

Article

Skeletal Rearrangements of the C₂₄₀ Fullerene: Efficient Topological Descriptors for Monitoring Stone–Wales Transformations

Denis Sh. Sabirov ^{1,*}  and Ottorino Ori ²¹ Laboratory of Mathematical Chemistry, Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russia² Actinium Chemical Research Institute, 00182 Rome, Italy; ottorino.ori@alice.it* Correspondence: diozno@mail.ru

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Abstract: Stone–Wales rearrangements of the fullerene surface are an uncharted field in theoretical chemistry. Here, we study them on the example of the giant icosahedral fullerene C₂₄₀ to demonstrate the complex chemical mechanisms emerging on its carbon skeleton. The Stone–Wales transformations of C₂₄₀ can produce the defected isomers containing heptagons, extra pentagons and other unordinary rings. Their formations have been described in terms of (i) quantum-chemically calculated energetic, molecular, and geometric parameters; and (ii) topological indices. We have found the correlations between the quantities from the two sets that point out the role of long-range topological defects in governing the formation and the chemical reactivity of fullerene molecules.

Keywords: fullerene C₂₄₀; Stone–Wales generalized transformation; sphericity; roundness

1. Introduction

Most chemical studies on fullerenes are focused on the reactions and compounds of C₆₀ and C₇₀, the two most abundant fullerenes. Nevertheless, the diversity of the sizes and shapes within the fullerenes' family is much wider. Indeed, there are many fullerene structures, smaller [1] and larger [2], which are produced in smaller amounts. The chemistry of such small and large fullerenes has growing experimental and theoretical interests.

We pay attention to the giant C₂₄₀ fullerene with icosahedral symmetry. Its structure is the next after C₆₀ in the series of icosahedral Goldberg polyhedra [3–5] having $60a^2$ vertices (where a is the integer). In the fundamental aspect, such chemical structures are very close to their mathematical models, so direct bridges between the chemistry and mathematics could be built, which means the possible correlations between the structural and topological (mathematical) indices and molecular (chemical) properties of the molecules [4–6]. It is noteworthy that the C₂₄₀ structure obtained with quantum chemical calculations corresponds to the idealized one, i.e., the highest symmetry (I_h) allowed by the topology of the molecule (there is a possibility of the Jahn–Teller symmetry reduction in the case of other icosahedral fullerenes, e.g., C₂₀ and C₈₀) [6]. In practical aspects, such giant cages as C₂₄₀ attract as they have a large size and may be classified as nano-objects, but they are still molecules. Due to their size, giant fullerenes are considered as nano-vessels for gas storage [7] and the closed structure makes C₂₄₀ a molecular Faraday cage screening the guest atoms/molecules from the external electric fields [8]. Note that C₂₄₀ (I_h) has not been yet synthesized nor isolated. Under arc-discharge fullerene synthesis, it should be produced in extremely minute quantities (it is also potentially insoluble compound due to its size; this makes an obstacle of its extraction) [9,10]. However, its complexes like C₆₀@C₂₄₀, C₂₄₀@C₅₆₀, and C₆₀@C₂₄₀@C₅₆₀ have been obtained and visualized with atom-force

microscopy [11–14]. As follows from these studies, the C_{240} molecule is most likely icosahedral. The thermodynamic [5,15,16] and dielectric properties [8,17–19] of C_{240} and other giant fullerenes have been studied with relevant computational techniques.

Giant fullerenes relate to the processes of classical fullerene formation [20]. They are proposedly formed from the C_2 gas and convert to C_{60} and C_{70} [21]. The presence of a large cavity (much larger than in C_{60}) makes giant fullerenes chemically unstable [21] and sensitive to various transformations. The Stone–Wales isomerization is one of such topological processes that may occur on the fullerene surface [22,23]. Since 1986 [24], it is well-known that Stone–Wales (SW) rotations have a theoretical role in connecting the isomers of a given C_n fullerene.

Under the action of the $SW_{5|6}$ operator (Figure 1a), the 1812 isomers of C_{60} are grouped in 13 sets. The larger one includes 1709 cages connected to C_{60} (I_h) through one or more $SW_{5|6}$ transformations whereas 31 isomers remain separated from the rest of the isomers [24]. Later, the introduction of the so-called generalized Stone–Wales transformations (Figure 1b) overcame this limitation offering a method of generating the complete C_{60} isomeric space starting from just one C_{60} isomers [25]. The instrumental role of chemical graphs in studying fullerene rearrangements was immediately evident [25]. The description of fullerene molecule C_n as a planar graph G made by n nodes (carbon atoms), $B = 3n/2$ edges (carbon–carbon bonds) forming $f_5 = 12$ pentagons and $f_6 = n/2 - 10$ hexagons is a convenient and powerful tool that is also suitable for computerized algorithms. Chemical graph G represents the topological skeleton of the molecule and allows a clear picture of the Stone–Wales isomerization mechanism. In Figure 1a, the $SW_{5|6}$ transformation (the so-called pyracylene rearrangement) that is capable of bridging C_n isomers with different symmetries is shown in the direct (bottom) and dual graph (top). In G the rotation of the central bond is obtained by cutting the two graph edges indicated by the red arrows and then by connecting, pairwise, the green and the orange nodes. This topological transformation is perfectly isomeric since the numbers of nodes, edges, and faces are conserved. The generation of the $SW_{5|6}$ rotation became even simpler when occurring on the dual fullerene graph $\bar{G}$ composed by $\bar{n} = \frac{n}{2} + 2$ dual nodes, which correspond to the faces of the direct C_n fullerene and $B = 3n/2$ edges. Both fullerene graphs, direct G and dual $\bar{G}$, have the same number of edges B . The top part of Figure 1a illustrates the pyracylene transformation in the dual graph $\bar{G}$. In this case the $SW_{5|6}$ rearrangement is obtained just by rotating the central edge (red arrow) evidencing a general feature of the SW transformations the dual space $\bar{G}$:

- In the dual space, a SW rotation consists in the reversible rotation of just one dual bond.

This straightforward mechanism allows the generation of extended topological defects, so-called generalized Stone–Wales transformations (gSW) that modify the fullerene surfaces in a peculiar fashion.

Figure 1b shows the typical gSW involving two $5|6$ pairs (shown in Figure 1a) and η pairs of the internal faces (white circles) included between those $5|6$. The white circles represent indifferently hexagons or pentagons. The surface transformation of the dual fullerene $\bar{G}$ (Figure 1b) corresponds therefore to the $gSW_{\eta=3}$ of size $\eta = 3$ whereas the generalized rotation $gSW_{\eta=0}$ of order $\eta = 0$ represents instead to the pyracylene rearrangement $SW_{5|6}$. Operators like gSW depend on integer parameter η (Figure 1b) and constitute only one set of the infinite class S of reversible non-local topological rearrangements. The extension (or the size) of the gSW defect is expressed by integer η .

- The gSW size η corresponds to the number of pairs of internal faces (white circles) included between the two $5|6$ pairs.

All SW operators represent full-isomeric rearrangements of the fullerene surface, which therefore preserve the numbers of direct nodes n , dual nodes $\bar{n}$, bonds B and faces. They also preserve the type of internal faces included in a dislocation dipole. Figure 1 gives nice examples of these topological modifications.

