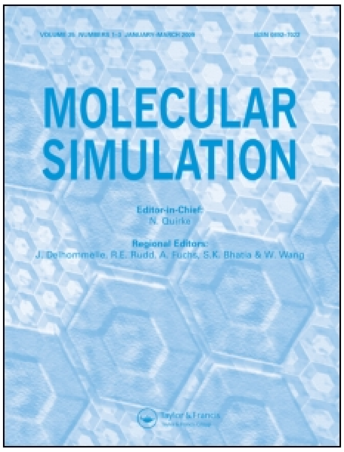

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Generalized Stone-Wales Transformations

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GENERALIZED STONE-WALES TRANSFORMATIONS[1]

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We introduce a large class of transformations allowing rearrangements of the fullerene surface. We call this set of rearrangements generalized Stone-Wales transformations (gSW) because the well-known Stone-Wales (or pyracylene) flip may be seen as the simplest representative of the novel gSW family. The interconversion between the two C_{28} fullerene isomers is presented as a simple example of gSW application. Further examples involving the *complete* generation of C_{60} and C_{70} isomer spaces are provided. In both cases, just *one* fullerene molecule is used as seed data. Some considerations on gSW energetics are also reported.

KEY WORDS: Generalised Stone-Wales transformations, fullerenes.

1. INTRODUCTION

In a theoretical paper [1] on C_{60} fullerene, Stone and Wales introduced their celebrated transformation that, by starting from the Buckminsterfullerene structure and moving two carbon atoms, is able to generate many alternative C_{60} isomers. This finding was further exploited by other authors [2, 3] aiming to generate C_{60} isomers with a lower structural symmetry. Figure 1 reproduces the reversible action of the Stone-Wales (SW) or pyracylene [4] rearrangement. Two pentagons and two hexagons are twisted around the central bond (often called the SW bond) producing a rotated configuration without changing the external connectivity. SW flips thus do not modify the topological fullerene constraints (a fullerene has n three-valent carbon atoms forming a network composed of 12 5-sided rings and $(n/2 - 10)$ 6-sided rings without

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[1] Preliminary results concerning this topic were presented at the meeting on NEW PERSEPCTIVES IN FULLERENE CHEMISTRY AND PHYSICS, Rome, October 10–12, 1994.

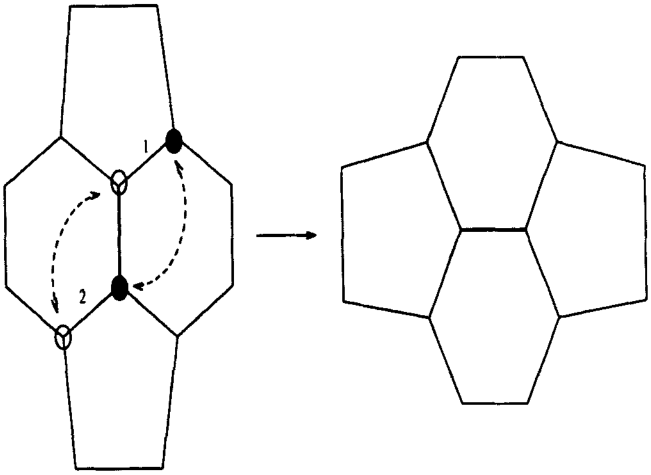

Figure 1 The Stone-Wales (SW) or pyracylene rearrangement. The four involved fullerene faces (2 pentagons and 2 hexagons) are shown. The primitive SW flip breaks the two labeled sigma bonds and forms new bonds between arrowed carbon atoms [1].

double bonds among carbon atoms) applicable to generic C_n molecules possessing SW bonds.

Due to its wide applicability, the SW transformation was considered in a large number of articles investigating structural and energetical properties of fullerenes. In a recent paper [4] reporting on the experimental isolation of C_{2v}- and D_3-type C_{78} fullerenes, Diederich and coworkers suggested that isomers with isolated pentagons often undergo SW interconversion during the fullerene growth process. This hypothesis has a strong practical implication: during the synthesis of a C_n fullerene, several isomers may be experimentally detected, with one molecule coming from each set of isolated-pentagon isomers interconnected via SW flips. This simple rule led immediately to the theoretical conclusion that both C_{82} and LaC_{82} should have a single predominant isomer [5].

