

## Kekulé Structures of Fullerene C<sub>70</sub>

Milan Randić<sup>a</sup> and Damir Vukičević<sup>b</sup>

<sup>a</sup>National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

<sup>b</sup>Faculty of Natural Sciences, Mathematics and Education, University of Split, Nikole Tesle 12, HR-21000 Split, Croatia

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Despite that, besides Buckminsterfullerene C<sub>60</sub>, fullerene C<sub>70</sub> is the next most stable structure, there are considerable differences in structural properties of these two most common fullerenes. The paper reports on numerous mathematical properties of the set of Kekulé structures of C<sub>70</sub>. Of over 50,000 Kekulé structures of fullerene C<sub>70</sub>, only 2780 Kekulé valence structures are distinct, while all the others are symmetry related. The subset of distinct Kekulé valence structures was examined and classified into six classes according to the degree of freedom (*df*), varying from *df* = 5 to *df* = 11. Enumeration of conjugated circuits R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> points to two symmetry related dominant Kekulé structures having the maximal number of 20 R<sub>1</sub>. There are 16 distinct symmetry unrelated Kekulé structures of C<sub>70</sub> that have no conjugated circuits R<sub>1</sub> at all.

### INTRODUCTION

Not long ago, in collaboration with H. Kroto, we examined the Kekulé valence structures of Buckminsterfullerene and their properties<sup>1,2</sup> and here we will first extend such investigations to C<sub>70</sub> and then make a comparison between the two fullerenes. In this article, we focus on mathematical properties of fullerene C<sub>70</sub>, which is the next most common fullerene after Buckminsterfullerene C<sub>60</sub>. As it is well known, the two fullerenes differ only in that C<sub>70</sub> has a »belt« of additional ten benzene hexagons in its structure, thus departing slightly from the spherical form of C<sub>60</sub>. In view of the close relationship of C<sub>70</sub> to C<sub>60</sub>, we decided to examine C<sub>70</sub> more closely and find out to what degree the apparent similarity between these two basic fullerenes extends to their mathematical properties, which describe their inner composition. As we will show, the two fullerenes show considerable differences in many properties though one might have expected otherwise.

### ANATOMY OF KEKULÉ VALENCE STRUCTURES

Ever since introduced by the Czech chemist<sup>3</sup> Friedrich August Kekulé von Stradonitz (1829–1896) in 1865,<sup>4</sup> Kekulé valence structures have played a major role in organic chemistry. However, following the historic work of Heitler and London<sup>5</sup> on stability of hydrogen molecule in 1927, which led to Valence Bond (VB) calculations, Kekulé valence structures received novel attention by becoming the basis for VB computations on polycyclic conjugated hydrocarbons. This work, initiated in particular by Linus Pauling,<sup>6,7</sup> Wheland<sup>8</sup> and other pioneers of the early Quantum Chemistry, still continues despite the widespread explosion of Molecular Orbital calculations. We may mention in particular the recent works of Klein and co-workers<sup>9,10</sup> and Jiang and co-workers,<sup>11,12</sup> who developed *ab initio* VB calculations that can be applied to benzenoid systems having two dozen and more  $\pi$ -electrons. However, despite the long history of Kekulé valence

\* Authors to whom correspondence should be addressed. (E-mail: mrandic@msn.com, vukicevi@pmfst.hr)

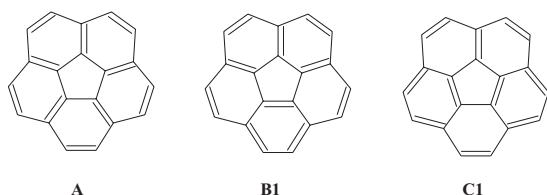


Figure 1. The three nonisomorphic Kekulé valence structures of corannulene. The first one is unique the other two, by rotation of  $72^\circ$ , generate the remaining Kekulé valence structures of corannulene.

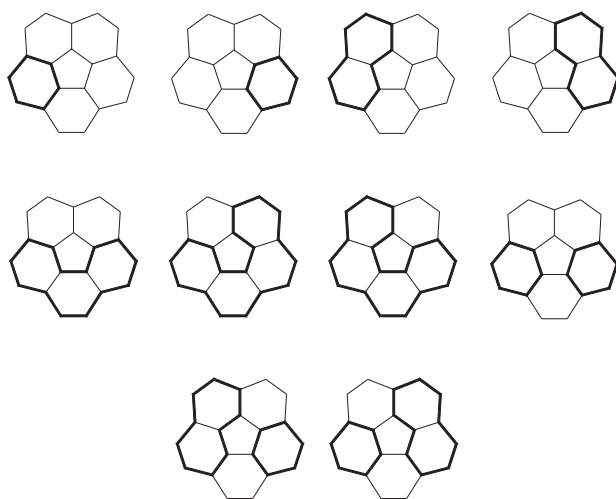


Figure 2. All conjugated circuits for the last Kekulé valence structure of Figure 1.

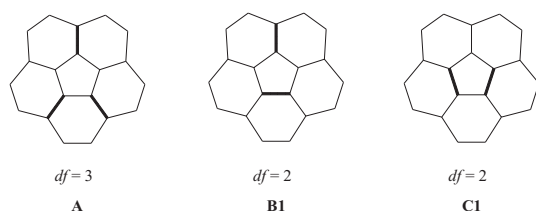


Figure 3. Illustration of CC bonds which when selected as CC double bonds determine the bond type character of all other CC bonds in the structure.

structures, it was relatively recently that several interesting properties of Kekulé valence structures, listed below, have surfaced. For a comprehensive review of these properties of polycyclic conjugated hydrocarbons, we direct the reader to the recent review article »Aromaticity in Polycyclic Conjugated Hydrocarbons.«<sup>13</sup> We will illustrate these properties of Kekulé valence structures on corannulene. Corannulene has 11 Kekulé valence structures, the three distinct of which (unrelated by symmetry operations) are shown in Figure 1. The conjugated rings of corannulene can be viewed as a portion of conjugated rings of fullerenes.