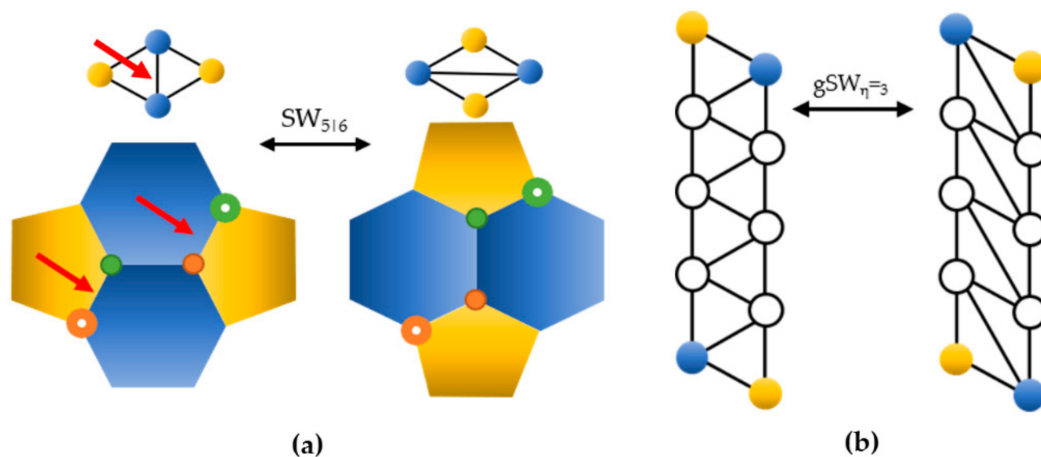


Figure 1. (a) Bottom Stone–Wales reversible transformation $SW_{5|6}$ on the fullerene direct graph G ; $SW_{5|6}$ rotates the central bond between green–orange pair. Red arrows indicate the bonds involved in the topological rearrangement. Top, $SW_{5|6}$ acting in the dual space $\bar{G}$. (b) The generalized Stone–Wales reversible rotation gSW of order $\eta = 3$ in the dual space. In both cases, blue (yellow) elements represent hexagonal (pentagonal) rings; white circles may be hexagonal or pentagonal faces indifferently and they are preserved before/after the gSW rotation.

In S another interesting group of operators is represented by the specific transformations that generate and then propagate 5|7 pairs in a hexagonal network [26,27]. In a regular hexagonal mesh, this original mechanism produces a peculiar linear extended defect, the so-called SW wave (SWw) with variable length η . Figure 2 describes in the dual graph the sequence of specific SW operators that create ($SW_{6|6}$) and move ($SW_{6|7}$) that wave in a graphenic lattice. The first rotation $SW_{6|6}$ (Figure 2a) of the arrowed dual edge creates the 5|7 double pairs (Figure 2b). The second rotation $SW_{6|7}$ separates them by the insertion of a couple of hexagons (Figure 2c). At this point, the propagation of the 5|7 pair has begun and successive $SW_{6|7}$ transformations propagate it in the lattice producing the topological SW wave. This topological defect SWw is known in the literature also under the name of dislocation dipole, whose length η corresponds to the minimal number of hexagon pairs between the 5|7 pairs. Figure 2 shows the dislocation dipoles (SWw) with $\eta = 0, 1$, and 2.

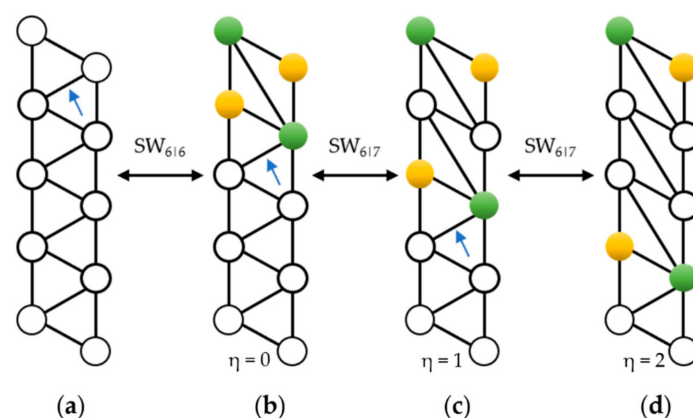


Figure 2. (a) $SW_{6|6}$ rotation of the arrowed bond creates in the pristine graphene dual lattice (white circles represent dual hexagons) the 5|7 double pair on the left. (b) A view of the 5|7 double pair; $SW_{6|7}$ applied to the arrowed bond moves one 5|7 pair one step down in the hexagonal mesh (c). After the second iterated $SW_{6|7}$ rotation SWw of order $\eta = 2$ is formed (d). Green (yellow) elements represent heptagonal (pentagonal) rings. The 5|7 double pair in (b) represents SWw of order $\eta = 0$. All Stone–Wales rearrangements are reversible.

Theoretically, the existence of extended topological defects such as SWw with $\eta \geq 3$ has been documented by molecular dynamics and *ab initio* studies [28,29] reporting about the presence of 5|7 dislocations in pristine graphene and at the grain boundaries of polycrystalline graphenic lattices. In the latter case, the authors state that these linear defects cannot be annealed by local reorganization of the honeycomb mesh. Specifically, work [28] affirmed that “neither an isolated pentagon, or a heptagon, or their pair 5|7” cannot be corrected by lattice rearrangements – an erroneous conclusion not considering that the SWw mechanism allows the 5|7 dislocations to be annealed by moving the 5|7 pair backward by applying the SW transformations (Figure 2) in the reverse direction.

Electronic properties of honeycomb planar systems indicate that single heptagon–pentagon dislocations are stable defects whereas 5|7 adjacent pairs are dynamically unstable [29]. The energy E_f of the formation of the 5|7 double pairs (Figure 2b) determined by the extended Hückel [30] and molecular mechanical simulations [31] depends on multiple structural factors:

- (i) the size of the honeycomb flat lattice around the defect, with E_f that assumes the minimum value $E_f \cong 6$ eV for “hexagonal layers” made by 9,000 carbon atoms [31];
- (ii) the presence a cylindrical curvature in the honeycomb mesh that facilitates furthermore the creation of the dislocation dipole by lowering the energy barrier to $E_f \cong 3$ eV for carbon nanotubes. Formation energy of the 5|7 double pair drops even more, down to $E_f \cong 2$ eV, when interstitial defects or ad-atoms are present in the networks [32,33].

Pentagon–heptagon pairs have been moreover detected by high-resolution TEM studies [34–37] whereby energetic particles, such as electrons and ions, generate 5|7 pairs in graphite layers or single-walled CNTs because of atom displacements.

We consider that both appearing elements favor the creation of dislocation dipoles, i.e., curvature and presence of hexagonal regions of variable size, are specific characteristics of fullerenes’ morphology. Therefore, the aim of this work is addressed, mainly from a topological corner, to the following basal theoretical questions:

- In which ways is the fullerene surface modified by SWw topological defects?
- Is the creation of SWw defects energetically favored?

In the following, the first attempt for answering the above points is made by taking into account the $C_{240} (I_h)$ molecule as a case study. The reasons for this choice are the high symmetry of the molecule and the previous of well-documented *ab initio* [16] and topological studies [27] about its stability. The next paragraph is devoted to the description of the mechanisms for the formation of dislocation dipoles on the $C_{240} (I_h)$ surface; then the energetic and topological considerations complete this work.

2. SW Waves on the $C_{240} (I_h)$ Fullerene

The theoretical evidences of the stability of 5|7 defects in various hexagonal systems [28–36] suggest the possibility to create extended defects even on the surface of a fullerene large enough to have graphene-like zones tiled only with hexagons. This section provides a concise introduction to the topological wave-like mechanism for the creation and the diffusion (or annihilation) of the pentagon–heptagon linear defect on the fullerene surface. The present investigation, combining extended topological rearrangements of the carbon networks and specific modifications of fullerene topology, sheds new light on possible mechanism that could be a base of fullerene formation and chemical properties.

Figure 3 shows the icosahedral C_{240} cage with $f_6 = 110$ hexagonal rings and the symmetry-independent rearrangements of type $SW_{6|6}$, which may take place on its surface (images sourced from the web [38]). Due to the icosahedral structure of the C_{240} molecule, one has in fact just three symmetry-independent ways A, B, and C of selecting quartets of hexagons admitting the $SW_{6|6}$ rotation. The three regions A, B, and C are shown in Figure 3a prior to applying the SW operator according to the mechanisms illustrated above (Figure 2). The $SW_{6|6}$ operator rotates the dual bonds pictured in black in each diamond in Figure 3a.

