Planar rearrangements of fullerenes

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A notion of planar rearrangement of fullerenes is proposed as a general framework for all conceivable rearrangements of fullerenes satisfying a minimum physicochemical condition. The planar rearrangement is defined as an edge relocation such that the planarity of a given Schlegel diagram remains undisturbed. Graph-theoretical properties of planar rearrangements are discussed and characteristics for establishing a hierarchy between them are pointed out. A number of graph-theoretical concepts have been introduced to provide means for classification and systematic generation of fullerene rearrangements. The simplest nontrivial rearrangements is shown to be the Stone–Wales rearrangement. © 2001 by Elsevier Science Inc.

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INTRODUCTION

A number of authors have studied rearrangements of fullerenes from various points of view. The first article to consider the possibility of rearranging one fullerene isomer to another was the famous study by Stone and Wales,[1] after which the simplest rearrangement became known as the Stone–Wales rearrangement. Several subsequent articles from various researchers examined energetic and mechanistic aspects of this hypothetical process.[2–7] Although different mechanisms were studied, all the results indicate that a high-energetic barrier is involved in this process.[2–4,6] Nevertheless, the high temperatures involved in the methods of preparation of fullerenes that are known so far could allow even such unfavorable transformations to occur. An auxiliary mechanism, including additional carbon atoms, was proposed as an autocatalytic pathway with a remarkably lower barrier.[6] Although it seems certain that carbon cages or their fragments rearrange during their growth, experimental evidence is still lacking.[7]

In the meantime, rearrangements have also been studied from a purely combinatorial point of view. Isomers of a given size were partitioned into equivalence classes according to their interconversions by the Stone–Wales rearrangement[8–9] as well as by its generalization.[5,10–12] Some more involved rearrangement mechanisms have been also proposed.[13–17]

In principle, one could devise a large number of different rearrangement schemes. A simple but extreme example is given by an arbitrary one-to-one mapping of atoms of one fullerene isomer to atoms of another, and subsequent replacement of all bonds, not preserved by the mapping, by those from the second isomer. Such a transformation could be interpreted as a rearrangement, but if the mapping was chosen randomly, the corresponding bond reorganization would not seem likely to occur.

The Stone–Wales (S–W) rearrangement is the simplest proposed mechanism. Many others between those two extreme cases could be imagined, yet no systematic attempt to produce all meaningful schemes has been reported so far. This article proposes a framework that unifies all considered rearrangement types and provides concepts that might be useful in a systematic generation and classification of all possible rearrangements. Although we are concerned mainly with combinatorial properties, we also take into account common chemical knowledge, especially when classification criteria are introduced. Nevertheless, the emphasis is on the graph-theoretical framework and its topological characteristics.

Throughout the article we will use graph-theoretical terminology and relations. The structural formulas of fullerenes will be represented by graphs with atoms being symbolized by vertices and chemical bonds by edges. The following discussion relies on planar diagrams of fullerene graphs that are obtained by drawing a graph in the plane so that no two edges cross. Planar diagrams are also called Schlegel diagrams or planar embeddings. For detailed exposition of graph-theoretical terminology used in chemistry, see a book by Trinajstic.[18]

CLASSIFICATION OF FULLERENE REARRANGEMENTS

The fullerene rearrangement is a bond relocation that transforms one fullerene isomer to another. This implies that the numbers of atoms and bonds, as well as atom valencies, remain unchanged during the transformation. Since all atoms in a fullerene are chemically equal, there is a large number of different rearrangements relating any given pair of fullerene structures. Our discussion is focused on a subset called planar rearrangements.

Definition: Let S be a Schlegel diagram of the fullerene A. A rearrangement of A to another fullerene, B, possibly equal, is *planar* if the structure of B can be realized by replacing the

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edges from S with the new ones so that the final diagram is planar again.

Real fullerene geometries are not planar, but nevertheless they are always embedded in an ellipsoidal shell of a small thickness compared with its diameters. Thus, fullerene structures can be imagined as confined to a thin sheet. The above definition reflects an intuitive feeling that the rearrangements that can be realized by moving and reconnecting atoms in such a thin sheet are energetically less demanding than those that require full separation of rearranging fragments and their movement out of the shell. Nevertheless, planar rearrangements still allow large bond reorganizations that certainly do not seem feasible, at least not if they are performed in a single step. On the other hand, some nonplanar rearrangements already mentioned in the literature[14–15] might be less demanding than some large planar rearrangements. So the distinction introduced by planar rearrangements serves mainly for topological classification and only partially reflects their physicochemical nature. Examples of planar rearrangements are shown in the figures throughout the text.

