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# On Instability of Fullerene $C_{72}$

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The most important fullerene is buckminsterfullerene $C_{60}$, obtained by leap-frog transformation of the fullerene $C_{20}$. The second smallest fullerene obtained by leap-frog transformation is $C_{72}$ (obtained from $C_{24}$). It is surprising that $C_{72}$ is unstable. The standard explanation of this fact is based on steric strain resulting from the existence of two hexagons, each surrounded by 6 hexagons. By analyzing the π-electron content, it is demonstrated that these hexagons show some »pentagon-like« behavior that may be the cause (or an additional cause) of the instability of $C_{72}$. Hence, it is shown that there may be topological (non-steric) reasons for the instability of $C_{72}$.

## INTRODUCTION

Buckminsterfullerene, $C_{60}$, is the first fullerene that was theoretically conceived and experimentally obtained.[1] Theoretically, $C_{60}$ may be viewed as being constructed by the leap-frog transformation of the fullerene $C_{20}$. The leap-frog transformation[2-4] is the transformation in which the dual of the original fullerene is formed and then truncated on all vertices.

Fullerene $C_{60}$ seems to be the most stable fullerene in nature. Hence, it would be reasonable to expect $C_{72}$, the second smallest fullerene obtained by leap-frog transformation, to be stable as well. Another reason for expecting stability of $C_{72}$ is that it has Kekulé structures in which all π-electrons belong to hexagons. Yet another reason for expecting stability of $C_{72}$ is that[2] it has a large band gap and bonding resonance energy, and thus a stable, closed-shell π-electron configuration.

In reality, the situation is different: $C_{72}$ is not stable. Its instability is usually explained by steric strain. Indeed, $C_{72}$ has two hexagons, each surrounded by 6 hexagons and because of this structural feature, the $C_{72}$ molecule must have a large amount of steric strain. Hexagon indices are described in *An Atlas of Fullerenes*.[2] The number of hexagons that are adjacent to exactly $i$ other hexagons is denoted by $h_i$. In this way, every fullerene isomer can be described by the 7-tuple ($h_0$, $h_1$, $h_2$, $h_3$, $h_4$, $h_5$, $h_6$). It is claimed that a fullerene is most stable if only one of the numbers $h_i$ is different from 0, and that there are some stable fullerenes that have two consecutive numbers $h_i$ and $h_{i+1}$ different. In the case of $C_{72}$:

$$(h_0, h_1, h_2, h_3, h_4, h_5, h_6) = (0,0,0,12,12,0,2)$$

which implies that $C_{72}$ has two »problematic« hexagons, namely hexagons surrounded by 6 other hexagons.

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The main point of this paper is to show that these two hexagons have unexpected properties regarding the distribution of π-electrons in Kekulé structures. Hence, here we offer a strictly topological (non-steric) argument that may contribute to clarifying the reasons for the lack of stability of the fullerene $C_{72}$.

Recently, two of the present authors (M. R., D. V.), together with Harry Kroto, analyzed the Kekulé structures of the $C_{60}$ fullerene.[5-7] Also, the properties of Kekulé structures of $C_{70}$ have been analyzed.[8-9] In these papers, it is taken into account that the importance of the Kekulé structure increases with the increase of the following values:

- number of independent conjugated cycles;
- degree of freedom;
- number of independent conjugated hexagons;
- number of conjugated hexagons;
- number of π-electrons belonging to hexagons.

We are not going to elaborate the relative importance of Kekulé structures or the identification of the most important ones, because it has been discussed in due detail elsewhere.[10]

A conjugated cycle is the cycle in which single and double bonds alternate. We say that two cycles are independent if they do not share a common edge. A set of cycles is independent if the cycles are independent pairwise. The degree of freedom is the smallest number of double bonds that completely determine the Kekulé structure, *i.e.,* it is the smallest subset of double bonds of the given Kekulé structure that is not contained in any other Kekulé structure. The number of π-electrons that belong to hexagons is the number of double bonds incident to hexagons (each double bond shared by two hexagons is counted twice and the double bonds shared by a pentagon and a hexagon are counted once, because it is taken that one electron belongs to the hexagon and the other to the pentagon).

The resonance graphs of the fullerenes are also analyzed in the papers.[5–7] The resonance graph of a fullerene is a graph the vertices of which are the Kekulé structures of the fullerene, and two vertices are adjacent if the corresponding Kekulé structures differ only in the position of three double bonds within a hexagon. This graph need not be connected,[7] in which case one of its components pertains to the most important Kekulé structures.

