycyclic conjugated hydrocarbons having with three C=C bonds
resonance graph	graph depicting which Kekulé valence structures have all C=C bonds in common except in a single ring
degree of freedom	the smallest number of C=C bonds in a Kekulé valence structure that fully determines the location of the remaining C=C bonds
inverse Clar problem	characterization of the subset of Kekulé valence structure which constitute a Clar structure
$\pi$ -electron ring partition	partition of $\pi$ -electrons to individual rings in polycyclic conjugated systems
numerical Kekulé structure	formula based on average $\pi$ -electron ring partition

<sup>a</sup> For more details consult the review article by one of the present authors on the aromaticity in polycyclic conjugated hydrocarbons.<sup>2</sup>

aromatic properties of conjugated hydrocarbons is one based on the count of how many times each benzene ring, when considering all Kekulé valence structures, has three C=C bonds.<sup>11</sup> As already mentioned<sup>5,23,29</sup> recently an alternative simple, elegant, and insightful approach to characterization of individual rings of polycyclic conjugated hydrocarbons has been outlined.<sup>37–47</sup> It considers partition of  $\pi$ -electrons to individual rings of polycyclic conjugated hydrocarbons. We decided therefore to examine a collection of fullerenes and report on the partition of  $\pi$ -electrons to their pentagonal and hexagonal rings in order to arrive at a novel description of their local structural characteristics. Detailed information on partitioning of  $\pi$ -electrons in fullerene C<sub>70</sub> and C<sub>72</sub> has been already reported.<sup>48,49</sup>

### CLAR $\pi$ -SEXTETS

Robinson and Armit<sup>50</sup> initiated the idea of a  $\pi$ -aromatic sextet, a model in which  $\pi$ -electron sextets are assigned to some benzene rings in polycyclic benzenoid hydrocarbons, but it was Clar who fully developed the notion of a  $\pi$ -aromatic sextet.<sup>36</sup> Apparently Robinson became skeptical and abandoned the notion of  $\pi$ -sextets.<sup>51</sup> Clar pointed out that some benzenoid systems have a single  $\pi$ -aromatic sextet formula in which benzene rings are either  $\pi$ -sextet rings or are “empty” rings. Such are the benzenoids of Figure 1. Clar referred to this class of benzenoid hydrocarbons as “fully benzenoid”. They have  $6n$   $\pi$ -electrons and are unusually stable, which has lead Clar to formulate his  $6n\pi$  rule for stable benzenoid hydrocarbons. The Clar “ $6n\pi$  Rule”, which is not widely known but has wide application, is far more general than the famous Hückel ( $4n+2$ ) rule, which is widely known but has very limited application (as it strictly holds only for monocyclic systems (annulenes). In passing we may mention that all “giant” benzenoids of Müllen and collaborators are “fully benzenoid” systems having  $6n\pi$  electrons.

Most benzenoid hydrocarbons, however, are not “fully benzenoid”. Some benzenoid systems can even have more than one Clar structure, a few of which are illustrated in Figure 2. According to the Clar model such systems involve “migrating  $\pi$ -sextets”, which are graphically represented by adding one or more arrows that indicate the molecule regions in which  $\pi$ -sextets migrate. The empirical approach of Clar was initially supported on observed shifts in UV spectra of structurally related benzenoids and the use of NMR data.

More recently it was shown that Clar’s model has valid quantum chemical justifications.<sup>43,54</sup>

The number of  $\pi$ -sextets for a molecule is important information, which need not be found easily for larger benzenoids and in particular fullerenes. Klavžar, Žigert, and Gutman<sup>55</sup> proposed a graphical enumeration of  $\pi$ -sextets for cata-condensed benzenoids. Figure 3 illustrates how one can obtain graphically the number of  $\pi$ -sextets in the Clar structure for such cases. The number of  $\pi$ -aromatic sextets is equal to the smallest number of line segments needed to cross all benzene rings. Generally the crossing of rings can be obtained in different ways; however, each solution will involve the same number of line segments. More recently it was pointed out by one of the present authors<sup>5,56</sup> that if the “crossing lines” are so chosen that they have the maximal number of crossing among themselves, that not only one will find the number of  $\pi$ -sextets but also one will determine the rings which are excluded for  $\pi$ -sextet migration.