To be valid, the above definition must be independent of the chosen Schlegel diagram. Indeed, this condition is fulfilled since a 2D-spherical embedding of a three-connected trivalent planar graph is known to be unique.[19] The planar map is obtained by choosing a ring that become a planar boundary within which inside the rest of the structure will be mapped. The definition might have been equivalently based on the unique 2D-spherical embedding, but Schlegel diagrams are easier to manipulate.

The notion of planar rearrangement introduces a relation between fullerene isomers of the same size. This is an equivalence relation since it is reflexive, symmetric, and transitive. Its reflexivity and symmetry are trivial to check, and the transitivity follows from simple reasoning. Let A, B and C denote three fullerene structures and suppose that A and B, as well as B and C can be rearranged pairwise in a planar manner. The rearrangements $B \rightarrow A$ and $B \rightarrow C$ can be done in the common planar map of B. Then, according to the definition, A and C have planar maps with equal vertex positions. Therefore, the transformation between A and C can be performed directly, without mediating by the structure B, so $A \rightarrow B$ and $B \rightarrow C$ imply $A \rightarrow C$.

Here arises an interesting but still open question: do all fullerene isomers of a given size belong to a single equivalence class induced by the planar rearrangement relation? The answer seems to be affirmative, but it does not look easy to prove. Another interesting question concerns the algorithm for finding the simplest planar rearrangement that interconverts any two given fullerene isomers.

For the purpose of the further discussion we define several notions specific to planar rearrangements. The edges to be removed and those to be formed will be called breaking edges and forming edges, respectively. All other edges will be referred to as intact. A superposition diagram (or simply a superposition) is a planar map of the initial fullerene isomer including both the breaking and forming edges. The initial and final diagrams are planar by definition, but their superposition does not have to be so. Rearrangements with planar superposition will be called continously planar rearrangements since they can be imagined as a continous process in which the breaking edges are gradually removed while the forming edges are gradually built up, with planarity retained in every moment.

The subgraph of the superposition diagram containing only breaking and forming edges and the incident vertices will be called a rearrangement subgraph. Due to the preservation of the vertex degrees, each vertex in the rearrangement subgraph is incident to an even number of edges, half of which are breaking edges and half of which are forming edges. Therefore, all vertices are arranged into cycles of alternating breaking and forming edges, here called rearrangement cycles. There can be more than one cycle and some cycles may have a common vertex but never a common edge. Rearrangement subgraphs and cycles are illustrated by the examples in Figures 1–6.

Rearrangement cycles enable us to establish a formal pairing of breaking and forming edges so that each breaking edge is paired with one of the incident forming edges. In isolated cycles such a pairing can be done in only two ways that correspond to two possible cyclic orientations. Although such a pairing could be interpreted as a specific conversion of breaking into the forming edges they are paired with, no such view is implied here and the mapping has only a purely formal meaning.

In continously planar rearrangements (those with a planar superposition diagram) each forming edge connects two vertices belonging to the same ring of the initial graph. Otherwise, it would be crossing some other edge and lead to a nonplanar—either final or superposition—diagram. If both the breaking and forming edges of a given pair connect vertices of the same ring, we say that the breaking edge is rotated into the forming edge and that they form a rotating pair. Indeed, with such a pair, the relocation of the breaking edge can be imagined as its rotation into the corresponding forming edge around their common vertex so that no other edge is crossed. Such a rotation may be oriented clockwise or counterclockwise. Figure 1 shows an example with only rotating pairs of breaking and forming edges, and the example in Figure 2 includes pairs that do not conform to the rotating relation.

Planar rearrangements provide a sufficient freedom to realize transformations of rather different complexity. The following four criteria are proposed to classify them:

1. Planarity of a superposition diagram
2. Disjoint rearrangement cycles
3. Rotating relation in all pairs of breaking and forming edges
4. Uniform orientation of the rotations affecting the same ring.

The above criteria are hierarchically ordered and those that satisfy a given condition are considered to be simpler than others. The planarity of the superposition diagram is chosen as the most important since nonplanar superpositions prevent valid definition of some other notions that appear helpful in analysis and generation of rearrangements (later defined as rearrangement skeletons). Two examples of nonplanar superpostions are taken from the literature[13–14] and shown in Figure 3 and Figure 4. Note that the second rearrangement may be interpreted in two ways, one of which has a planar superposition. It remains an open question if every rearrangement with a nonplanar superposition can be realized in a continously planar way. The answer does not appear to be affirmative, but remains to be proven.