Recently, the notion of π-electron content was introduced and analyzed.[11-15] The π-electron content of a face is the number of π-electrons that belong to that face. In the case of fullerenes, the number of π-electrons is equal to the number of double bonds that belong to the observed face. A self-explanatory example (for $C_{70}$) is given in Figure 1.

In this paper, we are going to analyze the connection between the importance of the Kekulé structures and the π-electron content of the $C_{72}$ faces.

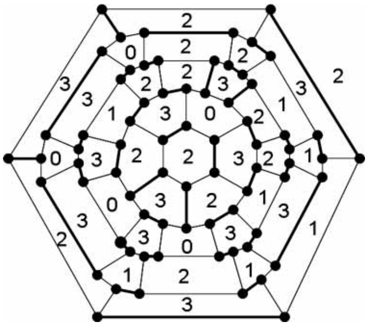

Figure 1. A Kekulé structure of $C_{70}$ and the corresponding π-electron content.

## PRELIMINARIES AND MAIN RESULTS

Up to isomorphism, there are four different faces of $C_{72}$. There are three types of hexagons (denoted by A, B, and C) and one type of pentagons (denoted by P). This is illustrated in Figure 2.

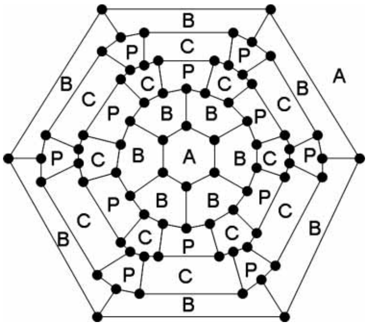

Figure 2. Labeling of the faces of $C_{72}$ by letters A, B, C and P. Isomorphic faces are denoted by the same letter.

We now define the isomorphism of Kekulé structures: Two Kekulé structures $K_1$ and $K_2$ are said to be isomorphic if there is an automorphism of the underlying graph that maps double bonds of $K_1$ to double bonds of $K_2$ and single bonds of $K_1$ to single bonds of $K_2$.

By means of appropriate computer software (slight modification of the software used in the research[5-7] of $C_{60}$ and research[8,9] of $C_{70}$), it can be established that there are 77400 Kekulé structures of $C_{72}$, which can be classified by symmetrical invariance into 3470 classes.

Also, it can be checked using the same program that the resonance graph of $C_{72}$ is not connected. Note that $C_{72}$ has one particular Kekulé structure $K^*$ (Figure 3), in which all double bonds are shared by hexagons. Every automorphism of $C_{72}$ maps $K^*$ to $K^*$.

Denote by MIC the connected component of the resonance graph of $C_{72}$ that contains $K^*$. In the sequel, we provide numerical evidence that this is the most important component of the resonance graph.

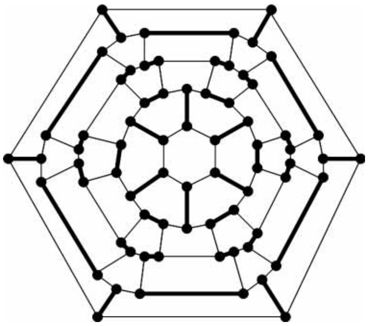

Figure 3. The most important Kekulé structure of $C_{72}$.

*Theorem 1.* – Let $K_1$ and $K_2$ be two isomorphic Kekulé structures. Then, they are either both in MIC or none of them is in MIC.

*Proof:* It is sufficient to prove that $K_1 \in \text{MIC} \Rightarrow K_2 \in$ MIC. Let $K_1\alpha_2\alpha_3\ldots\alpha_x K^*$ be the path from $K_1$ to $K^*$ and let $f$ be the automorphism of $C_{72}$ that maps $K_1$ to $K_2$. Then, $f(K_1)\, f(\alpha_2)\, f(\alpha_3)\ldots f(\alpha_x)\, f(K^*)$ is the path from $K_2 = f(K_1)$ to $K^* = f(K^*)$. ■

Let S be any subset of the set of Kekulé structures of $C_{72}$, such that for each two isomorphic Kekulé structures $K_1$ and $K_2$ either both $K_1$ and $K_2$ are in S or none of them is in S. Then, we say that S is an isomorphically invariant set. By convention, we assume that the empty set is isomorphically invariant.