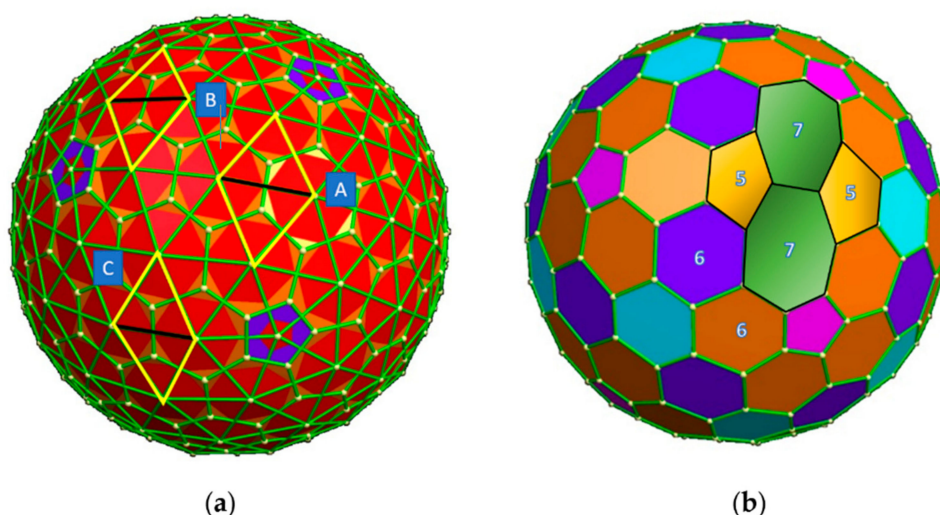


Figure 3. (a) Pristine C_{240} (I_h) fullerene has three symmetry-independent quartets of hexagons A, B, and C delimited by yellow diamonds whose corners correspond to the centers of the hexagons. (b) The $C_{240}^{\eta=0}$ structure generated by applying the $SW_{6|6}$ rotation to quartet A in (a). The double pair 5|7 and SW_w with length $\eta = 0$ are shown. Yellow (green) polygons represent pentagonal (heptagonal) rings. The pair 6|6 is ready for the $SW_{6|7}$ rotation and swap place with the nearby pair 5|7.

Our density functional theory (DFT) calculations show that, among the three isomers of the C_{240} (I_h) fullerene generated by the $SW_{6|6}$ operator applied to the quartets A, B, and C (Figure 3a), the energy effect favors the rotation of the quartet A. Indeed, the calculated ΔE values for modes A, B, and C equal 147.9, 323.5, and 347.4 kJ/mol (see Appendix A for the details of the calculations). Note that the structures obtained *via* the rotations of quartets A and B have the C_s symmetry whereas the structure derived by the quartet C rearrangement has no symmetry. The configuration of the molecule after the $SW_{6|7}$ rotation of quartet A is given in Figure 3b, which evidences the new 5|7 double pair. At this point, the SW wave with $\eta = 0$ has been created on the surface of the new isomer $C_{240}^{\eta=0}$ with $f_5 = 14$, $f_6 = 106$, and $f_7 = 7$. The two extra pentagons and the two heptagons are labeled with the number of respective edges in Figure 3b. According to the propagation mechanism (Figure 2c,d), the second $SW_{6|7}$ operator rotates the dual bond between the heptagon and the nearby hexagon (the arrowed dual bonds in Figure 2b,c), moving the 5|7 pair along the fullerene network. At each step η , the 5|7 pair swaps its place with a 6|6 one (see also Figure 3b); after η iterations of the $SW_{6|7}$ rearrangement, the C_{240}^{η} isomer is formed. Figure 4 shows the isomer with $\eta = 2$. The described propagation process is applied to the isolated 5|7 dislocation monopole as well as to the 5|7 double pair arising from the $SW_{6|6}$ rearrangement. It is worth mentioning that similar topological tools are used in other disciplines such as biology whereby wave-like diffusion processes and icosahedral patterns of viruses are normal mechanisms to model biochemical processes [39–42].

From the pure topological point of view, it is noteworthy that each fullerene network in the current study could be considered as the result of an instantaneous transformation generated by a single non-local generalized SW rotation. This kind of transformations, previously proposed in [25], constitutes a potentially infinite class of global rearrangements aiming to generate the entire isomeric space of a given C_n fullerene starting from a limited number (even only one) of inequivalent cages.

The final part of this section briefly introduces the topological invariants and how they measure the relative stability of fullerene isomers C_{240}^{η} modified by SW waves. Graph-theoretical results are presented and compared with energy values of the systems coming from quantum chemical simulations in the next sections. According to the topological modeling (TM) methods [43], chemical structures with n atoms and B bonds are schematically described as simple graphs G with n nodes and B edges. Geometrical, structural, and other physicochemical properties (maximal molecular symmetry being in the opinion of the authors the prominent, and somehow surprising, one) are embedded in the

graph topology as the study of distance-based invariants evidenced some decades ago in pioneering studies [44,45]. In this context, distances d_{ij} are integer numbers computed by counting the number of edges connecting two atoms i and j with the shortest path in G . The distances are graph invariants (i.e., they do not depend on the labeling of the nodes) and generate a vast parade of distance-based graph descriptors. Graph diameter is defined as $M = \max\{d_{ij}\}$.

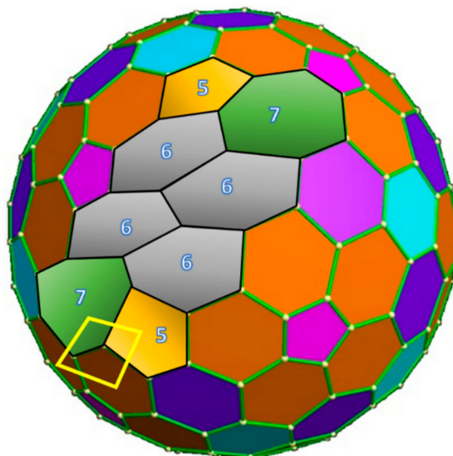


Figure 4. The molecule of the $C_{240}^{\eta=2}$ fullerene. It exhibits the extended dislocation dipole generated by applying two $SW_{6|7}$ rotation to the configuration shown in Figure 3b. The topological defect consists of two pairs of 5|7 and two pairs of 6|6 in between (the faces are numbered according to the number of carbon atoms in the ring). The molecule is ready for another $SW_{6|7}$ rearrangement involving the lower pair 5|7 and two neighboring hexagons (marked with yellow diamond) to produce the $C_{240}^{\eta=3}$ fullerene (not represented).

TM techniques mainly make use of two invariants W (1) and ρ^E (3) to measure graph compactness and roundness, respectively. Assuming $d_{ii} = 0$, the Wiener index W is derived as the semi-sum of all distances in G :

$$W(G) = \frac{1}{2} \sum_{i,j=1}^n d_{ij} = \sum_{i=1}^n w_i, \quad (1)$$

counting the contributions w_i arising from each node in the graph:

$$w_i = \frac{1}{2} \sum_{j=1}^n d_{ij}, \quad (2)$$

Intuitively, Equation (2) admits the minimum ($\underline{w}$) and maximum ($\overline{w}$) values for central (peripheral) nodes in G . The quotient ρ^E between the two w_i extremals:

$$\rho^E = \overline{w} / \underline{w}, \quad (3)$$

called extreme topological roundness denotes the topological symmetry of the graph: the lower (3) is the more symmetric G is (with the general constraint $\rho^E \geq 1$). We assign the role of the topological potential of the system described by G to the Wiener index and extreme topological roundness. Indeed, both quantities obey the minimum principle. Therefore, the TM model assumes that similar carbon systems arrange their structures to minimize W and ρ^E . Heuristically, this approach is confirmed by the fact that icosahedral fullerenes C_{60} and C_{240} minimize both indices in the respective isomeric sets. Recent works [46–48] on C_{66} and C_{84} molecules confirm that stable fullerenes combine high topological symmetry (low ρ^E) with high compactness (low W).

This fast and elegant computational approach is applicable to the evolution of the SW_w -defected fullerene molecules C_{240}^{η} . The electronic configurations of the atoms constituting the C_{240} isomers with defective structures in Figure 3; Figure 4 keep the sp^2 -hybridization state. On the other hand, surface

reconstructions induced by SWw cause complex modifications of “the electronic charge density and this varies the bond lengths within and around” [49], with effects also on the local curvature of the molecular cage.