The Clar structure of buckminsterfullerene has eight “migrating”  $\pi$ -sextets, as was for the first time reported by El Basil.<sup>57</sup> The Clar structure of C<sub>70</sub> has nine “migrating”  $\pi$ -sextets, as reported by the present authors.<sup>48</sup>

### NUMERICAL KEKULE VALENCE STRUCTURES

By combining the information in the set of a *numerical* Kekulé valence structure of a benzenoid system one can arrive at a *single* molecular formula for a polycyclic conjugated hydrocarbon. Thus one obtains an alternative characterization of benzenoid systems, which can replace the set of standard geometrical Kekulé valence structures as a representation of such systems. The numerical formula assigns to each benzene ring the average of the ring partitions found for that ring in the totality of Kekulé valence structures of the molecule. The ring partition of  $\pi$ -electron for individual Kekulé valence structures is obtained by the following rule:<sup>23</sup> Each C=C bond contributes two  $\pi$ -electrons to a ring if C=C bonds are not shared with adjacent rings. The C=C bonds common to two rings contribute one  $\pi$ -electron to each ring. By following this rule one can obtain from 0 to 6  $\pi$ -electrons for different rings in different molecules. In cata-condensed benzenoids on average terminal rings have a higher  $\pi$ -electron content than the inner rings and the smallest  $\pi$ -electron content belongs to the “kink”

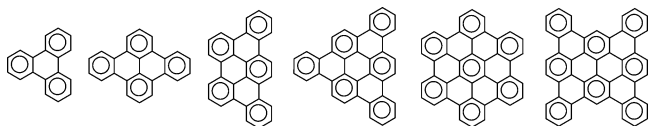


Figure 1. Fully benzenoid hydrocarbons.

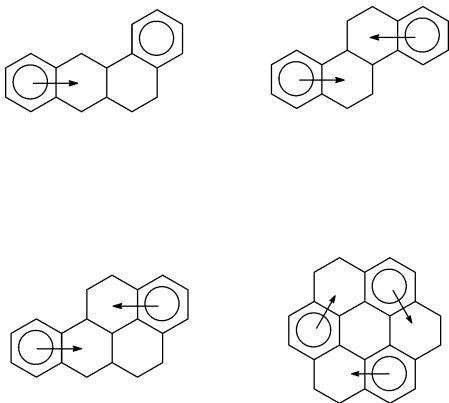


Figure 2. Benzenoid hydrocarbons with "migrating" sextets.

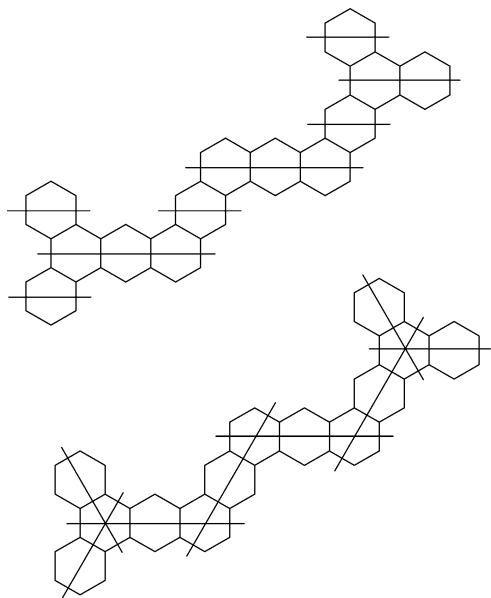


Figure 3. Graphical enumeration of  $\pi$ -sextets.

ring,<sup>58</sup> the rings at which the direction of the fusion of benzene rings change.

The calculated ring  $\pi$ -partition numbers reflect upon certain local structural characteristics of benzenoid systems. This is confirmed by finding that the smallest  $\pi$ -electron content for benzene rings corresponds to the "empty" rings of the Clar sextet model. For example, (see Figure 4), the central ring of triphenylene has a  $\pi$ -content of 2.0, the "empty" rings of dibenzopyrene have a  $\pi$ -content of 1.85, the central ring of coronene has a  $\pi$ -content of 1.5, while the central ring of perylene, which has two "essentially" single C—C bonds, that is CC bonds that are in all Kekulé valence structure single CC bonds, has a  $\pi$ -content of only 1.3333.<sup>37</sup> On the other hand, the largest  $\pi$ -electron content for benzene rings corresponds to rings which are the sites of the  $\pi$ -aromatic sextets in fully benzenoid hydrocarbons. For the six fully benzenoid systems of Figure 1 the rings having the maximal  $\pi$ -electron partitions (between 5.35 and 5.00) are terminal cata-condensed rings. The next highest