*Remark 2.* – From Theorem 1, it follows that MIC is an isomorphically invariant set. ■

Let K be any Kekulé structure. Denote by $ic(K)$, $df(K)$, $ih(K)$, $ch(K)$ and $pe(K)$, respectively, the maximal number of independent conjugated cycles of K, the degree of freedom of K, the maximum number of independent conjugated hexagons of K, the number of conjugated hexagons of K, and the number of π-electrons that belong to hexagons in K. It can be easily verified that the following theorem holds:

*Theorem 3.* – Let $i$ be any natural number. The sets:

$$ic_i = \{K : ic(K) = i\}$$

$$df_i = \{K : df(K) = i\}$$

$$ih_i = \{K : ih(K) = i\}$$

$$ch_i = \{K : ch(K) = i\}$$

$$pe_i = \{K : pe(K) = i\}$$

are isomorphically invariant. ■

We can also prove:

*Theorem 4.* – Let $S_1$ and $S_2$ be two isomorphically invariant sets. Then, the set $S_1 \cap S_2$ is also isomorphically invariant. ■

For any finite set X, we denote by $|X|$ the number of elements of the set X. Let S be any isomorphically invariant set. Denote $S^m = S \cap \text{MIC}$. Also, denote $S^{\text{ratio}} = |S^m| / |S|$.

Let X be any face of $C_{72}$ and let K be any Kekulé structure of $C_{72}$. Denote by $K(X)$ the π-electron content of the face X in the Kekulé structure K. Let S be any set of Kekulé structures. Denote

$$S(X) = \frac{\sum_{K \in S} K(X)}{|S|},$$

where $|S|$ is the number of the Kekulé structures in S. Let us illustrate this by three examples:

- $ch_4(C)$ is the average π-electron content of the hexagon when all Kekulé structures with 4 conjugated hexagons are taken into consideration;
- $df_5(A)$ is the average π-electron content of hexagon A when all Kekulé structures with degree of freedom equal to 5 are taken into consideration;
- $ic_7(B)$ is the average π-electron content of hexagon B when all Kekulé structures of the main component resonant graph that have the maximal number of independent cycles equal to 7 are taken into consideration.

*Theorem 5.* – Let $X_1$ and $X_2$ be two isomorphic faces and let S be the isomorphically invariant set of Kekulé structures. Then, $S(X_1) = S(X_2)$. ■

From this theorem, it follows:

*Remark 6.* – Let S be the isomorphically invariant set of Kekulé structures. To describe all faces, it is sufficient to calculate $S(A)$, $S(B)$, $S(C)$ and $S(P)$. ■

Now we can present our major results, which are given in the following five tables (the tables were obtained by a computer after about nine-hour long execution of the algorithm based on several mathematical theorems). All tables are structured as follows:

- The 1st column gives the prescribed value $i$;
- The 2nd column gives the number of Kekulé structures with value $i$ of the observed property;
- The 3rd column gives the number of Kekulé structures in the main component of the resonant graph with value $i$ of the observed property;
- The 4th column gives the ratio of the numbers in the third and second column;
- The 5th (resp. 6th, 7th, 8th) column gives the average π-electron content of the hexagon A (resp. hexagon B, hexagon C, pentagon P) when all the structures described in the 3rd item are taken into consideration;
- The 9th (resp. 10th, 11th, 12th) column gives the average π-electron content of the hexagon A (resp. hexagon B, hexagon C, pentagon P) when all the structures described in the 3rd item are taken into consideration.

The above five tables are given here:

TABLE I. Results pertaining to Kekulé structures with the same maximal number of independent conjugated cycles

| $i$ | $\lvert ic_i \rvert$ | $\lvert ic_i^{\mathrm{m}} \rvert$ | $ic_i^{\mathrm{ratio}}$ | $ic_i^{\mathrm{m}}(\mathrm{A})$ | $ic_i^{\mathrm{m}}(\mathrm{B})$ | $ic_i^{\mathrm{m}}(\mathrm{C})$ | $ic_i^{\mathrm{m}}(\mathrm{P})$ | $ic_i(\mathrm{A})$ | $ic_i(\mathrm{B})$ | $ic_i(\mathrm{C})$ | $ic_i(\mathrm{P})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 1086 | 0 | 0.000 | – | – | – | – | 1.989 | 1.960 | 1.983 | 1.726 |
| 5 | 13575 | 24 | 0.002 | 3.000 | 1.833 | 2.167 | 1.500 | 2.000 | 1.979 | 2.032 | 1.656 |
| 6 | 12487 | 160 | 0.013 | 2.663 | 1.944 | 2.219 | 1.394 | 2.091 | 2.030 | 2.044 | 1.577 |
| 7 | 15261 | 2364 | 0.155 | 2.211 | 2.040 | 2.186 | 1.406 | 1.847 | 2.146 | 2.103 | 1.443 |
| 8 | 7736 | 7736 | 1.000 | 1.663 | 2.197 | 2.226 | 1.300 | 1.663 | 2.197 | 2.226 | 1.300 |
| 9 | 27255 | 27255 | 1.000 | 1.413 | 2.298 | 2.302 | 1.164 | 1.413 | 2.298 | 2.302 | 1.164 |