We have performed the preliminary density functional theory (DFT) computations to monitor the topology effect on the geometrical parameters and molecular properties of the defected C_{240} cages. The DFT computations have been performed with standard procedures; the details are collected in Appendix A. We have computationally studied SWw on the C_{240} surface up to $\eta = 6$ (Figure 5). The $SW_{6|6}$ operator implies replacing six original hexagons with the emergence of four “defected” polygons (two 5|7 pairs). From the point of structural chemistry, we approximate SWw as a movement of one “defected” pair from the other due to similar operations. Thus, each C_{240}^η with $\eta = 0-3$ contains 12 original pentagons, 2 heptagons and 2 pentagons, static and migrating, generated by the wave (the remaining faces being hexagons). In Figure 5, static and dynamic defects are colored differently for clarity. The $C_{240}^{\eta=4}$ structure contains one migrating tetragon resulting from involving an original pentagon by SWw. In further structures, this tetragon converts to a new static pentagon. In other words, the wave shifts the position of the original pentagon in two operations. Note that the structures with $\eta = 3$ and $\eta = 5$ contain pentagon–pentagon fusions. These structural features are presented in Table 1.

Local curvature (k) is a key parameter we pay attention as it strongly correlates with the stability [1,2,50] and reactivity [51–53] of the fullerene species. The SWw transformations occur locally on the C_{240} surface. However, the calculated curvatures indicate the change in the shape throughout the whole surface (Equation (A2), Appendix A). To demonstrate it, we have chosen the curvature in the pentagon regions, both original and emerged upon SWw. As follows from Table 1, all pentagons have the same curvature in original C_{240} but SWw makes the curvatures more diversified. Accordingly, some of pentagons become more flattened as the others become more curved. Herewith, the structures with a tetragon ($C_{240}^{\eta=4}$) and fused pentagons ($C_{240}^{\eta=3}$ and $C_{240}^{\eta=5}$) manifest the highest curvatures in the set.

Sphericity (Ψ) is another parameter indicating the changes in the shape (Equation (A1), Appendix A). The calculated sphericities decrease from the starting value 0.9829 as the C_{240} system loses its initial icosahedral symmetry. Note that original C_{240} (I_h) and $C_{240}^{\eta=0}$ have very close values because the structure with $\eta = 0$ still has a low symmetry (C_5). The further changes are more pronounced. Nevertheless, Ψ does not become lower than 0.97 though SWw perturbs the shape. For comparison, Ψ may be significantly reduced ($\Psi < 0.9$) in highly functionalized fullerene compounds (e.g., C_{60} halogenides [54]). Sphericity (with associated quantity of volume, V) does not change monotonically with SWw propagation, i.e., there are no (and should not be) correlations between Ψ (or V) and η . However, we demonstrate below the correlations between these geometric parameters with topological ones.

Pristine and almost spherical C_{240} (I_h) has $n = 240$ direct nodes and $B = 360$, three symmetry-distinct sets of atoms (orbits) having multiplicities 60, 60, and 120, and 240 atoms with the same $\overline{w} = \underline{w} = 2312$. This last condition implies $W = 277,400$ and $\rho^E = 1$, indicating that the C_{240} (I_h) fullerene is a maximal roundness molecule even in presence of non-symmetry equivalent atoms (a special condition featured by tetrahedral C_{40} too [49]). We would like to remember here that the complete individuation of *all* families of non-transitive fullerenes with $\rho^E = 1$ is still an open task.

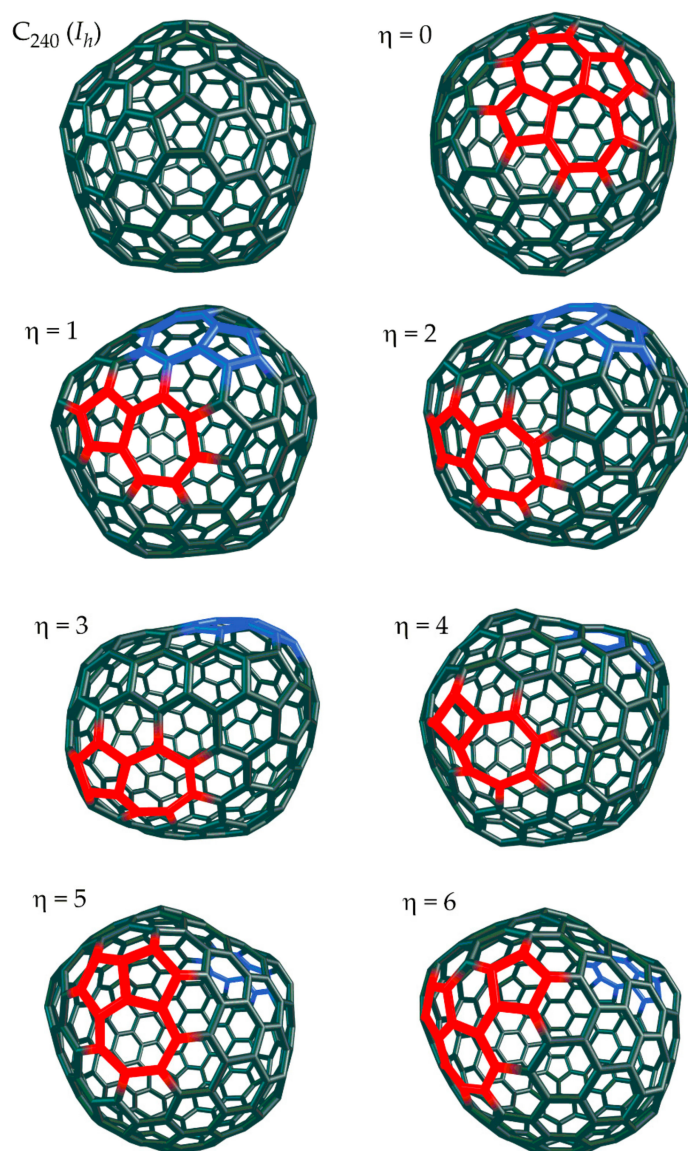


Figure 5. The DFT-optimized C_{240}^η fullerene structures. Blue and red colorings correspond to the static and migrating (Stone–Wales wave) defects, respectively (except for the case of $\eta = 0$ whereby the defect polygons are fused).

Table 1. Structural parameters of original and defected C_{240} fullerenes (DFT computations).

Fullerene Cage	Number of Polygons ¹	Volume (Å ³)	Sphericity, Ψ	Curvatures of Original Pentagons (Å ⁻¹)	Curvatures of Defected Pentagons (Å ⁻¹)	
					Static	Migrating
$C_{240}(I_h)$	12 110 0 0	1433.73	0.9829	0.2365	none	none
$C_{240}^{\eta=0}$	14 106 2 0	1436.10	0.9828	0.1850–0.2475	0.1641	0.1257
$C_{240}^{\eta=1}$	14 106 2 0	1430.11	0.9797	0.1763–0.2586	0.2112	0.1537
$C_{240}^{\eta=2}$	14 106 2 0	1425.73	0.9774	0.1763–0.2502	0.2171	0.1915
$C_{240}^{\eta=3}$	14 106 2 0	1420.88	0.9751	0.1763–0.2680	0.2151	0.2722
$C_{240}^{\eta=4}$	12 107 2 1	1417.49	0.9762	0.1754–0.3277	0.2135	0.3932 ² (tetragon)
$C_{240}^{\eta=5}$	14 106 2 0	1420.49	0.9750	0.1765–0.2589	0.2140 (0.2679)	0.2754
$C_{240}^{\eta=6}$	14 106 2 0	1421.94	0.9759	0.1578–0.2588	0.2140 (0.2383)	0.1939

¹ In the order: pentagons, hexagons, heptagons, tetragons. ² For tetragon. ³ Curvatures of static pentagons, which resulted due to SWw, are in parentheses.