– *Conjugated Circuits* (Figure 2): A close look at individual Kekulé valence structures of conjugated hydrocarbons as well as fullerenes reveals that such systems

have a number of circuits in which there is regular alternation of CC double and CC single bonds.<sup>14–16</sup> Conjugated circuits (measured by the number of carbon  $\pi$ -electron centres involved) can be of  $(4n+2)$  and  $(4n)$  size. The former make a positive contribution towards the molecular resonance energy (RE) while the latter make a negative (destabilizing) contribution to molecular stability as measured by RE. In Figure 2, we have illustrated conjugated circuits of one of the three distinct (nonisomorphic) Kekulé valence structures of corannulene.<sup>17</sup>

– *Degree of Freedom (df)* (Figure 3): Each Kekulé valence structure has a unique subset of CC double bonds, which does not appear in any other Kekulé valence structure. The cardinality of this subset is known as the innate degree of freedom of the Kekulé valence structure.<sup>18–20</sup> When this subset is inscribed within the molecular structure, the locations of all other CC double bonds are completely determined, *i.e.*, there is no choice of the locations of the remaining CC double bonds within the structure. Kekulé structures with a large degree of freedom contribute more to molecular stability while the Kekulé structures with a small degree of freedom show a »long-range order«. In Figure 3, we illustrate a selection of CC bonds for the three distinct Kekulé valence structures of Figure 1, two of which have  $df = 2$  and one has  $df = 3$ .

– *Resonance Theory*: Herndon<sup>21,22</sup> developed a simple and straightforward »Resonance Theory« for benzenoid hydrocarbons by showing that a simplified Hamiltonian based on the set of Kekulé valence structures suffices to reproduce very satisfactorily molecular stabilities (measured by the RE) previously calculated by MINDO calculations,<sup>23</sup> the semi-empirical SCF (Self-Consistent Field) theory developed by M. J. S. Dewar and C. de Llano. The Hamiltonian matrix elements between two Kekulé valence structures could be constructed by counting the number of CC double bonds at different locations in the two structures.

– *Equivalence between Resonance Expressions*: Schaad and Hess<sup>24</sup> were the first to observe that the expressions for RE obtained by counting conjugated circuits of different size and the expressions derived from the Resonance Theory of Herndon obtained from the Hamiltonian based on counting CC double bonds, which differ between a pair of Kekulé valence structures, are the same. Thus, the two conceptually distinct approaches turn out to be mathematically equivalent. As Klein and Trinajstić<sup>25</sup> pointed out, this equivalence leads to quantum chemical bases for the Conjugated Circuit Model. For more on the theoretical basis of the conjugated circuit model see numerous papers of Klein and collaborators.<sup>26–45</sup> Conjugated circuits model continues to be of interest not only for fullerenes but also for nanotubes.<sup>46</sup>

– *Resonance Graph* (Figure 4): If one considers only the relations between Kekulé valence structures which

differ in location of only three CC double bonds within a single benzene ring, one obtains a simplified VB interaction graph, known as the Resonance Graph.<sup>47–49</sup> Resonance graphs can be viewed as a collection of fused  $n$ -dimensional cubes, with  $n$  running from 1 to  $N$ , where  $N$  is the largest number of disjoint smallest conjugated circuits confined to a single benzene ring. The graph can be connected or disconnected, and the Kekulé valence structures that constitute the largest connected subgraph of the resonance graph contribute most to the molecular energy.

– *Information Content of Kekulé Valence Structure:* Gutman and Randić<sup>50</sup> came across a highly important observation concerning Kekulé valence structures which shows that a single Kekulé valence structure contains information on all the remaining Kekulé valence structures, which can one by one be derived from any selected structures after one has identified all conjugated circuits in such a structure, the number of which is  $(K-1)$ . All that is required to obtain other Kekulé valence structures from the considered one is to exchange CC single and CC double bonds within a single conjugated circuit. Figure 2 illustrates the theorem of Gutman and Randić on one of the Kekulé structures of corannulene by displaying ten conjugated circuits of that structure, each of which can produce one of the remaining ten Kekulé valence structures of corannulene.

–  *$\pi$ -Electron Ring Partition (Figure 5):* Kekulé valence structures are familiar to most chemists as a convenient geometrical representation for polycyclic conjugated hydrocarbons, but it was only very recently that the

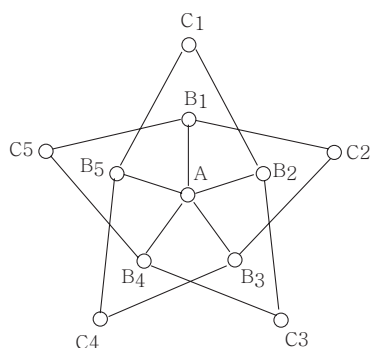


Figure 4. The resonance graph RG for corannulene: A, B<sub>1</sub> and C<sub>1</sub> are the three Kekulé valence structures of Figure 1. Structures B<sub>k</sub> and C<sub>k</sub> are obtained from B<sub>1</sub> and C<sub>1</sub>, respectively, by rotation  $(k-1)$  times 72°.

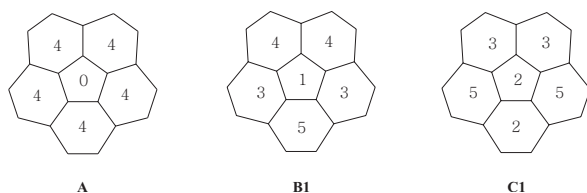


Figure 5. The partitioning of  $\pi$ -electrons for the three Kekulé valence structures of Figure 1.

notion of numerical Kekulé valence structures was proposed.<sup>51</sup> Numerical Kekulé valence structures are based on partition of  $\pi$ -electrons to individual rings of polycyclic conjugated hydrocarbons. CC double bond contributes both its  $\pi$ -electrons to a ring if it is not shared by other rings while if common to two rings, it shares  $\pi$ -electrons, one to each ring. When the contributions of all Kekulé structures are superimposed, individual rings vary in the number of  $\pi$ -electrons, revealing variations in local aromatic properties of individual rings.<sup>52–60</sup> In the case of fullerenes, all CC double bonds are shared between two rings; thus, ring partitions are simply given by the number of CC double bonds in each ring. Figure 5 shows the corresponding  $\pi$ -electron ring partitions for the three distinct Kekulé valence structures of corannulene C<sub>20</sub>H<sub>10</sub>. Each of the resulting partitions represents the numerical representation of the corresponding Kekulé valence structure. When the contributions from all 11 Kekulé valence structures are added, we obtain for the hexagonal rings 41/11 or 3.7272...  $\pi$ -electrons and for the central pentagon 15/11 or 1.3636  $\pi$ -electrons.