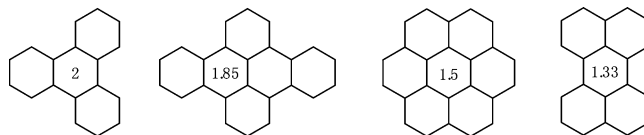


Figure 4.  $\pi$ -Ring partitions for "empty" rings.

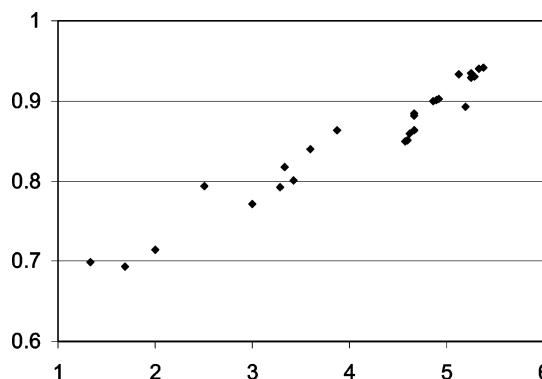


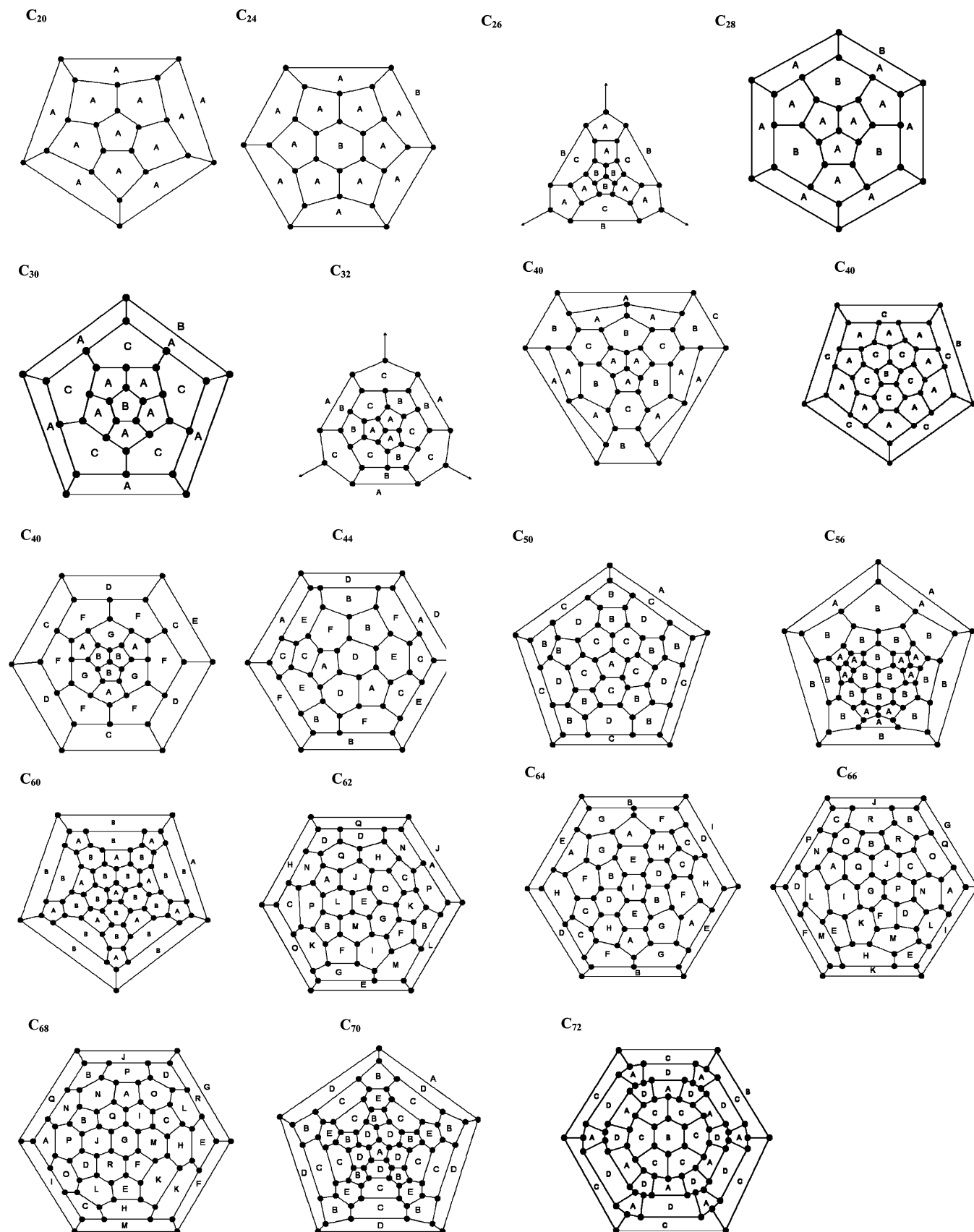
Figure 5. Plot of Polansky and Derflinger's ring indices against the  $\pi$ -electron ring partitions for 10 benzenoids.