3. Topological Simulations and Electronic Structure

3.1. Topological Modeling

The first step of the SW wave on the C_{240} (I_h) fullerene graph consists of a $SW_{6|6}$ bond flip that produces the 5|7 double pair (Figure 3b). This surface transformation decreases the lattice compactness to $W = 277,122$ derivable from the direct computation of the graph chemical distances d_{ij} and Equation (1). In our approximated model, this -0.11% variation of the Wiener index represents the gain in topological compactness allowed by the creation of the SW defect in the molecule $C_{240}^{\eta=0}$.

The subsequent $SW_{6|7}$ rotation ($\eta = 1$) splits the 5|7 pairs by inserting in between one pair 6|6 according to the topological mechanism described in (Figure 2a,b). This decreases by another -0.14% the value of the topological descriptor $W = 276,730$ for newly formed $C_{240}^{\eta=1}$. This “gaining” behavior holds for each propagation steps in the interval $\eta = [0, 3]$ of SWw over the fullerene surface, increasing the topological compactness of the system.

The reduction of the topological index W follows a quasi-parabolic trend (Figure 6). The curve evidences that the creation of an extended topological defect up to $\eta = 3$ is favored; the topology of the fullerene network allows the topological diffusion of the 5|7 pair over a quite extended region. The SWw propagation is then impeded by a small $+0.02\%$ increment of the topological index W having a local peak for $\eta = 4$. The Wiener index curve in Figure 6 evidences, and this result is reported here for the first time for the fullerene molecules, that the 5|7 defects are able to migrate on the fullerene surface to form extended linear defects. This is a specific behavior that matches similar findings previously reported for graphene planar layers [26] and curved carbon nanotubes and nanotori [33]. The present TM simulations show that creation of SW waves is allowed also on quasi-spherical surfaces tiled by hexagons. Based on this outcome, we may therefore propose the following important conjecture: the formation and propagation of the SW waves are allowed on surfaces tiled with hexagons independently of the surface genus.

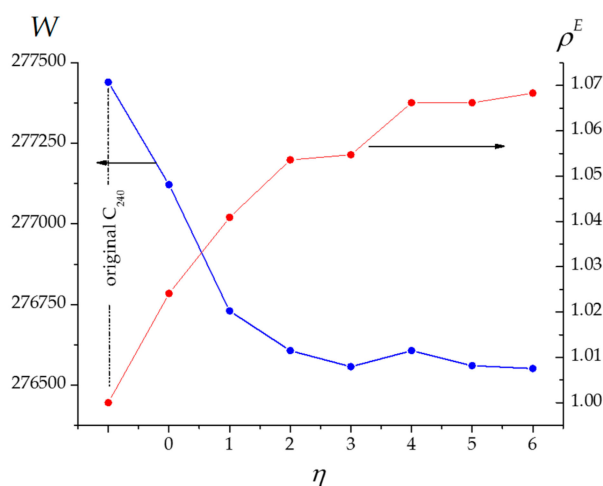


Figure 6. Changes in the Wiener index (W) and extreme topological roundness (ρ^E) upon the dislocation dipole propagation over the C_{240} surface, from the original I_h fullerene to $\eta = 6$.

This effect has a pure topological root and strongly correlates with the connectivity properties of the pentagon–heptagon pairs embedded in the hexagonal mesh and the “edge” effect induced by the presence of pristine pentagons on the surface. We note in fact here that the small barrier effect encountered by the 5|7 pair at $\eta = 4$ (Figure 6) is an effect generated by SWw colliding with one of the original pentagons of the C_{240} (I_h) fullerene. A different situation is encountered in the variations of the topological roundness (Equation (3)) of the system upon SWw diffusion, see Figure 6.

The generation of the 5|7 double pairs reduces the topological symmetry and moves the ρ^E curve upward after the first $SW_{6|6}$ rotation, with a topological increase $\rho^E = 1.0241$ for $C_{240}^{\eta=0}$ compared with

the unitary values of the original C_{240} (I_h). The successive $SW_{6|7}$ flip starts the dipole propagation still increasing the topological invariant ρ^E . The diffusion of the wave is opposed by the action of the invariant ρ^E , which shows a barrier effect confirmed at the successive steps in Figure 5. At $\eta = 2$ and 3, the ρ^E quantity shows an almost flat curve in the same region where W shows a local minimum (Figure 6). This result is quite interesting since it confirms that system, when the dislocation dipole has size $\eta = 2$ and 3, stops the obstacle to the creation of defective molecules ($C_{240}^{\eta=2}$ represented in Figure 4).

Topological invariants are listed in Table 2 and represented in Figure 6. We have found the inverse correlations between the extremal roundness (Table 2), volumes and sphericities of the C_{240} cages (Figure 7a). The found correlations are the same as in the case of the C_{84} isomeric series (made up with the isomers obeying the isolated-pentagon rule) [55] and similar to the findings of comprehensive work [56] on all possible isomers of C_{60} . The geometry and topology of the molecules obtain direct linkage in the relations of Ψ and ρ^E . Indeed, $\Psi \rightarrow 1-$ for sphere-like species whereas $\rho^E \rightarrow 1+$ in the case of structures with “equilibrated connectivity”. These terms, in the case of the fullerenes, coincide with the notion that is manifested with the found correlations. As for the correlation between the volume and extremal roundness of the C_{240} cages, it follows from the interdependence of the Ψ and V values (Figure 7b).

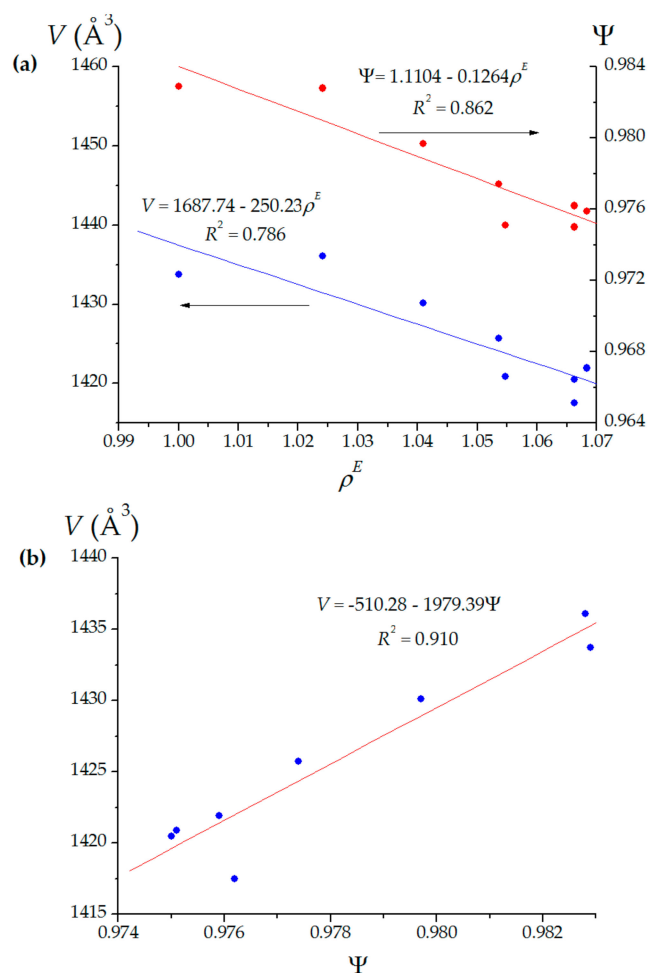


Figure 7. (a) Correlations between the extremal roundness, volume and sphericity of the C_{240} cages. (b) Linear correlation between the volume and sphericity of the C_{240} .

Table 2. Topological descriptors of the original and defected C₂₄₀ fullerenes.