Energetic aspects of the SW transformation were examined in detail by using Hückel model [6], semi-empirical and *ab initio* methods [14], and by local density theory coupled with the Car-Parinello method [15]. All the physical calculations indicate that the energy barrier involved in the SW transformation is so high that the conversion under the usually applied conditions does not seem probable. However, the authors agree that conditions under which fullerenes may be synthesized are sufficiently robust that SW transformation could still be possible. One should also take into account that the production conditions involve a number of yet unknown pre-fullerene species which might be more susceptible to SW conversion. On the other side one may speculate about some catalyst which would promote the transformation, or about chemical derivatives in which the transition state would be stabilized. As yet the SW transformation remains the only proposed mechanism for interconversion of fullerenes of the same size.

Diederich's hypothesis induced several researches to undertake the complete exploration of the SW-trajectories connecting isomers of a large number of fullerenes. This result was achieved firstly by Fowler and coworkers [6] who produced elegant isomerization maps, using SW bridges, for the complete set of isomers in the case of small fullerenes C_{24} to C_{40} and for the sole isolated-pentagon isomers within the range from C_{78} to C_{88}. In reference [7] the authors propose a classification according to SW interconvertibility of C_n isomers for $n \leq 70$. Analogous research [8,9,10] also pointed out that SW flips may accelerate the computerized exhaustive generation of fullerene isomers, usually done following Manolopoulos' string model [11]. The algorithmic synergy between SW transformation and strings shorthand is based on a simple reasoning: for each given C_n fullerene, once a valid string is (randomly) built, instead of immediately searching for a new one, one may generate directly a certain number of new isomers using SW flips. The good results, in terms of computational speed, one gets following this approach lead to a more general and intriguing question: Is it possible to find out a complete set of moves on the fullerene surface that, starting from a *single* C_n isomer, generate *all* its isomers?

This paper provides a partial answer to the above question, by introducing a novel class of reversible rearrangements, the generalized Stone-Wales transformations (in this paper also simply denoted as gSW), which extend the applicability of the simple SW flip. This result sheds additional light on the topological functioning of the SW transformation itself, and we also show how gSW transformations are the first set of moves proven to generate, in non-trivial cases, the complete set of isomers belonging to a given fullerene class, C_n.

2. TOPOLOGICAL NATURE OF gSW TRANSFORMATION

An effective manner, adopted herein, for representing the molecular topological structure is reached by drawing a C_n fullerene graph in its reciprocal space, where $(n/2+2)$ graph nodes represent fullerene faces and $3n/2$ bonds between them correspond to adjacent faces. Dual structures are easily brought back to the usual ones, made from carbon atoms, by applying the same operation.

Dual diagrams given in Figure 2 show how gSW transformations work. The key element for the existence of a gSW-transformable set of faces is the presence of a SW subunit enlarged by inserting an even number k of other faces (the shaded ones in Figure 2), with $k = 0, 2, 4 \ldots$. These faces have exactly four bonds in common with the others and actively participate in gSW transformation, by allowing modification of their connectivity. We can see that, after the gSW application, the positions of the four SW faces (black and white ones in Figure 2) get reversed, as in the simple SW move in Figure 2B, whereas the position of the shaded faces remains unchanged. By varying k, we generate a potentially infinite class of reversible rearrangements, which will be classified in term of k itself. As gSW *order* ω we define the number of chemical bonds connecting the hexagons belonging to the SW subunit (see dotted lines in Figure 2A). Thus gSW elements will be labeled by $k-1$, under the assumption that the order of a rearrangement is the smallest one admitted by a given gSW-transformable set of faces.