$\pi$ -electron content belongs to peripheral rings adjacent to two internal rings in the maximal  $\pi$ -electron partitions, the  $\pi$ -ring content of which is 4.80 or less. All this clearly points to a certain possible structural and functional interpretation of the  $\pi$ -electron ring partitions, but what?

#### ON INTERPRETATION OF $\pi$ -ELECTRON RING PARTITIONS

There are many local ring indices for benzene rings of benzenoid hydrocarbons that have been considered in the literature such as the following: the "characterograms" of Polansky and Derflinger (1967);<sup>25</sup> the ring aromaticity indices of Herndon and Ellzey (1974);<sup>59</sup> the local aromaticity indices of one of the present authors (1974–1980);<sup>11,19,60</sup> and benzene characteristics of Aida and Hosoya (1980)<sup>61</sup> to a more recent local indices including a harmonic oscillator model of Krygowski and collaborators<sup>34</sup> and nucleus-independent  $^{13}\text{C}$  chemical shifts of Schleyer and collaborators<sup>62</sup> computed at the center of benzene rings or 1 Å above the center of rings. One is tempted to consider each such local ring index as an index of local aromaticity—but do all these different constructions legitimate indicators of local aromaticity? Balaban and Randić<sup>29</sup> recently compared the above-mentioned scales and others as estimators of the local aromaticity of rings in polycyclic benzenoids—an attempt which also presumed that local indices characterize local aromaticity. However, it was a significant finding that when attempting to correlate  $\pi$ -electron ring partitions and other local aromaticity indices for all benzenoids (cata-condensed and peri-condensed), despite similar trends that were evident when different classes of benzenoids were treated separately, lower correlations coefficients were obtained. For example, the correlation between the ring values for  $\pi$ -electron partitions and HOMA values (of Krygowski et al.) leads to the correlation coefficient  $r = 0.7680$  (and  $r^2$  of 0.590), which suggests that the two quantities do not necessarily characterize the same molecular characteristics.

In Figure 5 we show a correlation between the  $\pi$ -ring partitions and  $\pi$ -ring characters of Polansky and Derflinger. As one can see the two local descriptors correlate quite well.