The second criterion separates cases where more than one pair of breaking and forming edges are incident at the same vertex. This leads to an ambiguity in the definition of the rearrangement cycles, which otherwise enable unique partition
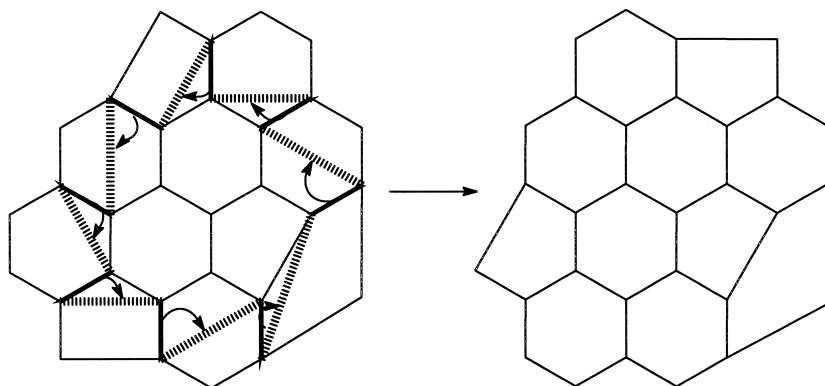
Figure 1. A rearrangement example taken from Astakhova and Vinogradov.[13] The superposition diagram is shown on the left, with the breaking and forming edges represented by the bold and dashed lines, respectively. The rearrangement subgraph contains a single rearrangement cycle. The arrows relate pairs of breaking and forming edges.
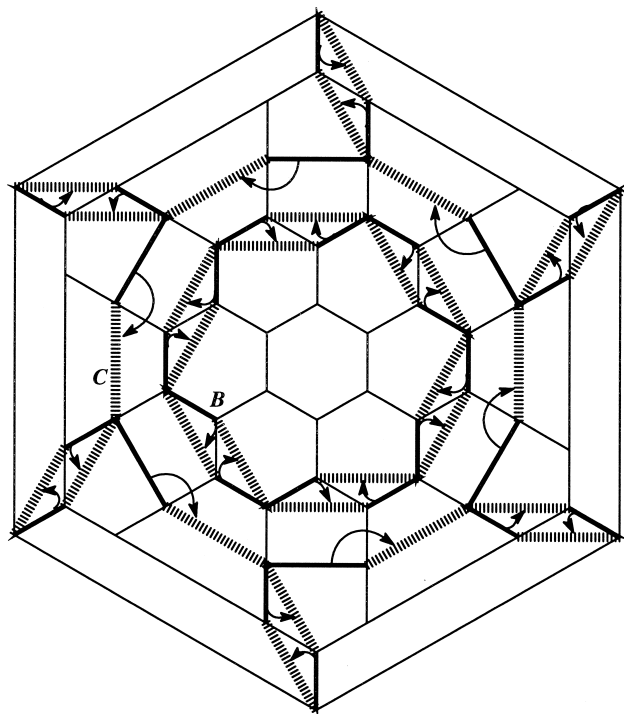

Figure 2. An example of the rearrangement with nonrotating pairs of breaking and forming edges. These are in the middle rearrangement cycle, C, which is joined with six S–W rearrangements. Note that these six S–W rearrangements could be replaced by the rearrangement as in the innermost part, B, of the diagram.

rings are affected; one is increased in size and another is equally decreased. With nonrotating pairs, more rings are affected, as two of them are joined into one and another is split into two new rings; see example in Figure 2. That is why such cases appear more complicated.

The last condition on uniform orientation of the rotations affecting the same ring in the initial diagram also makes it easier to control changes of ring sizes. When this condition is met, the affected rings form a chain(s) in which every member increases in size at the cost of the next ring. An example with nonuniform orientation of the rearrangement cycle is given in Figure 6.

All rearrangements falling into the same complexity class can be further ordered in respect to e.g., the changes in ring sizes induced by rotations, or—more universally—the number of breaking bonds.

SIMPLE PLANAR REARRANGEMENTS

The rearrangements that fulfill all four discussed criteria and an additional one-that rotations change ring sizes only by one, we will call simple planar rearrangements as they are easy to characterize in detail.