TABLE II. Results pertaining to Kekulé structures with the same degree of freedom

| $i$ | $\lvert df_i \rvert$ | $\lvert df_i^{\mathrm{m}} \rvert$ | $df_i^{\mathrm{ratio}}$ | $df_i^{\mathrm{m}}(\mathrm{A})$ | $df_i^{\mathrm{m}}(\mathrm{B})$ | $df_i^{\mathrm{m}}(\mathrm{C})$ | $df_i^{\mathrm{m}}(\mathrm{P})$ | $df_i(\mathrm{A})$ | $df_i(\mathrm{B})$ | $df_i(\mathrm{C})$ | $df_i(\mathrm{P})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 1557 | 0 | 0.000 | – | – | – | – | 1.981 | 1.963 | 1.933 | 1.775 |
| 6 | 16809 | 60 | 0.004 | 2.500 | 1.950 | 2.150 | 1.483 | 2.014 | 1.988 | 2.010 | 1.666 |
| 7 | 21604 | 2204 | 0.102 | 2.273 | 2.015 | 2.166 | 1.441 | 1.993 | 2.082 | 2.085 | 1.500 |
| 8 | 9196 | 7065 | 0.768 | 1.720 | 2.175 | 2.209 | 1.330 | 1.651 | 2.209 | 2.216 | 1.300 |
| 9 | 24037 | 24013 | 0.999 | 1.473 | 2.268 | 2.272 | 1.215 | 1.473 | 2.268 | 2.272 | 1.215 |
| 10 | 4096 | 4096 | 1.000 | 1.066 | 2.479 | 2.490 | 0.854 | 1.066 | 2.479 | 2.490 | 0.854 |
| 11 | 100 | 100 | 1.000 | 0.480 | 2.770 | 2.780 | 0.370 | 0.480 | 2.770 | 2.780 | 0.370 |
| 12 | 1 | 1 | 1.000 | 0.000 | 3.000 | 3.000 | 0.000 | 0.000 | 3.000 | 3.000 | 0.000 |

TABLE III. Results pertaining to Kekulé structures with the same maximal number of independent conjugated hexagons

| $i$ | $\lvert ih_i \rvert$ | $\lvert ih_i^{\mathrm{m}} \rvert$ | $ih_i^{\mathrm{ratio}}$ | $ih_i^{\mathrm{m}}(\mathrm{A})$ | $ih_i^{\mathrm{m}}(\mathrm{B})$ | $ih_i^{\mathrm{m}}(\mathrm{C})$ | $ih_i^{\mathrm{m}}(\mathrm{P})$ | $ih_i(\mathrm{A})$ | $ih_i(\mathrm{B})$ | $ih_i(\mathrm{C})$ | $ih_i(\mathrm{P})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 289 | 0 | 0.000 | – | – | – | – | 1.869 | 1.882 | 1.893 | 1.913 |
| 1 | 408 | 0 | 0.000 | – | – | – | – | 2.103 | 1.944 | 1.865 | 1.841 |
| 2 | 4512 | 0 | 0.000 | – | – | – | – | 2.007 | 1.955 | 1.954 | 1.756 |
| 3 | 3366 | 0 | 0.000 | – | – | – | – | 2.303 | 1.949 | 1.968 | 1.699 |
| 4 | 12867 | 0 | 0.000 | – | – | – | – | 2.000 | 2.021 | 2.058 | 1.587 |
| 5 | 6198 | 76 | 0.012 | 3.000 | 1.868 | 2.237 | 1.395 | 2.033 | 2.045 | 2.079 | 1.537 |
| 6 | 12405 | 108 | 0.009 | 2.500 | 1.972 | 2.194 | 1.417 | 1.762 | 2.165 | 2.102 | 1.439 |
| 7 | 4028 | 4028 | 1.000 | 2.179 | 2.061 | 2.212 | 1.363 | 2.179 | 2.061 | 2.212 | 1.363 |
| 8 | 6072 | 6072 | 1.000 | 1.534 | 2.226 | 2.219 | 1.299 | 1.534 | 2.226 | 2.219 | 1.299 |
| 9 | 27255 | 27255 | 1.000 | 1.413 | 2.298 | 2.302 | 1.164 | 1.413 | 2.298 | 2.302 | 1.164 |