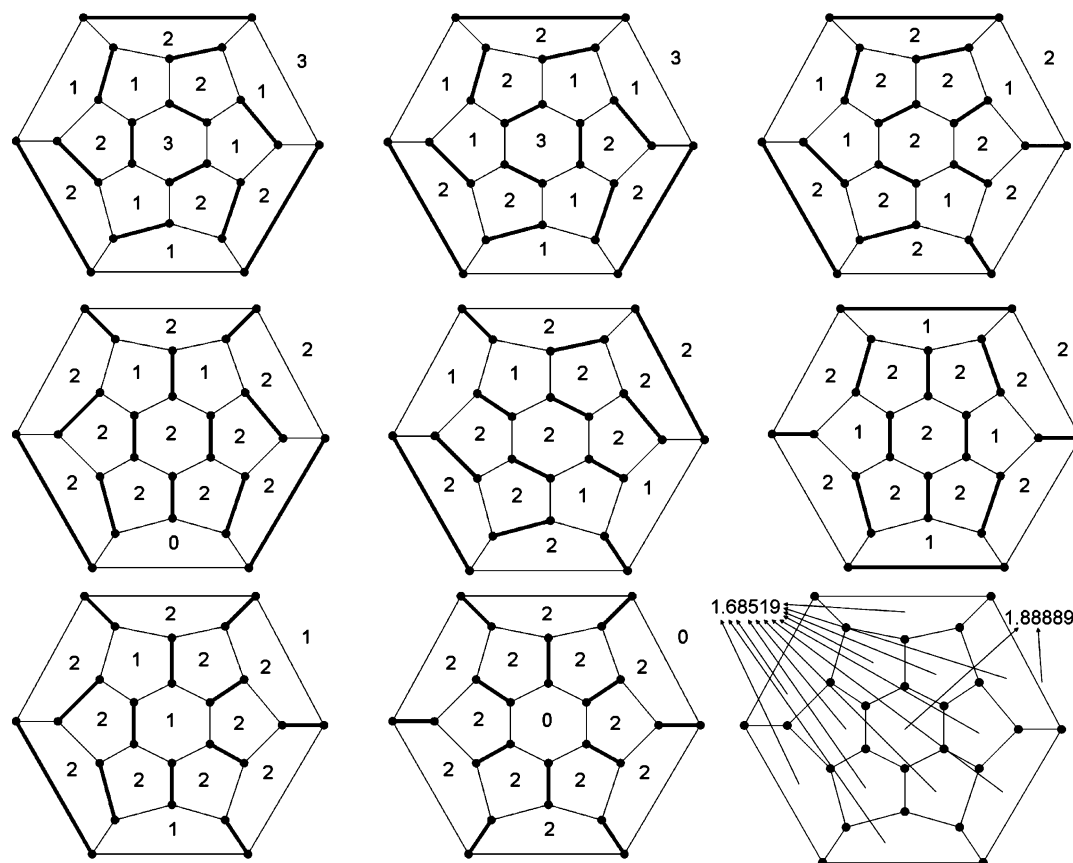


**Figure 6.** The 19 fullerenes considered. The same label is used for the equivalent rings.

One can even detect a grouping of points belonging to aromatic sextets at the top right-hand side. One thus concludes that the two local descriptors, one based on HMO calculations and the other on VB structures, pertain to the

local structural features of benzenoid hydrocarbons. We maintain that these descriptors do not necessarily characterize local aromaticity but local density distributions of  $\pi$ -electrons of benzenoid systems.





**Figure 7.** Symmetry nonequivalent Kekulé valence structures of fullerene  $C_{24}$  with the partition of  $\pi$ -electrons to individual rings.

In order to strengthen the statement that the  $\pi$ -electron ring partitions are not kind novel local aromaticity indicators, assume for the moment the opposite, that the  $\pi$ -electron ring partition is an index of local aromaticity. Then by *adding* all local aromatic contributions one ought to obtain a global molecular aromaticity measure. However, when one adds all  $\pi$ -electron ring partitions in a molecule one obtains  $N$ , the number of  $\pi$ -electrons in a molecule. Thus isomers tetracene would be equally aromatic to fully benzenoid like triphenylene—which is absurd. Hence, the  $\pi$ -electron ring partitions represent the local  $\pi$ -electron *density*. Obviously by adding local density distributions one obtains the total amount of  $\pi$ -electrons. What the  $\pi$ -electron ring partitions have shown is that there are significant variations in the local  $\pi$ -electron density not only in benzenoid but also in non-benzenoid hydrocarbons. In this article we explore variations in the local  $\pi$ -electron density among a selection of fullerenes.

#### $\pi$ -CONTENT FOR PENTAGONAL AND HEXAGONAL RINGS OF FULLERENES

In this section we will report on the  $\pi$ -electron content for pentagonal and hexagonal rings for the following 19 fullerenes:  $C_{20}$ ,  $C_{24}$ ,  $C_{26}$ ,  $C_{28}$ ,  $C_{30}$ ,  $C_{32}$ ,  $C_{40}$  (three isomers),  $C_{44}$ ,  $C_{50}$ ,  $C_{56}$ ,  $C_{60}$ ,  $C_{62}$ ,  $C_{64}$ ,  $C_{66}$ ,  $C_{68}$ , and  $C_{74}$ , all illustrated in Figure 6. There are two novel aspects arising when calculating the partitioning of  $\pi$ -electrons in fullerenes, which are absent when calculating the  $\pi$ -electron content for benzenoid or non-benzenoid hydrocarbons: (1) The calculations are simplified due to the fact that in fullerenes *all* C=C bonds are *shared* by two adjacent rings, hence each C=C contributes always just one  $\pi$ -electron to a ring. (2) The

search is complicated because the number of Kekulé valence structures in fullerenes is so large that one has to use a computer in order to construct and analyze them.