Fullerene Cage	W	M ¹	$\bar{w}$	$\bar{w}$	ρ^E
C ₂₄₀ (I _h)	277,440	19	1156	1156	1
C ₂₄₀ ^{η=0}	277,122	19	1140	1167.5	1.0241
C ₂₄₀ ^{η=1}	276,730	19	1125.5	1171.5	1.0409
C ₂₄₀ ^{η=2}	276,607	19	1118.5	1178.5	1.0536
C ₂₄₀ ^{η=3}	276,557	19	1124	1185.5	1.0547
C ₂₄₀ ^{η=4}	276,607	19	1118.5	1192.5	1.0662
C ₂₄₀ ^{η=5}	276,560	19	1125	1199.5	1.0662
C ₂₄₀ ^{η=6}	276,551	19	1120	1196.5	1.0683

¹ M is the graph diameter M = max{d_{ij}}.

3.2. DFT Simulations on Energetic and Molecular Parameters of the Defected C₂₄₀ Cages

We have assessed the possibility of SWw transformations on the C₂₄₀ cage from the thermodynamic point of view. For this purpose, we have operated with the DFT-computed total energies of the original and defected cages (see Appendix A for the details of the DFT study). As expected, the energies of all SWw-generated C₂₄₀ cages are much higher as compared with the pristine one (Table 3). However, the energy effects of the stepwise transitions between C₂₄₀^{η=0} shows that some of the transitions may be favorable. Indeed, the transitions are endothermic up to C₂₄₀^{η=3} → C₂₄₀^{η=4} and exothermic for the two next steps (Table 3). The exothermicity is explainable in terms of the structural chemistry of fullerenes. The structure C₂₄₀^{η=5}, a participant of the two exothermic steps, has two adjacent pentagons. This is the instability factor making the conversion C₂₄₀^{η=5} → C₂₄₀^{η=6} favorable. As for η = 4, the precursor of C₂₄₀^{η=5}, it has the tetragon–heptagon junction, and exothermicity C₂₄₀^{η=4} → C₂₄₀^{η=5} indicates that such an introduction of tetragon to the C₂₄₀ cage makes the structure less favorable as compared with one containing the fused pentagons.

Table 3. Energetic and molecular parameters of original and defected C₂₄₀ fullerenes (DFT computations).

Fullerene Cage	Relative Energy, E _{rel} (kJ/mol) ¹	Energy Effect, ΔE (kJ/mol) ²	Dipole Moment, μ (D)	ε _{HOMO} (eV)	ε _{LUMO} (eV)	HOMO–LUMO Gap (eV)
C ₂₄₀ (I _h)	0	n/a	0	−5.53	−4.30	1.23
C ₂₄₀ ^{η=0}	147.8	147.8	0.86	−5.26	−4.46	0.80
C ₂₄₀ ^{η=1}	315.5	167.7	0.51	−5.18	−4.41	0.76
C ₂₄₀ ^{η=2}	430.4	114.9	1.57	−5.30	−4.57	0.72
C ₂₄₀ ^{η=3}	510.5	80.1	2.53	−4.98	−4.70	0.28
C ₂₄₀ ^{η=4}	642.6	132.1	0.83	−4.89	−4.61	0.27
C ₂₄₀ ^{η=5}	489.2	−153.5	4.62	−4.94	−4.83	0.10
C ₂₄₀ ^{η=6}	384.0	−105.2	3.57	−5.03	−4.79	0.24

¹ Calculated as E_{rel} = E(C₂₄₀^η) − E(C₂₄₀^{original}). ² Calculated as ΔE = E(C₂₄₀^η) − E(C₂₄₀^{η−1}).

The HOMO–LUMO gap is another indicator of the fullerene stability [55] (HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals, respectively). It is calculated as the difference in the HOMO and LUMO energies. In our isomeric C₂₄₀ series, only the original structure manifests the largest gap value that indicates its stability. Other (defected) cages, as follows from the orbital energies, should be kinetically unstable. We have tried to collate the obtained HOMO–LUMO gaps with the results of the TM modeling and found a correlation between the gap and extreme topological roundness values (Figure 8). Indeed, both values, being different in their origin, should

reflect the stability of the C_{240} cages. However, the correlation is weak ($R^2 = 0.861$) and requires further investigation, which includes a larger number of the defected fullerene structures.

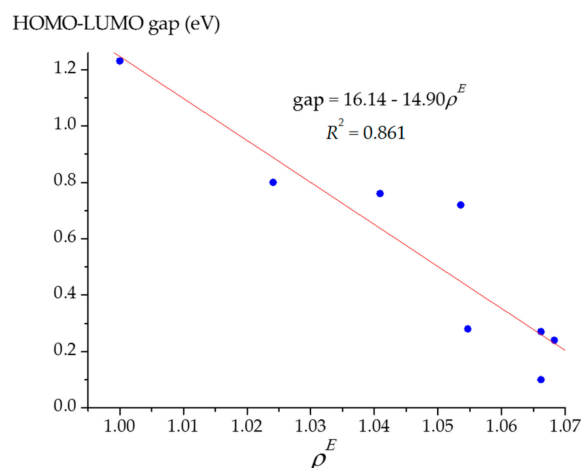


Figure 8. Correlation between the HOMO–LUMO gap and extreme topological roundness of the C_{240} cages.

4. Discussion

The results of the TM simulations are summarized in Table 2 and Figure 6. The analysis of the evolution of the topological compactness W of the isomers C_{240}^η (Figure 6) allows observing how the generation $\eta = 1$ of the SW dipole causes an immediate decrease in the network invariant $W = 277,122$ (Equation (1)). In our topological model, this negative variation in the Wiener index represents the topological gain in the graph compactness in respect to the pristine C_{240} (I_h) fullerene. The creation of the SW defect is therefore able to make the fullerene cage more compact. The successive $SW_{6|7}$ rotations further augment the topological compactness of the structure, the reduction in W showing an almost parabolic trend for the first propagation steps $\eta = 1, 2, 3$. This characteristic behavior of the W index, which favors the expansion of the SW wave, has a pure topological root and it relates to the connectivity properties of the hexagonal regions partially covering the fullerene surface. This result, in fact, matches with previously reported behaviors of SW waves when they propagate in pure honeycomb lattices [26]. The topological diffusion of the $5|7$ pair with creating extended dislocation dipoles is stopped at $\eta = 4$ and W reaching a local maximum ($W = 276,607$). Here, the SW wave “collapses” with one of the pentagons of the pristine icosahedral fullerene with the creation of a 4-ring of carbon atoms.

Figure 6 shows instead that the topological order gets diminished by the creation and the propagation of the SW wave. The increase in the extreme topological roundness ρ^E (Equation (3)) represents, in fact, an evident “topological response” of the cage to the diffusion of the pentagon-heptagon pairs over the fullerene surface. The evolution of ρ^E demonstrates a characteristic plateau ($\eta = 3, 4$ with $\rho^E \cong 1.05$ and $\eta = 4, 5, 6$ with $\rho^E \cong 1.06$) where the topological symmetry of the C_{240}^η cages remains pretty uncanged, opening the door for the presence of extended dislocation dipoles embedded in the fullerene mesh.

In summary, the main outcomes of the TM simulations state that isomers C_{240}^η have greater compactness (lower W) than the parent C_{240} (I_h), favoring the creation and the propagation of the SWw defects over the fullerene surface. In these molecules, however, at each step of the SWw propagation, the ρ^E index increases (lowering their extreme topological roundness) and obstructs the diffusion of the SWw itself; this barrier effect is reduced in the case of the large η values.

The DFT-estimated energy parameters, in general, indicate endothermicity of the transformations towards the defected fullerene isomers. Thus, such SW processes may take place under high-energy (nonequilibrium) conditions (plasma, interstellar environments etc. [20,21]). The computed HOMO–LUMO gaps also reveal the kinetic instability of the defected cages (in contrast to the parent one having the

largest gap). We do not deeply discuss the HOMO–LUMO vs. ρ^E plot (Figure 8). There values seem correlated, but the justification of the trend requires extending the correlation field.