TABLE IV. Results pertaining to Kekulé structures with the same number of conjugated hexagons

| $i$ | $\lvert ch_i \rvert$ | $\lvert ch_i^{\mathrm{m}} \rvert$ | $ch_i^{\mathrm{ratio}}$ | $ch_i(\mathrm{A})$ | $ch_i(\mathrm{B})$ | $ch_i(\mathrm{C})$ | $ch_i(\mathrm{P})$ | $ch_i(\mathrm{A})$ | $ch_i(\mathrm{B})$ | $ch_i(\mathrm{C})$ | $ch_i(\mathrm{P})$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 289 | 0 | 0.000 | – | – | – | – | 1.869 | 1.882 | 1.893 | 1.913 |
| 1 | 228 | 0 | 0.000 | – | – | – | – | 2.026 | 1.943 | 1.846 | 1.873 |
| 2 | 2070 | 0 | 0.000 | – | – | – | – | 1.991 | 1.920 | 1.897 | 1.851 |
| 3 | 3192 | 0 | 0.000 | – | – | – | – | 2.083 | 1.966 | 1.953 | 1.733 |
| 4 | 4437 | 0 | 0.000 | – | – | – | – | 2.153 | 1.960 | 1.950 | 1.732 |
| 5 | 7288 | 0 | 0.000 | – | – | – | – | 2.068 | 1.990 | 2.005 | 1.660 |

(continued)

TABLE IV. cont.

| $i$ | $\vert ch_i \vert$ | $\vert ch_i^{\mathrm{m}} \vert$ | $ch_i^{\mathrm{ratio}}$ | $ch_i$(A) | $ch_i$(B) | $ch_i$(C) | $ch_i$(P) | $ch_i$(A) | $ch_i$(B) | $ch_i$(C) | $ch_i$(P) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 7680 | 96 | 0.013 | 2.750 | 1.875 | 2.125 | 1.542 | 2.016 | 2.042 | 2.055 | 1.567 |
| 7 | 6980 | 652 | 0.093 | 2.402 | 1.917 | 2.035 | 1.647 | 1.974 | 2.075 | 2.081 | 1.514 |
| 8 | 6822 | 2036 | 0.298 | 2.095 | 2.024 | 2.095 | 1.532 | 1.860 | 2.125 | 2.135 | 1.430 |
| 9 | 6456 | 4548 | 0.704 | 1.821 | 2.108 | 2.125 | 1.464 | 1.776 | 2.144 | 2.154 | 1.406 |
| 10 | 8492 | 7234 | 0.852 | 1.651 | 2.179 | 2.184 | 1.362 | 1.626 | 2.198 | 2.200 | 1.331 |
| 11 | 7840 | 7600 | 0.969 | 1.551 | 2.237 | 2.250 | 1.255 | 1.542 | 2.242 | 2.253 | 1.247 |
| 12 | 6375 | 6146 | 0.964 | 1.393 | 2.319 | 2.334 | 1.115 | 1.385 | 2.324 | 2.337 | 1.108 |
| 13 | 4020 | 4020 | 1.000 | 1.307 | 2.374 | 2.401 | 1.007 | 1.307 | 2.374 | 2.401 | 1.007 |
| 14 | 2638 | 2614 | 0.991 | 1.102 | 2.463 | 2.477 | 0.876 | 1.099 | 2.465 | 2.478 | 0.874 |
| 15 | 1276 | 1276 | 1.000 | 1.034 | 2.505 | 2.528 | 0.794 | 1.034 | 2.505 | 2.528 | 0.794 |
| 16 | 772 | 772 | 1.000 | 0.801 | 2.609 | 2.618 | 0.640 | 0.801 | 2.609 | 2.618 | 0.640 |
| 17 | 276 | 276 | 1.000 | 0.848 | 2.598 | 2.620 | 0.641 | 0.848 | 2.598 | 2.620 | 0.641 |
| 18 | 168 | 168 | 1.000 | 0.500 | 2.750 | 2.750 | 0.417 | 0.500 | 2.750 | 2.750 | 0.417 |
| 19 | 76 | 76 | 1.000 | 0.553 | 2.737 | 2.750 | 0.421 | 0.553 | 2.737 | 2.750 | 0.421 |
| 21 | 24 | 24 | 1.000 | 0.250 | 2.875 | 2.875 | 0.208 | 0.250 | 2.875 | 2.875 | 0.208 |
| 24 | 1 | 1 | 1.000 | 0.000 | 3.000 | 3.000 | 0.000 | 0.000 | 3.000 | 3.000 | 0.000 |