Let us illustrate the search for  $\pi$ -ring partitions on  $C_{24}$ , one of the smaller fullerenes considered. Fullerene  $C_{24}$ , which has only two hexagons separated by a belt of 12 pentagons, has only 54 Kekulé valence structures, eight of which, illustrated in Figure 7, are nonequivalent. Integers from 0 to 3 distributed in individual fullerene rings indicate the number of C=C bonds in each ring, which is the same as the number of  $\pi$ -electrons associated with each ring. Observe that pentagonal rings in  $C_{24}$  can have either one or two C=C bonds, and only in a fullerene having isolated pentagons can one have pentagonal faces with an inscribed zero (that is pentagons without C=C bonds). The smallest of these is buckminsterfullerene  $C_{60}$ . In contrast hexagonal rings can have inscribed integers 0–3. The unique numerical formula for fullerene  $C_{24}$  is obtained by averaging the  $\pi$ -content of individual rings over all Kekulé valence structures.

#### RESULTS

In Table 2 we have listed for the 19 fullerenes considered partitions of  $\pi$ -electrons to their pentagonal and hexagonal rings. For each fullerene rings were ordered alphabetically, starting with rings having the smallest  $\pi$ -electron content and ending with the ring having the largest  $\pi$ -electron content. With few exceptions most of the fullerenes of Table 2 have less than a dozen symmetry-nonequivalent rings. The exceptions are as follows:  $C_{62}$  having 6 different pentagons and 11 different hexagons;  $C_{64}$  having 3 different pentagons

**Table 2.** Partition of  $\pi$ -Electrons to Individual Rings in Fullerenes Considered

fullerene	5-ring	$\pi$ -content	6-ring	$\pi$ -content
C <sub>20</sub>	A	1.66667		
C <sub>24</sub>	A	1.68519	B	1.88889
C <sub>26</sub>	A	1.66667	C	1.93651
	B	1.69841		
C <sub>28</sub>	A	1.66667	B	2.00000
C <sub>30</sub>	A	1.63576	C	2.00000
	B	1.82119		
C <sub>32</sub>	A	1.61806	C	2.06944
	B	1.64583		
C <sub>40</sub>	A	1.68056	B	1.97222
			C	2.00000
C <sub>40</sub>	A	1.58185	C	2.09786
	B	1.60142		
C <sub>40</sub>	A	1.64583	E	1.95139
	B	1.65046	F	2.00000
	C	1.66435	G	2.03704
	D	1.68519		
C <sub>44</sub>	A	1.52597	D	2.03463
	B	1.60173	E	2.06710
	C	1.63203	F	2.13853
C <sub>50</sub>	A	1.39565	C	2.08365
	B	1.55826	D	2.15792
C <sub>56</sub>	A	1.66667	B	2.00000
<b>C<sub>60</sub></b>	<b>A</b>	<b>1.40000</b>	<b>B</b>	<b>2.16000</b>
C <sub>62</sub>	A	1.49121	G	1.98241
	B	1.54837	H	1.99304
	C	1.54885	I	2.00863
	D	1.56012	J	2.04797
	E	1.58970	K	2.05101
	F	1.65390	L	2.06220
			M	2.06540
			N	2.06620
			O	2.07891
			P	2.11920
			Q	2.13719
C <sub>64</sub>	A	1.46956	D	1.97474
	B	1.47908	E	2.00951
	C	1.53371	F	2.10158
			G	2.15782
			H	2.18179
			I	2.18444
C <sub>66</sub>	A	1.43513	G	1.89684
	B	1.45292	H	1.95426
	C	1.48096	I	2.03850
	D	1.54436	J	2.06425
	E	1.58240	K	2.07186
	F	1.63209	L	2.07256
			M	2.10645
			N	2.11191
			O	2.11496
			P	2.12713
			Q	2.14357
			R	2.14698
C <sub>68</sub>	A	1.41985	G	1.86539
	B	1.43446	H	1.98158
	C	1.47517	I	2.03408
	D	1.47778	J	2.06825
	E	1.55564	K	2.07299
	F	1.59825	L	2.11588
			M	2.13330
			N	2.13398
			O	2.14385
			P	2.15765
			Q	2.16141
			R	2.17048
C <sub>70</sub>	A	1.39241	C	1.99446
	B	1.46598	D	2.17009
			E	2.18199
C <sub>72</sub>	A	1.39354	B	1.74418
			C	2.15400
			D	2.16175