The title defect introduced to the honeycomb carbon-containing system is called a dislocation dipole. In the case of the fullerenes, we associate it with nonzero dipole moments (Table 3) of the defected fullerene cages (indeed, it is impossible to make such attribution in the case of introducing a dislocation dipole to the infinite systems, like graphene [57], as their dipole moment is not defined). The influence of the defects on the polarizability of fullerenes has been studied in a few works concluding the increase with the topological defects (see in review [58]). In further studies, we will investigate this important property in the context of SW waves.

As usually considered, the title defect also generates negative-curvature regions on the fullerene surface. In our estimates deduced from the pyramidity angles (Equation (A2)), we have found the atoms with decreased curvatures of the surroundings but which are still positive. Thus, the presence of the pair 5|7 is not the only condition of the negatively curved surface. Additionally, upon SWw, more curved regions also emerge, especially with tetragon inclusion or pentagon–pentagon fusions. Curvature is an important parameter for assessing the reactivity of fullerenes and their derivatives [1,50–53]. We think that our estimates may be useful for assessing chemical properties of the giant fullerenes, hollow [4–6,50] or filled (as a part of carbon nano-onions [59,60]).

The calculated curvature values correspond to the local changes in the C_{240} structures upon SWw. Sphericity is another parameter reflecting the general change in the shape of the molecule. As expected, it goes down with introducing the defects. More important here, sphericity, a geometric structural parameter, is correlated with extreme roundness, a topological structural parameter. This indicated the deducibility of the structural and energetic parameters from the topology of the molecules.

5. Conclusions and Prospective

In the present work, topological, energetic and structural modifications induced on the C_{240} fullerene by the presence of a propagating expanding SWw have been investigated for the first time. Although cage compactness is enhanced for the dislocation-dipole isomers, their energies increase with the size η of the SW dislocation. This means a relatively low probability of the formation of these defective fullerenes. However, the existence of these defective isomers, especially those molecules with large η , which combine low W with non-increasing ρ^E , may relate to special thermodynamic conditions like during fullerene growth or in interstellar media.

As found, the extreme topological roundness correlate with volumes and sphericities of the C_{240} cages. Such correlations are general for fullerene structures (as they have also been found for other isomeric series). Considering these regularities, we consider the efficiency of the presented topological approach for structural studies on fullerenes and deducing their molecular properties.

These results are perfectly in line with the topological determination of the relative stability of smaller fullerenes. The ability of W in selecting the most compact cage as the physically stable one is documented by the non-trivial case of the C_{60} fullerene [44] that, among its 1812 non-isomorphous isomers, minimizes the Wiener index in correspondence to the C_{60} (I_h) with $W = 8340$ and $\rho^E = 1$. In more complex C_{66} case [46], the stability of the whole set of 4478 isomers has been ranked with maximizing two graph properties, i.e., topological compactness (low W) and topological roundness (low ρ^E). As concluded, the most stable C_{66} isomers minimize both graph invariants and, hence, may be found in the local minima of the (W, ρ^E) plane. We recently found that this purely topological approach works also for the C_{84} fullerene. Its most stable forms have minimal graph invariants W and ρ^E [47,48]. The latter result also evidences the computational convenience of the TM simulations that rank just in a matter of minutes the topological stability of 51,592 distinct C_{84} isomers. Thus, we highlight that the TM approximated method is generally applicable to the formation and stabilization mechanisms of complex sp^2 carbon structures, like large fullerenes. As an additional advance, topological studies allow quick sieving the possible structures before detailed but time-consuming *ab initio* computations.

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Appendix A. Details of Quantum Chemical and Auxiliary Calculations

All optimizations were performed by the density functional theory method PBE/3 ζ implemented in the Priroda program [61]. The 3 ζ basis set describes the electronic configuration of carbon atoms as contracted Gaussian-type functions (11s,6p,2d)/[6s,3p,2d] combined with uncontracted ones (10s,3p,3d,1f). Previously, this method was used in diverse computational studies on fullerenes, including structure simulations [62–64], DFT-assisted spectral characterization of fullerene compounds [62,65–67], assessing their molecular and energetic parameters [68–71], kinetic and thermodynamic studies of fullerene reactions [62,72–78]. The method is also applied to related compounds such as polycyclic aromatic hydrocarbons [68,79,80] and endofullerenes [69–71,81]. The accuracy and reliability of PBE/3 ζ were discussed in the mentioned papers. Based on the previous advances, we consider the suitability of the method to the purpose of this work (e.g., the method works well in the case of giant fullerenes [16], perfectly reproduces experimental IR and NMR spectra of fullerene compounds [62,65–67] and volumes of fullerene cages [64]).

We used the Cartesian coordinates of the atoms for calculating the volumes, sphericities, and curvatures of the fullerene cages. The term volume of the fullerene cage means the volume of the polyhedron made up with nuclei of the atoms of the cage (i.e., nuclear volume). The algorithm for the volume calculations has been previously presented (in general, it implies the triangulation of the fullerene cage, i.e., its partition over the disjoint pyramid primitives having one common vertex in the center of mass of the cage) [64]. The sphericities (Ψ) of the C₂₄₀ cages are calculated as previously described [47,54]:

$$\Psi = \frac{\pi^{1/3}(6V)^{2/3}}{A} \quad (\text{A1})$$

where V and A are the volume and the surface area of the fullerene cage. Sphericity is the ratio of the surface area of a sphere, having the same volume as the given particle, to the surface area of the particle.

The local curvature of each site (atom) is calculated using the optimized geometry of a fullerene as [63]

$$k = 2\sin \theta_p/a, \quad (\text{A2})$$

where a is the average distance between the site and its three neighbors, and θ_p is the pyramidity angle of the site. The local curvature of polygons are the average values of the constituting atoms.

References

1. Lu, X.; Chen, Z. Curved pi-conjugation, aromaticity, and the related chemistry of small fullerenes (<C₆₀) and single-walled carbon nanotubes. *Chem. Rev.* **2005**, *105*, 3643–3696. [CrossRef]
2. Kovalenko, V.I.; Khamatgalimov, A.R. Regularities in the molecular structures of stable fullerenes. *Russ. Chem. Rev.* **2006**, *75*, 981–988. [CrossRef]
3. Goldberg, M. A class of multi-symmetric polyhedra. *Tohoku Math. J. First Ser.* **1937**, *43*, 104–108.
4. Schewerdtfeger, P.; Wirz, L.N.; Avery, J.E. The topology of fullerenes. *WIREs Comput. Mol. Sci.* **2015**, *5*, 96–145. [CrossRef]