Our studies point out that the gSW has enough power to generate the *complete* isomer space, starting from a *single* known fullerene, for such complex cases as C_{60} and C_{70}. For a large set of fullerenes ($n \leq 70$) we performed in fact a computerized analysis

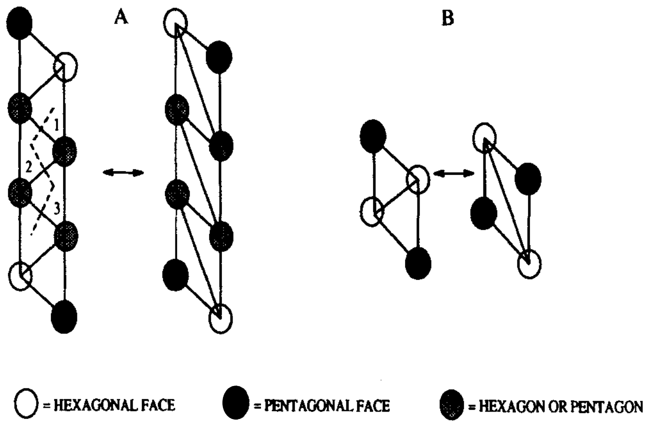

Figure 2 A: The generalized Stone-Wales rearrangement. The shown gSW-transformable set of faces involves eight of them: it contains the *necessary* SW subgroup (black and white faces) embracing four shaded faces. On the rearranged configuration, shown on the right, the two SW pentagons are in the positions previously occupied by SW hexagons. The number of dotted chemical bonds one has to traverse to join the two SW hexagon gives the order ω of the transformation. This one has order three, and we will call it gSW_3. B: The Stone-Wales rearrangement may be seen as a gSW of zeroth order gSW_0.

in order to examine the separation of isomers into equivalence classes when only the gSW transformations of order less than or equal to some limit were considered. Table 1 reports on C_{28}, C_{60} and C_{70} examples. The maximal order of gSW is denoted in the uppermmost row. For each class of gSW move, the resulting distribution is characterized by two numbers: the first is the number of classes into which isomers with at least one gSW pattern of a considered type are distributed, and the second number denotes the number of isomers with no gSW pattern of the considered type.

Table 1 starts from a primitive SW application ($\omega_{MAX} = 0$). In this case we see that one C_{28} isomers does not admit gSW rearrangement, while the same is true for 31 of the C_{60} isomers and 92 of the C_{70} isomers. By increasing the gSW order, we are able to connect the C_{28} isomers (for details see next paragraph), whereas both C_{60} and C_{70} isomer spåces present two large distinct sets of gSW-transformable molecules and, for both cases, six isomers without gSW_ω patterns, with $\omega = 0, 1$. With $\omega_{MAX} = 3$, the

Table 1 Examples of gSW Applications to C_n fullerenes with $n = 28, 60, 70$. By using gSW_w transformations up to a given maximal order ω_{MAX}, it allows one to split the set of isomers according to the reported pairs (a, b), where: a is the number of isomer subsets admitting gSW_ω rearrangements; b is the number of isomers which do not admit any of those gSW_ω patterns.

n	*Maximal order of gSW transformation*				
	0	1	3	5	7
28	(1, 1)	(1, 0)			
60	(13, 31)	(2, 6)	(1, 1)	(1, 0)	
70	(77, 92)	(2, 6)	(1, 2)	(1, 1)	(1, 0)

gSW-transformable isomers almost completely span the two spaces, with just 1 C_{60} and 2 C_{70} not included. Isomer generation comes to completion when $\omega_{MAX} = 5$ for C_{60} ($\omega = 0, 1, 3, 5, 7$ for C_{70}).

This result represents a relevant theoretical finding for exhaustive isomer search not previously reported in literature.

From physical point of view gSW transformations are even less favored than the simple SW, as already indicated in [16]. The gSW can be regarded as a set of simple transformations occurring simultaneously. Evidently, the corresponding energetic barrier could amount to a multiple of that estimated for simple SW. Nevertheless, in the recent article [17] Chernoztonskii suggested a transformation of the Buckminsterfullerene into the structure he named as barrelene. It is one of D_{6h} isomers of C_{60} which may be visualized by drawing a hexagon and surrounding it first with a belt of 6 pentagons, then by three belts of 6 hexagons, and finally again with a belt of 6 pentagons. Chernozatonskii proposes the transformation into barrelene as the only way to explain observation of rectangular close-packed layer structure of ellipsoid molecules obtained under rapid compression of Langmuir-Blodget film of Buckminsterfullerene molecules [18]. The implied transformation may be achieved by 12 primitive SW transformations which occur simultaneously (or one gSW). The validation of the barralene structure will be a strong indication of the feasibility of the gSW transformation.