TABLE V. Results pertaining to Kekulé structures with the same number of $\pi$-electrons that belong to hexagons

| $n$ | $\vert pe_i \vert$ | $\vert pe_i^{\mathrm{m}} \vert$ | $pe_i^{\mathrm{ratio}}$ | $pe_i^{\mathrm{m}}$(A) | $pe_i^{\mathrm{m}}$(B) | $pe_i^{\mathrm{m}}$(C) | $pe_i^{\mathrm{m}}$(P) | $pe_i$(A) | $pe_i$(B) | $pe_i$(C) | $pe_i$(P) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 48 | 1089 | 8 | 0.007 | 1.500 | 2.000 | 1.750 | 2.000 | 2.121 | 1.869 | 1.778 | 2.000 |
| 49 | 2640 | 132 | 0.050 | 2.000 | 1.917 | 1.833 | 1.917 | 2.293 | 1.839 | 1.862 | 1.917 |
| 50 | 3384 | 306 | 0.090 | 2.412 | 1.853 | 1.912 | 1.833 | 2.284 | 1.898 | 1.888 | 1.833 |
| 51 | 5648 | 576 | 0.102 | 1.750 | 2.028 | 1.931 | 1.750 | 2.039 | 1.979 | 1.931 | 1.750 |
| 52 | 7101 | 1530 | 0.215 | 1.988 | 2.003 | 1.999 | 1.667 | 2.090 | 1.984 | 2.001 | 1.667 |
| 53 | 6828 | 1716 | 0.251 | 2.007 | 2.026 | 2.056 | 1.583 | 1.948 | 2.057 | 2.035 | 1.583 |
| 54 | 8422 | 3026 | 0.359 | 1.594 | 2.146 | 2.089 | 1.500 | 1.800 | 2.111 | 2.090 | 1.500 |
| 55 | 7644 | 3756 | 0.491 | 1.899 | 2.106 | 2.161 | 1.417 | 1.870 | 2.113 | 2.159 | 1.417 |
| 56 | 6828 | 3564 | 0.522 | 1.515 | 2.219 | 2.195 | 1.333 | 1.582 | 2.218 | 2.185 | 1.333 |
| 57 | 7104 | 4992 | 0.703 | 1.518 | 2.246 | 2.251 | 1.250 | 1.601 | 2.226 | 2.257 | 1.250 |
| 58 | 5088 | 3780 | 0.743 | 1.667 | 2.241 | 2.315 | 1.167 | 1.606 | 2.258 | 2.307 | 1.167 |
| 59 | 4632 | 3780 | 0.816 | 1.200 | 2.372 | 2.344 | 1.083 | 1.255 | 2.362 | 2.345 | 1.083 |
| 60 | 3848 | 3529 | 0.917 | 1.462 | 2.342 | 2.415 | 1.000 | 1.469 | 2.339 | 2.417 | 1.000 |
| 61 | 2244 | 2040 | 0.909 | 1.259 | 2.415 | 2.459 | 0.917 | 1.235 | 2.423 | 2.455 | 0.917 |
| 62 | 2130 | 2058 | 0.966 | 1.052 | 2.488 | 2.503 | 0.833 | 1.068 | 2.483 | 2.506 | 0.833 |
| 63 | 1168 | 1156 | 0.990 | 1.355 | 2.449 | 2.575 | 0.750 | 1.346 | 2.452 | 2.574 | 0.750 |
| 64 | 681 | 669 | 0.982 | 0.789 | 2.602 | 2.599 | 0.667 | 0.793 | 2.601 | 2.601 | 0.667 |
| 65 | 540 | 540 | 1.000 | 1.000 | 2.583 | 2.667 | 0.583 | 1.000 | 2.583 | 2.667 | 0.583 |
| 66 | 170 | 170 | 1.000 | 1.024 | 2.606 | 2.724 | 0.500 | 1.024 | 2.606 | 2.724 | 0.500 |
| 67 | 132 | 132 | 1.000 | 0.500 | 2.750 | 2.750 | 0.417 | 0.500 | 2.750 | 2.750 | 0.417 |
| 68 | 54 | 54 | 1.000 | 1.000 | 2.667 | 2.833 | 0.333 | 1.000 | 2.667 | 2.833 | 0.333 |
| 69 | 12 | 12 | 1.000 | 0.000 | 2.917 | 2.833 | 0.250 | 0.000 | 2.917 | 2.833 | 0.250 |
| 70 | 12 | 12 | 1.000 | 0.500 | 2.833 | 2.917 | 0.167 | 0.500 | 2.833 | 2.917 | 0.167 |
| 72 | 1 | 1 | 1.000 | 0.000 | 3.000 | 3.000 | 0.000 | 0.000 | 3.000 | 3.000 | 0.000 |