More information on all the above mentioned interesting and intriguing properties of Kekulé valence structures can be found in a recent comprehensive review article on aromaticity of polycyclic conjugated hydrocarbons of one of the present authors.<sup>13</sup> In summary, let us mention that the parameters  $R_n$ , which were empirically estimated, satisfy the inequality:

$$R_1 > R_2 > R_3 > R_4$$

Hence, the dominant role in determining molecular RE comes from the smallest conjugated circuits. In addition, we should also comment on the »classical« Hückel  $(4n+2)$  rule, which is known to hold only for monocyclic structures. It constitutes a great achievement of MO theory, because it explained the difference between the stability of benzene C<sub>6</sub>H<sub>6</sub> and elusive cyclobutadiene C<sub>4</sub>H<sub>4</sub>. All attempts to extend the Hückel rule to polycyclic conjugated hydrocarbons failed. However, one can view conjugated circuits as a natural generalization of the Hückel  $(4n+2)$  rule, but note that we have moved from an MO point of view to a VB point of view. Individual conjugated circuits represent monocyclic systems and hence do not violate the Hückel rule. The count of conjugated circuits not only allows one to obtain expressions for the molecular resonance energy RE but also allows classification of polycyclic conjugated hydrocarbons as aromatic and antiaromatic. According to this classification, conjugated systems having only  $4n+2$  conjugated circuits form the class of highly aromatic systems, while those having only  $4n$  conjugated circuits are highly antiaromatic.<sup>13,15</sup> Structures having both  $4n+2$  and  $4n$  conjugated circuits belong to a class »in-between«, compounds that will show some aromatic and some antiaromatic characteristic.

## PROPERTIES OF $C_{70}$ KEKULÉ VALENCE STRUCTURES

Fullerene  $C_{70}$ , the skeleton of which is illustrated in Figure 6, has 25 hexagons and 12 pentagons. It has 52,168 Kekulé structures as it was first reported by Gutman *et al.*<sup>61</sup> and confirmed here using our back-tracking algorithm previously developed for the study of Kekulé valence structures of Buckminsterfullerene. The maximal number of the smallest conjugated circuits  $R_1$  is 20, found in two Kekulé valence structures illustrated in Figure 7. In Table I, we list enumeration of Kekulé structures hav-

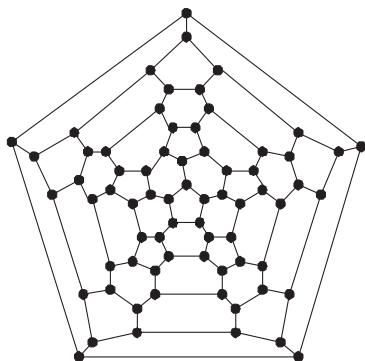


Figure 6. The skeleton of  $C_{70}$ .

TABLE I. Distinct (nonisomorphic) and the total number of Kekulé structures having  $k$  conjugated circuits  $R_1$

Number of $R_1$	Number of nonisomorphic structures	Total number of structures	Quotient
0	16	205	12.81
1	17	340	20.00
2	94	1730	18.40
3	128	2520	19.69
4	179	3270	18.27
5	280	5400	19.29
6	327	6285	19.22
7	369	6970	18.89
8	375	7150	19.07
9	291	5490	18.87
10	265	4826	18.85
11	171	3220	18.83
12	119	2220	18.66
13	77	1370	17.79
14	33	610	18.48
15	23	350	15.22
16	9	150	16.67
17	3	30	10.00
18	3	30	10.00
19	0	0	
20	1	2	2

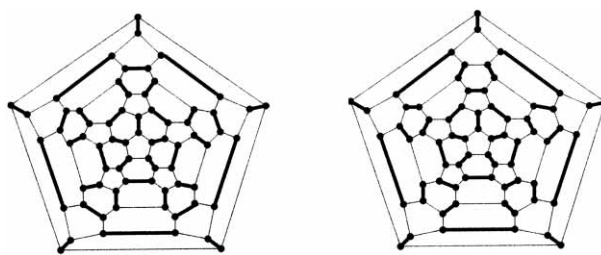


Figure 7. The two Kekulé valence structures having the maximal number (20) of the smallest conjugated circuits  $R_1$ .

ing a different number of  $R_1$ . The middle columns relate to symmetry distinct structures and the total number of Kekulé structures having  $k$  conjugated circuits  $R_1$ , while the quotient of the two is in the last column. Note that it is not possible to have a Kekulé structure with 19  $R_1$ , *i.e.*, one less than the maximal number, because if hexagons CC double and CC single bonds are exchanged in one, this will also affect adjacent hexagons and reduce the maximal number of CC double bonds in them. As we see, the quotient is rather constant for most cases, except for the cases with a very large number of  $R_1$  and the case of zero  $R_1$  conjugated circuits. The symmetry group of  $C_{70}$  has 20 elements, which reduce the 52,168 Kekulé structures to 2780 distinct Kekulé structures. Hence, in the following we need to examine more closely the properties of this smaller subset of Kekulé structures of  $C_{70}$ . In contrast to the case of Buckminsterfullerene of 12,500 different Kekulé structures, there were 158 distinct Kekulé structures. Hence in the case of  $C_{60}$ , distinct Kekulé structures make 1.26 % of all structures but in the case of  $C_{70}$  the distinct Kekulé valence structures make 5.33 % of all structures.