We end this section, by noticing that generating isomers by mean of gSW can be a time consuming process. Computational techniques have been devised for *fast* gSW application and are reported elsewhere [2].

3. AN APPLICATION: THE C_{28} FULLERENE

We conclude this work by reporting on the topological move allowing a direct interconversion between C_{28} isomers. This fullerene can have two forms [7,11], presenting respectively a D_2 and a T_d symmetry. Their dual representations are given in Figure 3, where the numbered faces isolate the surface portion affected by the gSW transformation. One can see that a gSW_1, the simplest among gSW after the trivial pyracylene flip gSW_0, is able to bridge between the C_{28} isomers, and Figure 4 gives the detail of such a move.

4. CONCLUSIONS

We introduced a new class of fullerene reversible transformations called the generalized Stone-Wales transformations or gSW. They augment the applicability of the primitive Stone-Wales (SW) flip, which represents the simplest gSW element. Using a given C_n isomer as a seed, this series of moves has the capability to build complete set of isomers for large fullerene (testing up to C_{70} revealed a single isomer which cannot be obtained in this way) by simply finding topological bridges among them. Further extension of the gSW class is also possible. An upcoming paper will report on those findings [13].

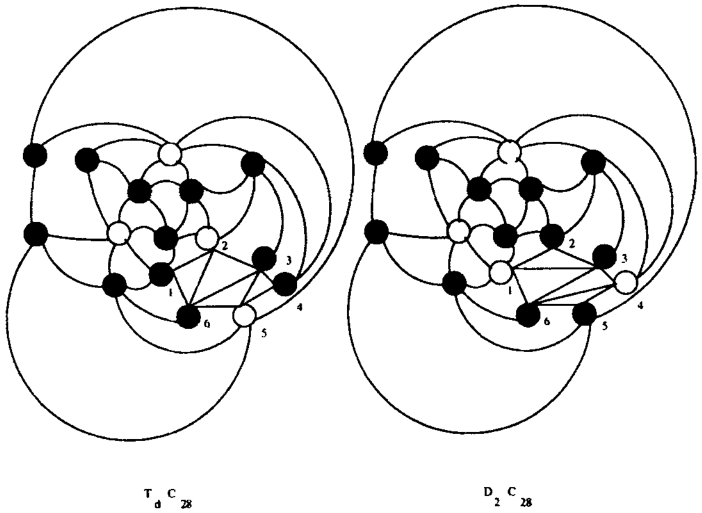

Figure 3 Black (white) balls represent pentagons (hexagons). The dual topological structures of the two C_{28} fullerene isomers are shown. D_2 C_{28} self-racemises when SW rearranged [6]. A reversible gSW$_1$ move, consistently applied at the labeled faces, is the simplest topological transformation interconnecting them.

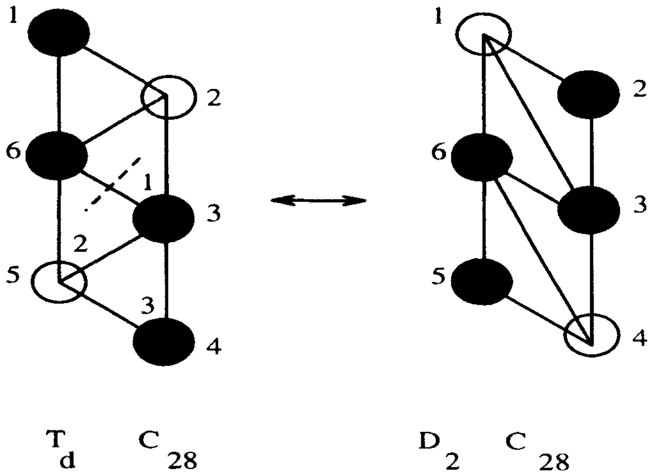

Figure 4 Black (white) balls represent pentagons (hexagons). gSW$_1$ interconverting the two C_{28} fullerene isomers is given. The reported rearrangement does not change molecular topology outside the represented region of the fullerene surface.

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