Let us consider possibilities in generating simple planar rearrangements. After choosing the first pair of breaking edges and the corresponding forming edge there are three possibilites shown in Figure 7. In the first of them the next rotating pair closes the rearrangement cycle with the previous pair and the requirement for disjoint rearrangement cycles prevents inclusion of any other edges into the rearrangement cycle. This corresponds to the Stone–Wales rearrangement.

Otherwise, the next pair may be chosen in two ways, also shown in Figure 7, and this continues until the rearrangement cycle is closed. With each rotating pair one may associate the intact edge that connects the two nonidentical vertices of the breaking and forming edge. The intact edges associated with adjacent rotating pairs are incident and they form a path that also must be closed into a cycle. The cycle containing intact edges associated with all rotating pairs in the rearrangement cycle is called a rearrangement skeleton. It represents the part of the structure around which the rearrangement happens; for illustration see Figure 8. The rearrangement skeleton is in a unique correspondence with all the breaking edges. If only the rearrangement skeleton is specified, it is clear that the breaking edges must be all those that are incident to the rearrangement skeleton. There remains an ambiguity in deducing the positions
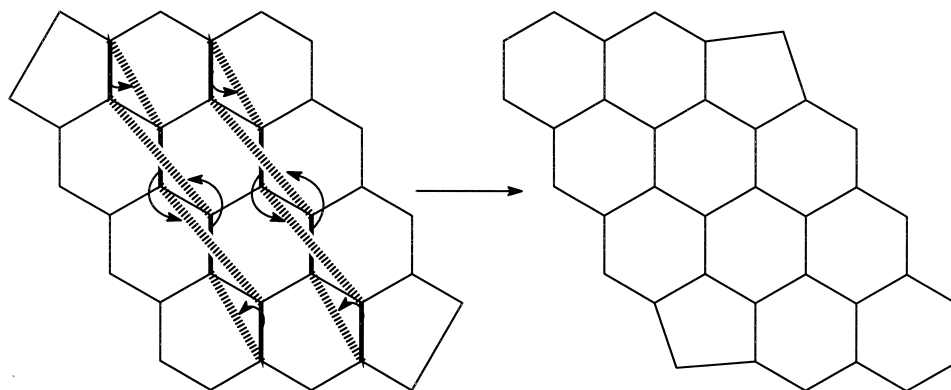
of the rearrangement into separate, less dependent, parts. From the chemical point of view, the atoms where the cycles join undergo large local electronic disturbance, which is an additional reason for considering them to be more complex and chemically demanding. An example of probably the simpliest rearrangement with joined cycles is taken from Chiu et al.[16] and shown in Figure 5.

Generation of new rearrangements requires attention to two conditions: (i) the alternating breaking and forming edges must close into cycle(s); and (ii) the perturbed rings must be again only five- or six-membered. When the breaking and forming edges are paired into rotating pairs, ring perturbations are easier to control and follow since, with each rotation, only two

Figure 3. An example of a non-planar superposition diagram, taken from Astakhova and Vinogradov.[13]
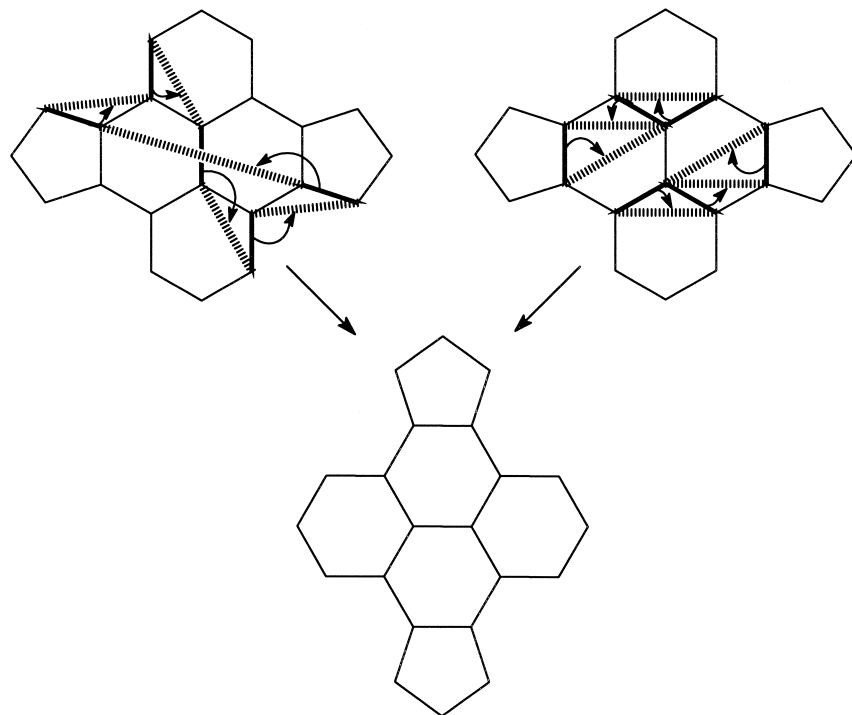