In Figure 7, we have already illustrated the Kekulé structures with the maximal number of  $R_1$  conjugated circuits. It is not difficult to see that of the 20  $R_1$  conjugated circuits in these two structures (which are symmetry related) we can select at most nine disjoint conjugated circuits. One such possibility is illustrated in Figure 8, in which five hexagons of the central hexagonal belt are se-

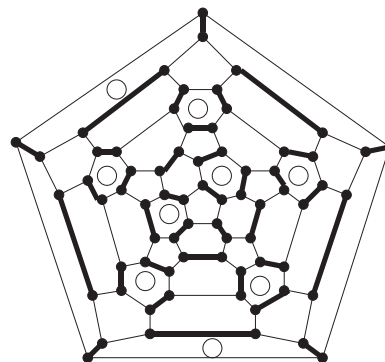


Figure 8. One choice of selecting nine disjoint conjugated circuits forming the Clar structure of  $C_{70}$ .

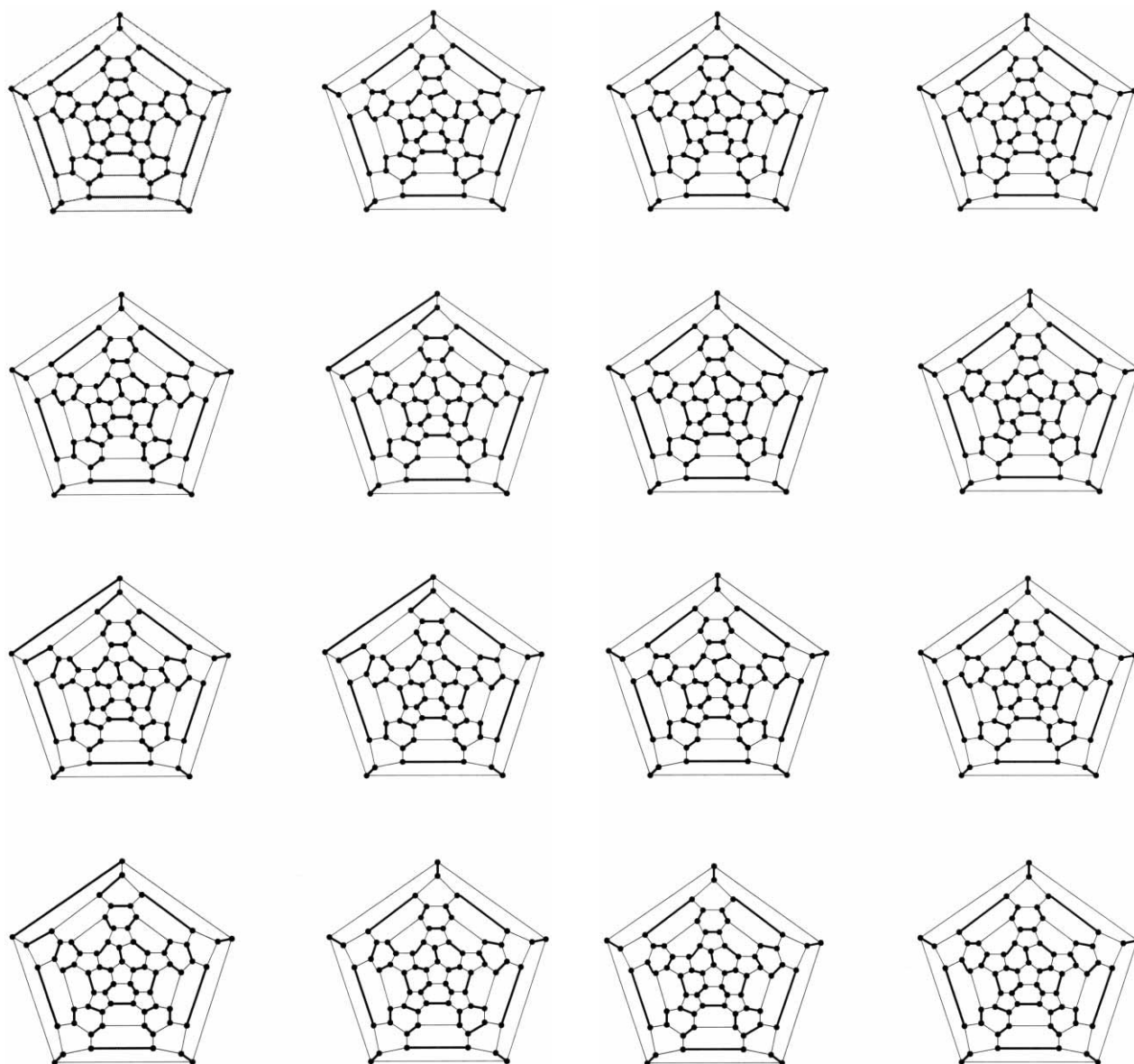


Figure 9. The 16 most important Kekulé valence structures of  $C_{70}$  having 16 or more conjugated circuits  $R_1$ .

lected, leaving inside and outside the belt five hexagons adjacent to the central innermost pentagon and five adjacent to the outermost pentagon (representing the periphery of the  $C_{70}$  figure). Each group of these five pentagons allow two additional disjoint  $R_1$  conjugated circuits, totalling nine. The resulting structure, having nine  $R_1$  and eight CC double bonds, represents the Clar structures of  $C_{70}$ . The Clar structure of Buckminsterfullerene has eight  $R_1$  conjugated circuits and six CC double bonds. In Figure 9, we have illustrated the 16 most important (according to the theory of resonance circuits) Kekulé valence structures of  $C_{70}$  having 16 or more conjugated circuits  $R_1$  and in Figure 10 we similarly show 16 the least important Kekulé valence structures of  $C_{70}$  having no conjugated circuits  $R_1$  at all.

Table II shows the count of disjoint conjugated circuits  $R_1$ . As can be seen from the last row of Table II, in  $C_{70}$  there are 212 different and symmetry unrelated Clar structures and the total of 3872 Clar structures. In this respect, there is considerable difference between  $C_{70}$  and  $C_{60}$ , which has only one distinct Clar structure and five Clar structures in all. We will examine the Clar structures of  $C_{70}$  more closely in the next section.