and 6 different hexagons; and C<sub>66</sub> and fullerene C<sub>68</sub> having 6 different pentagons and 12 different hexagons.

Observe that among the fullerenes considered the  $\pi$ -content of pentagons can be as low as 1.39242, the value found in C<sub>24</sub>, and as high as 1.82119, the value found in C<sub>30</sub>. The  $\pi$ -content of the pentagons in buckminsterfullerene is 1.40000, which is close to the lower bound shown above. The presence of small values of the  $\pi$ -content for pentagons means that the “surplus” of  $\pi$ -electrons will be available for distribution among the hexagonal rings. The smallest  $\pi$ -content among hexagonal rings is 1.74418, found in C<sub>72</sub>, while the highest  $\pi$ -content is 2.18444, which is found in C<sub>70</sub>. It is interesting and may not have been expected to see that the  $\pi$ -content of pentagonal rings can be as high as and even higher than the lowest  $\pi$ -content of some hexagonal rings. However, a close look at the rings in fullerene C<sub>72</sub> shows that the benzene ring with the lowest  $\pi$ -content is surrounded by six hexagons. Thus this ring is in the center of a local fragment representing coronene, which in the case of coronene represents an “empty” benzene ring. Hence, the low  $\pi$ -content found for the “central” hexagon of the coronene fragments C<sub>72</sub> is in agreement with Clar’s model of the  $\pi$ -aromatic sextets; it should not be surprising, in fact it should have been expected.

#### CONCLUDING REMARKS

The outlined partition of  $\pi$ -electrons to rings of fullerene offers novel insights into the local structure of fullerenes. As we have seen from Table 2 not all pentagonal rings are equal nor are the hexagonal rings even though the differences between the  $\pi$ -content of rings of the same size are not excessive. It remains to be seen how will these local variations in  $\pi$ -content of rings, that is, variation in local  $\pi$ -electron density, manifest themselves experimentally. The numerical indices of individual rings, besides providing data for numerical characterization of fullerenes, may be of some theoretical interest. In early MO theory days Polansky and Derflinger<sup>25</sup> extracted numerical ring indices from molecular orbitals of benzenoids. It has been generally accepted that these indices characterize local aromatic properties, but in view of the present work on the partition of  $\pi$ -electrons such interpretation is in doubt. Namely, it seems more likely that the results of Polansky and Derflinger also relate to local  $\pi$ -electron densities. It remains to be seen if similar calculations, when performed on fullerenes, will result in ring indices that correlate with the reported  $\pi$ -electron content of fullerene rings here.

There is yet another potential use of results reported in Table 2—this time for the need of chemical documentation. The ring indices (with possible exceptions when degeneracy is present) allow in a rather simple way a unique assignment of numerical labels to symmetry nonequivalent rings. One starts by assigning the label 1 to the rings having the highest  $\pi$ -electron content. One continues by assigning the label 2 to the rings having the next highest  $\pi$ -electron content, and so on. In this way therefore one can assign labels to rings, or vertices of the dual graphs, which inform one at a glance on the relative importance of rings and the variations of  $\pi$ -electrons distributions in fullerenes, at least as projected by the model based on  $\pi$ -electron ring partition.

Even more interesting, both from the positions of structural chemistry and chemical documentation, will be to examine

the classification of the  $\pi$ -ring partitions, as they may lead to a unique numerical representation of fullerenes based on a seven digit code, which would be based on the count of  $\pi$ -electrons in hexagonal rings (which for fullerenes may be 3, 2, 1, 0) and  $\pi$ -electrons in pentagonal rings (which for fullerenes may be 2, 1, 0).<sup>63</sup>

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