Figure 4. A rearrangement example taken from Astakhova and Vinogradov.[14] The final diagram is given in the bottom part. Note that the same diagram can be produced with a nonplanar and planar superposition diagram, shown in the top row.
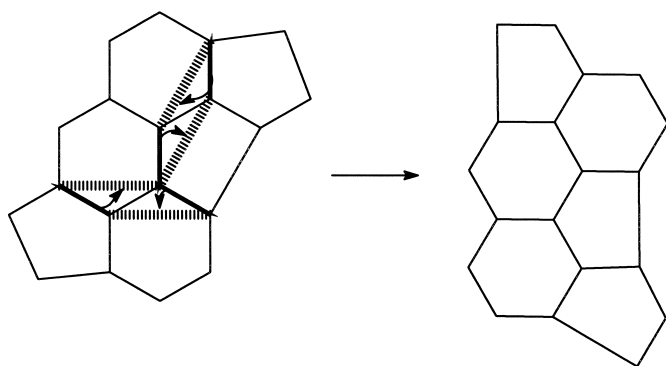

Figure 5. The smallest example with joined rearrangement cycles, taken from Chiu et al.[16]

of the forming edges, but there are only two possible choices: a given breaking edge is incident to two edges of the rearrangement skeleton; by choosing one of them as associated to the considered breaking edge, the position of the forming edge is immediately determined. Once the choice is made for one breaking edge, it is automatically fixed for all others. This ambiguity may be resolved by assigning an orientation to the rearrangement skeleton so that its edges go from breaking to forming edges in the assigned direction. In this way the simple planar rearrangements may be uniquely reduced to the oriented
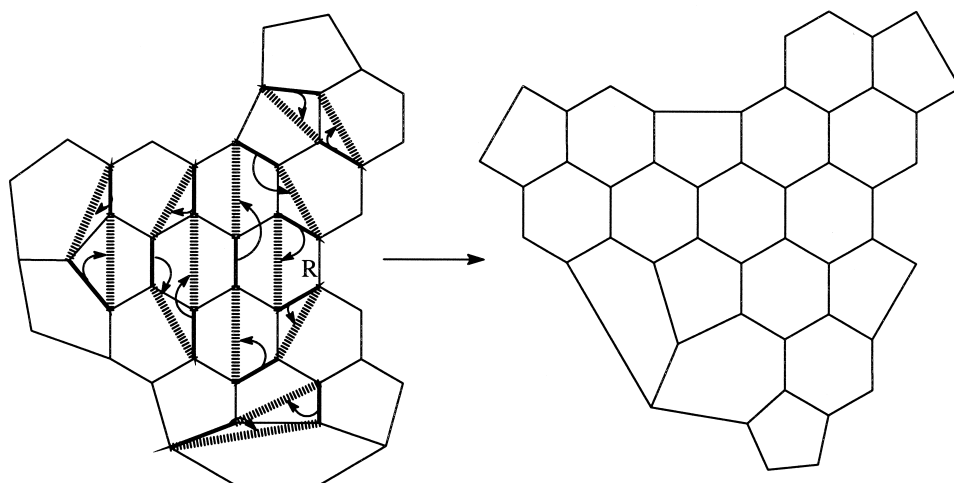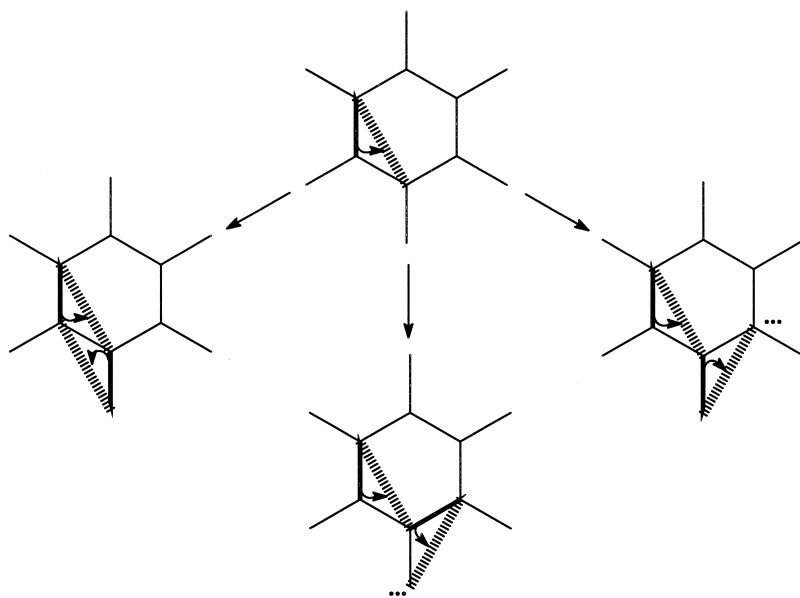
Figure 6. A rearrangement example with oppositely oriented rotations in the ring R.