#### Clar Structures of Fullerene $C_{70}$

Clar structures of Buckminsterfullerene obtained by placing the aromatic  $\pi$ -sextets in eight out of twenty hexagonal rings in  $C_{60}$  were first reported by El-Basil.<sup>62,63</sup> Since each sextet is obtained by superposition of two Kekulé

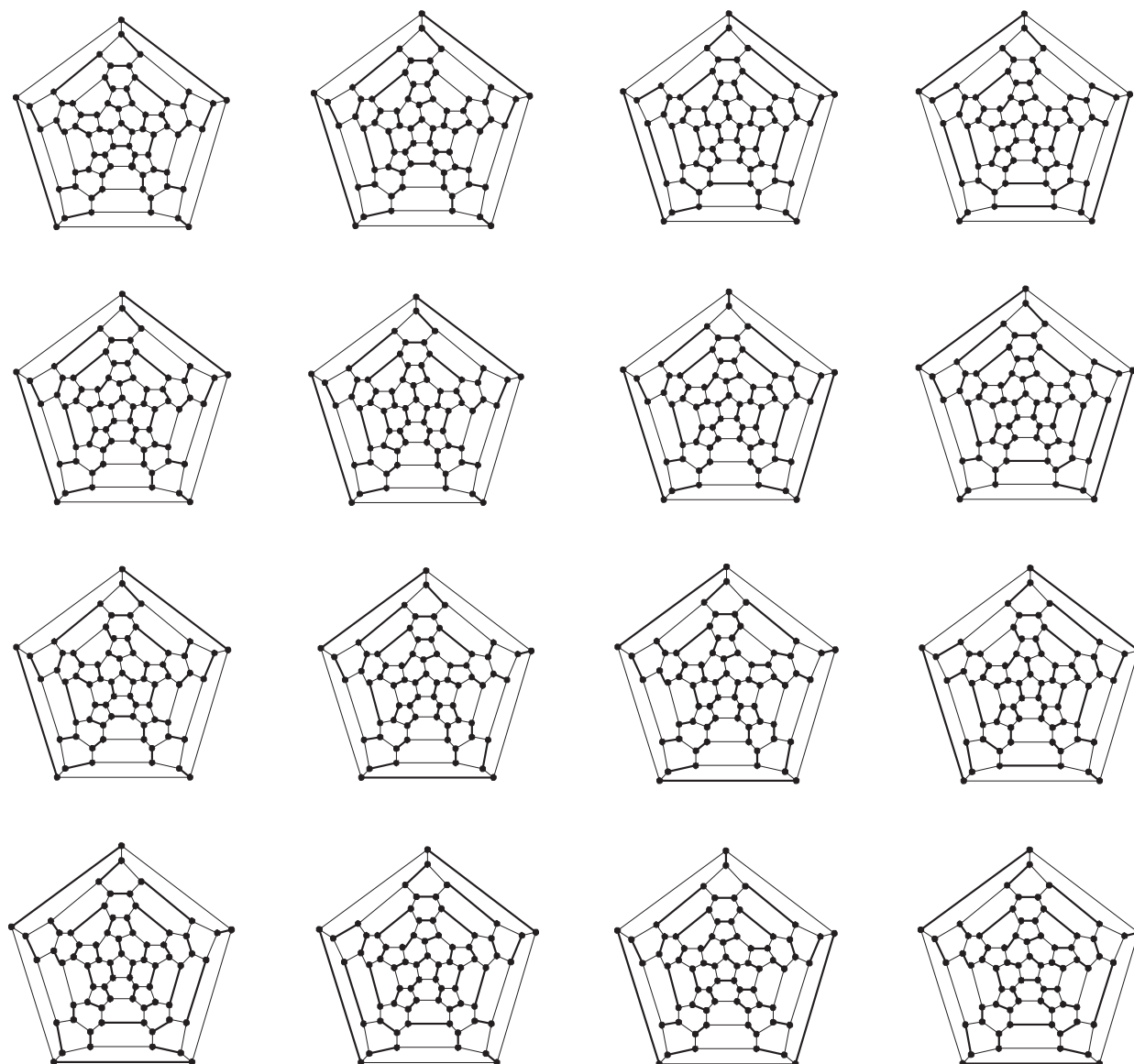


Figure 10. The 16 least important Kekulé valence structures of  $C_{70}$  having no conjugated circuits  $R_1$  at all.

TABLE II. The count of disjoint conjugated circuits  $R_1$

Number of disjoint $R_1$	Number of nonisomorphic structures	Total number of structures	Quotient
0	16	205	12.81
1	26	500	19.23
2	200	3675	18.38
3	167	3250	19.46
4	320	5951	18.60
5	793	14893	18.78
6	331	6320	19.09
7	257	4702	18.29
8	458	8800	19.21
9	212	3872	18.26

structures of benzene, it follows that a single  $C_{60}$  Clar structure involves  $2^8$  or 256 Kekulé valence structures. In the case of  $C_{70}$ , it follows similarly that a single  $C_{70}$  Clar structure involves  $2^9$  or 512 Kekulé valence structures. In total, as we can see from the last row of Table II, there are 3872 Kekulé structures that contribute to the Clar structure of  $C_{70}$ . Instead of depicting that many Kekulé valence structures, we will outline a simple procedure that allows one to easily construct them, if wanted. For that purpose, in Figures 11–13 we have depicted components which when combined produce the required Kekulé valence structures. First, Figure 11 shows two diagrams of  $C_{70}$ , in which only a single hexagon has inscribed three CC double bonds. By rotating the figure by  $72^\circ$ , one can obtain the remaining eight structures, there being ten such components in all. Figure 12 shows three

diagrams of C<sub>70</sub> with partially inscribed CC double bonds in the central part involving the central pentagon and the five adjacent hexagons. The three diagrams are nonisomorphic and except for the first, which is unique (its only isomorphism is identity), the other two can generate, by rotating the figure by 72°, four additional (isomorphic) diagrams, thus totalling together with the first unique diagram in all 11 components. Finally, Figure 13 again shows three diagrams of C<sub>70</sub> with partially inscribed CC double bonds in the periphery involving the outside pentagon and the five adjacent hexagons. The three diagrams are again nonisomorphic and except for the first, which is unique (its only isomorphism is identity), the remaining two can generate, by rotating the figure by 72°, four additional (isomorphic) diagrams, thus totalling together with the unique diagram in all 11 components. By choosing any structure given in Figure 11, any in Figure 12 and any in Figure 13 and joining their double bonds, we get one of Kekulé structures involved in the Clar structure of C<sub>70</sub>. When we also consider components obtained by rotating the diagrams shown in this way, we can construct  $2 \cdot 2 \cdot 2 \cdot 2 \cdot 2 \cdot 11 \cdot 11 = 3872$  (*i.e.*, all) Kekulé structures participating in defining the Clar structures of C<sub>70</sub>.