It can be seen (in Table II) that all Kekulé structures of $C_{72}$ have degrees of freedom from 5 to 12. The Kekulé structure with (maximal) degree of freedom 12 is presented in Figure 3. Kekulé structures with degrees of freedom equal to, respectively, 5, 6,…,11 are presented in the following figures:

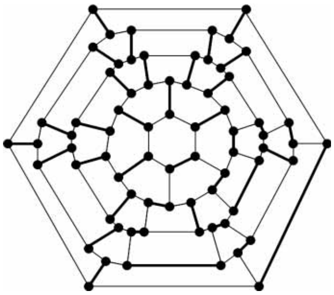

Figure 4. Kekulé structure with *df* = 5.

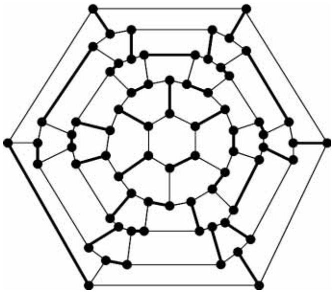

Figure 5. Kekulé structure with *df* = 6.

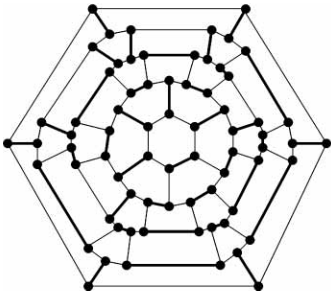

Figure 6. Kekulé structure with *df* = 7.

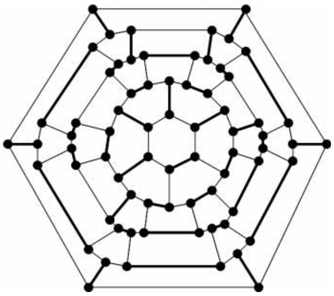

Figure 7. Kekulé structure with *df* = 8.

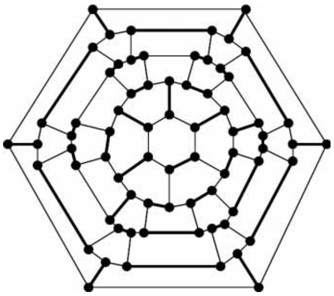

Figure 8. Kekulé structure with *df* = 9.

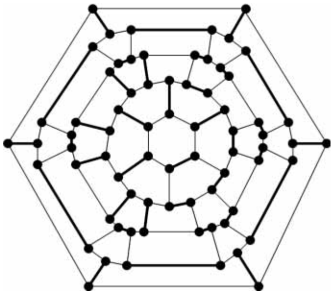

Figure 9. Kekulé structure with *df* = 10.

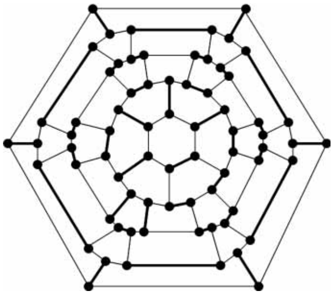

Figure 10. Kekulé structure with *df* = 11.

## DISCUSSION

First note that the values of $ic_i^{\text{ratio}}$, $df_i^{\text{ratio}}$ $ih_i^{\text{ratio}}$, $cf_i^{\text{ratio}}$, and $pe_i^{\text{ratio}}$ increase (with a few exceptions) with the increment of *i*. When *i* is small, these values tend to 0 and when *i* is large, these values tend to 1. This means that almost all Kekulé strucutures of low importance are outside MIC and almost all of those of high importance belong to MIC. This holds irrespective of the criterion used (maximal number of independent conjugated cycles, degree of freedom, maximal number of independent conjugated hexagons, number of conjugated hexagons, or number of π-electrons that belong to hexagons). Especially note that for the 7 highest values of *i* the values of the second and third rows of Tables IV and V coincide, *i.e.*, all structures with 7 highest values of numbers of conjugated hexagons and π-electron content belong to the most important component of the resonance graph. All this leads to the conclusion that MIC represents the most important component of the resonance graph of $C_{72}$. Hence, the study of Kekulé structures within the MIC is particularly relevant.