Figure 7. The three possible ways to continue the initial pair of the breaking and forming edges under the restriction that each one changes ring size by only one. The leftmost case is the Stone–Wales rearrangement, and the other two lead to trivial rearrangement.

rearrangement skeletons. However, it turns out that except for the Stone–Wales rearrangements, the simple planar rearrangements are trivial as they do not induce any change in the fullerene structure.

Theorem

The rearrangements represented by the cyclic rearrangement skeletons do not induce any change in the fullerene graph.

Proof

The skeleton of the Stone–Wales rearrangement is a single edge and the theorem does not refer to it. The rings affected by the rearrangement are those having vertices in common with the skeleton. Due to the cyclic character of the skeleton, S, the affected ring, R, shares with the skeleton not only a vertex but a continous sequence of edges, P. The edges of R incident to two ending vertices of P are the only breaking edges that affect the size of R, since no other edge of R may be incident to P and
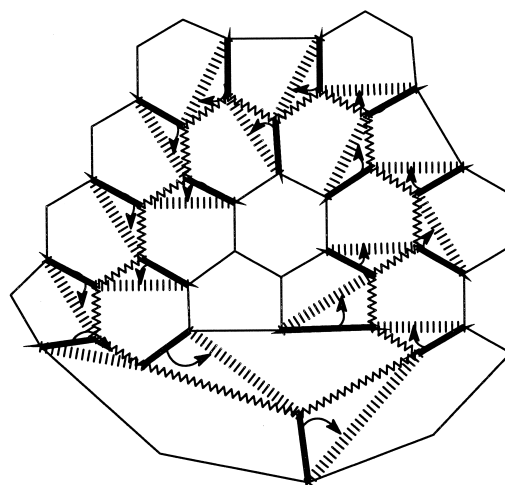

Figure 8. A superposition diagram of a simple planar rearrangement. The rearrangement skeleton is drawn by wavy lines.

every edge incident to S is a breaking edge. These two breaking edges rotate with the same orientation, one of them reducing the size of R and the other increasing. Since the induced change is the same for all pairs of breaking and forming edges, the two rotations cancel each other and the resultant change is zero. Note that S cannot have more than one P in common with R, since no two breaking edges may be incident to each other (the condition of disjoint rearrangement cycles). However, even if this condition was released, the above arguments would apply as well.

Nevertheless, if the carbon atoms were isotopically labelled, or if we had a heterofullerene, the initial and final isomer might be distinguishable. In that case the simple planar rearrangements, which differ from the Stone–Wales rearrangements, might have a real meaning, too.

CONCLUSIONS

Several graph-theoretical notions for characterization of all conceivable rearrangements have been introduced. A distinct class of planar rearrangements has been defined and the topological criteria for their classification have been proposed. The simple planar rearrangements were defined and shown to include only the Stone–Wales type as a nontrivial rearrangement. All other simple rearrangements were shown to induce no change in the fullerene structure with identical vertices/atoms.

So far, the field of fullerene rearrangements has been studied only occasionally. It seems that this is a rather complex area, rich in topological structures and still unexplored. We hope that the present report defines a useful conceptual frame and provides a stimulus for further study.

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