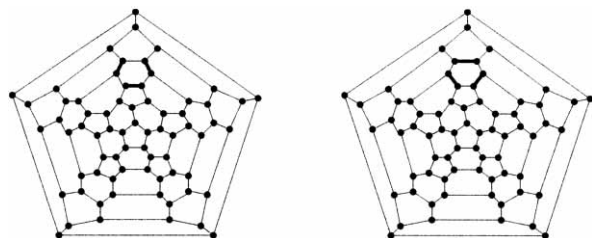


Figure 11. Two diagrams of C<sub>70</sub> in which only a single hexagon has inscribed three CC double bonds.

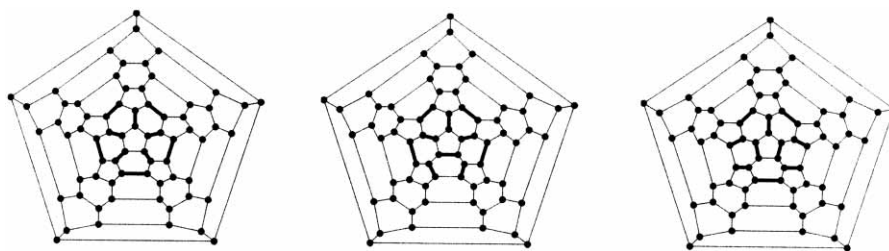


Figure 12. Three diagrams of C<sub>70</sub> with partially inscribed CC double bonds in the central part involving the central pentagon and the five adjacent hexagons.

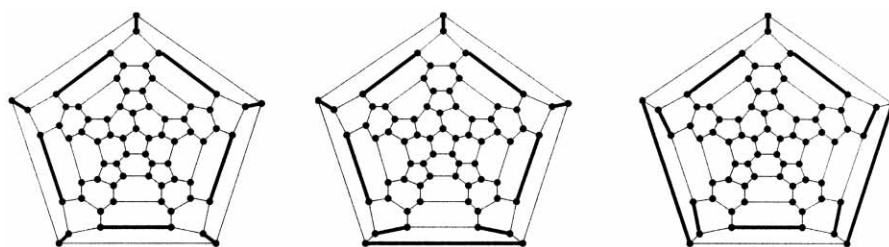


Figure 13. Three diagrams of C<sub>70</sub> with partially inscribed CC double bonds in the periphery involving the outside pentagon and the five adjacent hexagons.

### Resonance Graph

According to *ab initio* VB calculations on  $\pi$ -conjugated hydrocarbons, Klein and collaborators found that only a subset of all Kekulé valence structures contribute significantly to molecular stability (that is, to the total molecular energy). They identified these Kekulé valence structures as those which can be obtained from the dominant Kekulé valence structure by successive exchange of CC single and CC double bonds within any of the single benzene hexagons. All Kekulé valence structures that can be generated in this fashion belong to the main component of the Resonance Graph (RG). A class of 3872 Kekulé valence structures contributing to the Clar structure belong to the valence structures of the main component of the Resonance Graph, which however contains additional valence structures. In Table III, the left columns show the number of nonisomorphic and the total number of Kekulé valence structures forming the main component of the Resonance Graph. As can be seen from Table III, there are in all 17,454 valence structures in the Resonance Graph, of which 3872 belong to the class forming Clar structures. If we consider only nonisomorphic structures, the total of which is 3872, only about a fourth, *i.e.*, 932, are Kekulé structures of the RG, but if we consider all Kekulé valence structures, then out of 52168 valence structures only about 1/3, *i.e.*, 17,454, make a significant contribution to molecular energy computations.

A close look at Table III shows that all Kekulé valence structures having 13 R<sub>1</sub> and more belong to the main component of the RG, with the exception of a single structure (shown in Figure 14), while at the same time all Kekulé valence structures having 5 R<sub>1</sub> and less do not belong to the main component of RG. The ratio of the number

TABLE III. The number of nonisomorphic and the total number of Kekulé valence structures forming the main component of the Resonance Graph

Number of $R_1$	Main component		Number of $R_1$	Other	
	Number of non-isomorphic structures	Total number of structures		Number of non-isomorphic structures	Total number of structures
0	0	0	0	16	205
1	0	0	1	17	340
2	0	0	2	94	1730
3	0	0	3	128	2520
4	0	0	4	179	3270
5	0	0	5	280	5400
6	3	50	6	324	6235
7	37	700	7	332	6270
8	118	2240	8	257	4910
9	171	3300	9	120	2190
10	186	3532	10	79	1294
11	160	3050	11	11	170
12	109	2050	12	10	170
13	77	1370	13	0	0
14	32	600	14	1	10
15	23	350	15	0	0
16	9	150	16	0	0
17	3	30	17	0	0
18	3	30	18	0	0
19	0	0	19	0	0
20	1	2	20	0	0
Total	932	17454		1848	34714

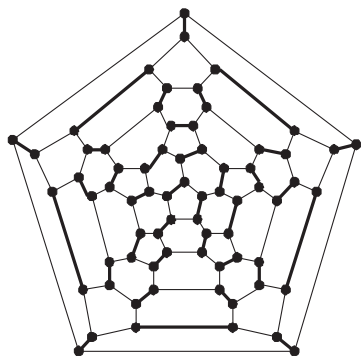


Figure 14. Kekulé valence structures having 14  $R_1$  (six of which are disjoint) and not belonging to the main component of the RG.