As the importance of the observed class of Kekulé structure grows, one should expect that the number of π-electrons that belong to each of the hexagons will increase and that number of π-electrons that belong to each of the pentagons will decrease. Similar results should be obtained also if we restrict ourselves to the main component.

Analyze first the pentagon P. Functions $ic_i$, $df_i$, $ih_i$, $cf_i^{\text{ratio}}$, $pe_i$, $df_i^{\text{m}}$ and $pe_i^{\text{m}}$ are decreasing. Functions $ic_i^{\text{m}}$, $ih_i^{\text{m}}$, and $ch_i^{\text{m}}$ are decreasing if we disregard one exception. Also, function $ch_i$ is decreasing if we disregard two exceptions. Hence, the π-electron content of pentagon P behaves according to intuition.

Analyze now hexagons of type B. Functions $ic_i$, $df_i$, $df_i^{\text{m}}$, $ic_i^{m}$, and $ih_i^{m}$ are increasing. Functions $ic_i$, $df_i$, and $ch_i^{m}$ are increasing if we disregard two exceptions. Functions $ep_i$ and $ep_i^{m}$ show, in general, increasing tendencies, but with several exceptions. Again, we see that the π-electron contents of hexagons B behave according to intuition.

Next, we analyze the hexagon of type C. Functions $ic_i$, $df_i$, $pe_i$, $df_i^{\text{m}}$, and $pe_i^{\text{m}}$ are increasing, $ih_i$, $ic_i^{\text{m}}$, $ih_i^{\text{m}}$, and $ch_i^{\text{m}}$ are increasing if we disregard one exception, whereas $ch_i$ is increasing if we disregard two exceptions. Hence, again, the π-electron contents of hexagons C behave according to intuition.

It remains to analyze the hexagons of type A. Functions $ic_i^{\text{m}}$, $df_i^{\text{m}}$, and $ih_i^{\text{m}}$ are strictly decreasing, $df_i$ is decreasing if we disregard one exception whereas $ch_i^{\text{m}}$ is decreasing if we disregard two exceptions. All other functions show, in general, a decreasing tendency, but with several exceptions. We can see that the behavior of the π-electron content of a type A hexagon is contra-intuitive. It behaves in a »pentagon-like« manner. As Kekulé structures become more and more important, this hexagon has fewer and fewer π-electrons. Returning to the 7-tuple:

$$(h_0, h_1, h_2, h_3, h_4, h_5, h_6) = (0,0,0,12,12,0,2),$$

one again concludes that the presence of hexagons of type A is the cause of the instability of $C_{72}$. However, we have shown that the instability is not solely a result of steric strain, but also features related to the (topology-dependent) distribution of π-electrons in Kekulé structures may significantly contribute to it.

The method put forward and applied in the present work may also provide a new insight into the properties of other fullerenes, and help forecast their stability.

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## SAŽETAK

### O nestabilnosti fulerena $C_{72}$

**Damir Vukičević, Ivan Gutman i Milan Randić**

Najvažniji fuleren je Buckminster fuleren $C_{60}$. Ovaj fuleren je dobiven *leap-frog* transformacijom fulerena $C_{20}$. Sljedeći najmanji fuleren koji se može dobiti *leap-frog* transformacijom je $C_{72}$ (dobiven iz $C_{24}$). Iznenađujuće je da je ovaj fuleren nestabilan. Standardno objašnjenje njegove nestabilnosti je njegov nepovoljan

prostorni raspored uzrokovan dvama heksagonima koji su okruženi sa po 6 heksagona. Analizirajući π-elektronski sadržaj ovih heksagona pokazano je da je ponašanje ovih heksagona sličnije ponašanju pentagona nego ponašanju heksagona, što također može biti uzrokom (ili dodatnim uzrokom) nestabilnosti fulerena $C_{72}$. Dakle, u ovom radu se ukazuje i na postojanje topoloških razloga (koji nemaju veze s prostornim rasporedom) za nestabilnost ovog fulerena.