of Kekulé valence structures having between 6  $R_1$  and 12  $R_1$  belonging to the main component increases as the number of  $R_1$  conjugated circuits increases. We can compare the results obtained for the  $C_{70}$  fullerene with similar results for the  $C_{60}$  buckminsterfullerene. Just as in the case of buckminsterfullerene, the resonance graph of  $C_{70}$

is too complex to be graphically presented. However, we know that instead of the 8-dimensional cube being the largest  $n$ -dimensional cube possible for  $C_{60}$ , now we have the 9-dimensional cube as the largest  $n$ -cube possible. In addition, the resonance graph of  $C_{70}$  involves numerous fused 8-dimensional cubes, 7-dimensional cubes and smaller  $n$ -cubes, all constituting a single connected component of the resonance graph. In their variational resonance valence bond study of the ground state of  $C_{60}$ , Flocke, Schmalz and Klein<sup>6</sup> used the 5828 (that form the main component of the RG from the total of 12,500 Kekulé valence structures of  $C_{60}$ ) based on the Heisenberg model for Hamiltonian, which considers electron correlation as a result of exchange interactions. Such Hamiltonian has been used extensively in solid state physics and can be derived as the dominant terms in cluster expansions or degenerate perturbation methods.<sup>64–66</sup> The calculations on conjugated hydrocarbons thus definitively demonstrated the significance of the main component of the RG. The difference between such calculations made on benzenoid hydrocarbons and nonbenzenoid conjugated systems (which include fullerenes) is that in the case of benzenoid systems RG has a single component.

Of the 12,500 Kekulé valence structures of  $C_{60}$ , at most 5828 play an important role for stabilization of the molecule. Wu, Schmalz and Klein<sup>9</sup> have shown using an extended Heisenberg Hamiltonian with next-nearest-neighbour and ring permutation terms, including only the spin pairing corresponding to 5828 Kekulé valence in the case of  $C_{60}$ , recovered 99.90 % of the energy that is obtained using the full Kekulé basis, and using the extended Heisenberg model on the same 5828 Kekulé basis structures they recovered as much as 99.96 % of the full Kekulé basis result. It is clear that the subset of Kekulé valence

TABLE IV. Count of nonisomorphic Kekulé structures having a different number of disjoint  $R_1$  conjugated circuits

Number of disjoint $R_1$	Main component		Number of disjoint $R_1$	Other	
	Number of non-isomorphic structures	Total number of structures		Number of non-isomorphic structures	Total number of structures
0	0	0	0	16	205
1	0	0	1	26	500
2	0	0	2	200	3675
3	0	0	3	167	3250
4	0	0	4	320	5951
5	0	0	5	793	14893
6	5	80	6	326	6240
7	257	4702	7	0	0
8	458	8800	8	0	0
9	212	3872	9	0	0
Total	932	17454		1848	34714



structures that makes a single connected component of the resonance graph are the important valence structures, while the 6672 structures can be overlooked when energetic properties of C<sub>60</sub> are considered. Thus, in the case of C<sub>70</sub>, we can expect results of similar quality by using 17,454 valence structures instead of 52,168.

If we focus attention on the count of disjoint conjugated circuits R<sub>1</sub>, then we find that all Kekulé valence structures having nine, eight or seven disjoint R<sub>1</sub> conjugated circuits belong to the main component of RG, while all Kekulé valence structures having five and less disjoint R<sub>1</sub> conjugated circuits do not belong to the main component of RG. As can be seen from Table IV, of the 331 nonisomorphic Kekulé structures having six disjoint R<sub>1</sub> conjugated circuits only five belong to the main component of RG. The structure that does not belong to RC has already been illustrated in Figure 14.

Table V shows the count of conjugated circuits in the main component of the resonance graph. The distances shown relate to the dominant two Kekulé valence structures as the origin. The rows give conjugated circuits and columns give the distances.

#### Degree of Freedom

Table IV shows the distribution of the innate degree of freedom within the totality of 52,158 Kekulé valence structures of C<sub>70</sub>. The innate degree of freedom, *df*, is defined as the smallest number of CC double bonds that completely determines the location of all the remaining CC double bonds in a Kekulé valence structure. As can be seen from Table VI, the maximal degree of freedom in C<sub>70</sub> is 11, there being four valence structures with *df* = 11. Of the Kekulé structures belonging to the main component of RG, four have the degree of freedom six, while the smallest possible degree of freedom for C<sub>70</sub> is five. Comparison of Table IV and Table VI shows that the count of disjoint R<sub>1</sub> better discriminates between Kekulé valence structures belonging to the main component of RG than the degree of freedom.

#### $\pi$ -Electron Ring Partitions

We will end this analysis of Kekulé valence structures of C<sub>70</sub> fullerene by examining the distribution of  $\pi$ -electrons within the hexagonal rings of C<sub>70</sub>. In Figure 15, we have illustrated partition of the 70  $\pi$ -electrons to the 25 hexagons (on the left in Figure 15) and the 12 pentagons (on the right in Figure 15). Since the structure of fullerenes is closed, the partition of  $\pi$ -electrons is accomplished very simply by counting the CC bonds in each ring. As can be seen from Figure 15, for the selected Kekulé structure we have 18 hexagons with three  $\pi$ -electrons, four hexagons with two  $\pi$ -electrons and three hexagons to which a single  $\pi$ -electron is assigned. The total number of  $\pi$ -electrons assigned to the 25 hexagons is therefore

Table V. The count of conjugated circuits in the main component of the resonance graph. The distances shown relate to the dominant two Kekulé valence structures as the origin. The rows give conjugated circuits and columns give the distances

Number of conjugated cycles	Minimal distance from one of the two main Kekulé structures									
	0	1	2	3	4	5	6	7	8	9
6	0	0	0	0	0	0	0	20	30	0
7	0	0	0	0	0	0	0	470	200	30
8	0	0	0	0	0	0	1370	770	100	0
9	0	0	0	0	0	1250	1560	460	30	0
10	0	0	0	0	350	2032	1020	130	0	0
11	0	0	0	0	1330	1330	390	0	0	0
12	0	0	0	220	1230	560	40	0	0	0
13	0	0	0	700	490	180	0	0	0	0
14	0	0	30	350	220	0	0	0	0	0
15	0	0	200	110	40	0	0	0	0	0
16	0	0	80	70	0	0	0	0	0	0
17	0	20	10	0	0	0	0	0	0	0
18	0	20	10	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0
20	2	0	0	0	0	0	0	0	0	0

TABLE VI. Count of nonisomorphic Kekulé structures having a different number of innate degrees of freedom

Degree of freedom	Main component		Other		
	Number of non-isomorphic structures	Total number of structures	Degree of freedom	Number of non-isomorphic structures	Total number of structures
5	0	0	5	110	2080
6	4	70	6	712	13540
7	159	3020	7	812	15390
8	456	8750	8	209	3652
9	266	4902	9	5	52
10	43	680	10	0	0
11	4	32	11	0	0
Total	932	17454		1848	34714

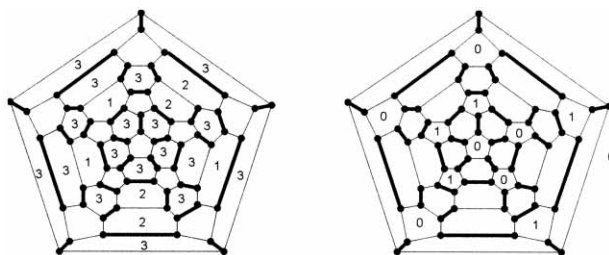


Figure 15. Partition of the 70  $\pi$ -electrons to the 25 hexagons (on the left) and the 12 pentagons (on the right).

TABLE VII. Count of rings having the same partitioning of  $\pi$ -electrons in hexagonal rings

$\pi$ -electron ring partition	Main component		$\pi$ -electron ring partition	Other	
	Number of non-isomorphic structures	Total number of structures		Number of non-isomorphic structures	Total number of structures
1.84	0	0	1.84	38	605
1.88	5	80	1.88	77	1440
1.92	3	50	1.92	158	2860
1.96	31	590	1.96	200	3950
2.00	25	480	2.00	234	4521
2.04	68	1300	2.04	273	5240
2.08	93	1790	2.08	243	4570
2.12	76	1420	2.12	202	3870
2.16	146	2860	2.16	172	3195
2.20	92	1722	2.20	104	1980
2.24	100	1880	2.24	71	1300
2.28	117	2250	2.28	43	730
2.31	36	640	2.31	18	260
2.36	66	1160	2.36	10	160
2.40	38	720	2.40	5	33
2.44	6	80	2.44	0	0
2.48	20	320	2.48	0	0
2.52	6	80	2.52	0	0
2.56	0	0	2.56	0	0
2.60	4	32	2.60	0	0
Total	932	17,454		1848	34,714
Average		2.1928			2.0564

65, which is the maximal number possible. Note that five of the »belt« hexagons have the maximal possible number of  $\pi$ -electrons per ring, which is three, but the other five hexagons of the »belt« region have one or two. Thus, in comparison with Buckminsterfullerene, where all hexagons can attain the maximal number of three  $\pi$ -electrons, that is not the case here. Here, the presence of additional hexagons in fact decreases, rather than increases, the local aromaticity of the hexagonal rings. We obtain, on average, for this particular Kekulé valence structure 2.60  $\pi$ -electrons per ring. The remaining five  $\pi$ -electrons belong to 12 pentagons, giving on average 0.41667  $\pi$ -electrons for pentagons.

In Table VII, we have collected information on partitioning of  $\pi$ -electrons to hexagonal rings for all nonisomorphic Kekulé valence structures as well as for the total number of Kekulé valence structures belonging to the main component of the resonance graphs and to the remaining part of the RG. As can be seen even just by superficial examination of Table VI, most hexagonal rings of the main RG component have between 2.04 and 2.36  $\pi$ -electrons, while most of the hexagonal rings of the Kekulé valence structures not belonging to RG have be-

tween 1.88 and 2.24  $\pi$ -electrons. This observation alone suffices to indicate quite clearly that Kekulé valence structures of RG are more significant and will contribute more to the molecular stability than the Kekulé structures that do not belong to RG. In the last row of Table VII, we show the average  $\pi$ -electron content of hexagonal rings of  $C_{70}$  for Kekulé valence structures belonging to the main component of RG and also for those not belonging to the main component of RG. The difference between the two values, 2.1928 and 2.0564, does not appear large, but when the two numbers are multiplied by 25, the total number of hexagonal rings in  $C_{70}$ , then we can better appreciate the importance of the Kekulé valence structures that constitute the resonance graph.

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## SAŽETAK

### Kekuléove strukture fulerena C<sub>70</sub>

Milan Randić i Damir Vukičević

Bez obzira na to što je fuleren C<sub>70</sub> drugi najstabilniji fuleren nakon C<sub>60</sub> Buckminsterfullerena, među ovim fulerenima postoje značajne strukturne razlike. U radu se iznosi mnoštvo matematičkih svojstava Kekuléovih struktura fulerena C<sub>70</sub>. Od preko 50000 Kekuléovih struktura fulerena C<sub>70</sub>, samo je 2780 struktura koje nisu izomorfne. Ove strukture su klasificirane s obzirom na stupnjeve slobode (*degree of freedom, df*) u 6 klasa koje se kreću od *df* = 5 do *df* = 11. Prebrojavanjem konjugiranih prstenova R<sub>1</sub>, R<sub>2</sub> i R<sub>3</sub> utvrđeno je da postoje dvije najznačajnije strukture sa 20 R<sub>1</sub> konjugiranih prstenova i da su one međusobno izomorfne. S druge strane postoji 16 neizomornih Kekuléovih struktura fulerena C<sub>70</sub> koje uopće nemaju konjugiranih prstenova R<sub>1</sub>.