5. Yoshida, M.; Ōsawa, E. Molecular mechanics calculations of giant- and hyperfullerenes with icosahedral symmetry. *Fullerene Sci. Tech.* **1992**, *1*, 55–74. [[CrossRef](#)]
6. Sabirov, D.S.; Ōsawa, E. Information entropy of fullerenes. *J. Chem. Inf. Model.* **2015**, *55*, 1576–1584. [[CrossRef](#)]
7. Suyetin, M.V.; Vakhrushev, A.V. Guided carbon nanocapsules for hydrogen storage. *J. Phys. Chem. C* **2011**, *115*, 5485–5491. [[CrossRef](#)]
8. Zope, R.R. Electronic structure and static dipole polarizability of $C_{60}@C_{240}$. *J. Phys. B: At. Mol. Opt. Phys.* **2008**, *41*, 085101. [[CrossRef](#)]
9. Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; John Wiley & Sons: New York, NY, USA, 2006.
10. Taylor, R. *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*; Imperial College Press: London, UK, 1999.
11. Mordkovich, V.Z.; Umnov, A.G.; Inoshita, T.; Endo, M. The observation of multiwall fullerenes in thermally treated laser pyrolysis carbon blacks. *Carbon* **1999**, *37*, 1855–1858. [[CrossRef](#)]
12. Mordkovich, V.Z.; Shiratori, Y.; Hiraoka, H.; Umnov, A.G.; Takeuchi, Y. A path to larger yields of multishell fullerenes. *Carbon* **2001**, *39*, 1929–1941. [[CrossRef](#)]
13. Mordkovich, V.Z.; Takeuchi, Y. Multishell fullerenes by laser vaporization of composite carbon–metal targets. *Chem. Phys. Lett.* **2002**, *355*, 133–138. [[CrossRef](#)]
14. Mordkovich, V.Z.; Shiratori, Y.; Hiraoka, H.; Takeuchi, Y. Synthesis of multishell fullerenes by laser vaporization of composite carbon targets. *Phys. Solid State* **2002**, *44*, 603–606. [[CrossRef](#)]
15. Noël, Y.; De La Pierre, M.; Zicovich-Wilson, C.M.; Orlando, R.; Dovesi, R. Structural, electronic and energetic properties of giant icosahedral fullerenes up to C_{6000} : Insights from an *ab initio* hybrid DFT study. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13390–13404. [[CrossRef](#)] [[PubMed](#)]
16. Pankratyev, E.Y.; Khatymov, R.V.; Sabirov, D.S.; Yuldashev, A.V. On the upper bound of the thermodynamic stability of fullerenes from small to giant. *Physica E* **2018**, *101*, 265–272. [[CrossRef](#)]
17. Zope, R.R.; Baruah, T.; Pederson, M.R.; Dunlap, B.I. Static dielectric response of icosahedral fullerenes from C_{60} to C_{2160} characterized by an all-electron density functional theory. *Phys. Rev. B* **2008**, *77*, 115452. [[CrossRef](#)]
18. Langlet, R.; Mayer, A.; Geuquet, N.; Amara, H.; Vandescuren, M.; Henrard, L.; Maksimenko, S.; Lambin, P. Study of the polarizability of fullerenes with a monopole–dipole interaction model. *Diamond Relat. Mater.* **2007**, *16*, 2145–2149. [[CrossRef](#)]
19. Calaminici, P.; Carmona-Espindola, J.; Geudtner, G.; Köster, A.M. Static and dynamic polarizability of C_{540} fullerene. *Int. J. Quantum Chem.* **2012**, *112*, 3252–3255. [[CrossRef](#)]
20. Irle, S.; Zheng, G.; Wang, Z.; Morokuma, K. The C_{60} formation puzzle “solved”: QM/MD simulations reveal the shrinking hot giant road of the dynamic fullerene self-assembly mechanism. *J. Phys. Chem. B* **2006**, *110*, 14531–14545. [[CrossRef](#)]
21. Ōsawa, E. Formation mechanism of C_{60} under nonequilibrium and irreversible conditions—An annotation. *Fuller. Nanotub. Carbon Nanostruct.* **2012**, *20*, 299–309. [[CrossRef](#)]
22. Stone, A.J.; Wales, D.J. Theoretical studies of icosahedral C_{60} and some related species. *Chem. Phys. Lett.* **1986**, *128*, 501–503. [[CrossRef](#)]
23. Monthieux, M.; Charlier, J.C. Giving credit where credit is due: The Stone–(Thrower)–Wales designation revisited. *Carbon* **2014**, *75*, 1–4. [[CrossRef](#)]
24. Kumeda, Y.; Wales, D.J. *Ab initio* study of rearrangements between C_{60} fullerenes. *Chem. Phys. Lett.* **2003**, *374*, 125–131. [[CrossRef](#)]
25. Babić, D.; Bassoli, S.; Casartelli, M.; Cataldo, F.; Graovac, A.; Ori, O.; York, B. Generalized Stone–Wales transformations. *Mol. Simul.* **1995**, *14*, 395–401. [[CrossRef](#)]
26. Ori, O.; Cataldo, F.; Putz, M.V. Topological anisotropy of Stone–Wales waves in graphenic fragments. *Int. J. Mol. Sci.* **2011**, *12*, 7934–7949. [[CrossRef](#)] [[PubMed](#)]
27. Ori, O.; Putz, M.V.; Gutman, I.; Schwerdtfeger, P. Generalized Stone–Wales transformations for fullerene graphs derived from Berge’s switching theorem. In *Ante Graovac—Life and Works*; Gutman, I., Pokrić, B., Vukićević, D., Eds.; University of Kragujevac: Kragujevac, Serbia, 2014; pp. 259–272.
28. Liu, Y.; Yakobson, B.I. Cones, pringles, and grain boundary landscapes in graphene topology. *Nano Lett.* **2010**, *10*, 2178–2183. [[CrossRef](#)] [[PubMed](#)]
29. Carpio, A.; Bonilla, L.L.; de Juan, F.; Vozmediano, M.A.H. Dislocations in graphene. *New J. Phys.* **2008**, *10*, 053021. [[CrossRef](#)]

30. Zhoua, L.G.; Shib, S.Q. Formation energy of Stone–Wales defects in carbon nanotubes. *Appl. Phys. Lett.* **2003**, *83*, 1222–1224. [CrossRef]
31. Collins, P.G. Defects and disorder in carbon nanotubes. In *Oxford Handbook of Nanoscience and Technology: Frontiers and Advances*; Narlikar, A.V., Fu, Y.Y., Eds.; Oxford University Press: Oxford, UK, 2011; Volume 2. [CrossRef]
32. Ewels, C.P.; Heggie, M.I.; Briddon, P.R. Adatoms and nanoengineering of carbon. *Chem. Phys. Lett.* **2002**, *351*, 178–182. [CrossRef]
33. Samsonidze, G.G.; Samsonidze, G.G.; Yakobson, B.I. Energetics of Stone–Wales defects in deformations of monoatomic hexagonal layers. *Comput. Mater. Sci.* **2002**, *23*, 62–72. [CrossRef]
34. Nordlund, K.; Keinonen, J.; Mattila, T. Formation of ion irradiation induced small-scale defects on graphite surfaces. *Phys. Rev. Lett.* **1996**, *77*, 699–702. [CrossRef]
35. Krashennnikov, A.V.; Nordlund, K.; Sirviö, M.; Salonen, E.; Keinonen, J. Formation of ion-irradiation-induced atomic-scale defects on walls of carbon nanotubes. *Phys. Rev. B* **2001**, *63*, 245405. [CrossRef]
36. Hashimoto, A.; Suenaga, K.; Gloter, A.; Urita, K.; Iijima, S. Direct evidence for atomic defects in graphene layers. *Nature* **2004**, *430*, 870–873. [CrossRef]
37. Kotakoski, J.; Krashennnikov, A.V.; Kaiser, U.; Meyer, J.C. From point defects in graphene to two-dimensional amorphous carbon. *Phys. Rev. Lett.* **2011**, *106*, 105505. [CrossRef] [PubMed]
38. RobertLovesPi: Polyhedra, tessellations, and more. Available online: <https://robertlovespi.net/c240-fullerene-1/> (accessed on 27 April 2020).
39. Pyshnov, M.B. Topological solution for cell proliferation in intestinal crypt. I. Elastic growth without cell loss. *J. Theor. Biol.* **1980**, *87*, 189–200. [CrossRef]
40. Branden, C.I.; Tooze, J. *Introduction to Protein Structure*, 2nd ed.; Garland Science: New York, NY, USA, 1999; pp. 1–302.
41. Twarock, R. Mathematical virology: A novel approach to the structure and assembly of viruses. *Philos. Trans. R. Soc. A* **2006**, *364*, 335–3373. [CrossRef]
42. Dechant, P.-P.; Wardman, J.; Keef, T.; Twarock, R. Viruses and fullerenes – symmetry as a common thread? *Acta Crystallogr. A* **2014**, *70*, 162–167. [CrossRef]
43. Iranmanesh, A.; Ashrafi, A.R.; Graovac, A.; Cataldo, F.; Ori, O. Wiener index role in topological modeling of hexagonal systems-from fullerenes to graphene. In *Distance in Molecular Graphs – Applications*; Gutman, I., Furtula, B., Eds.; University of Kragujevac: Kragujevac, Serbia, 2012; pp. 135–155.
44. Ori, O.; D’Mello, M. A topological study of the structure of the C₇₆ fullerene. *Chem. Phys. Lett.* **1992**, *197*, 49–54. [CrossRef]
45. Babić, D.; Klein, D.J.; Sah, C.H. Symmetry of fullerenes. *Chem. Phys. Lett.* **1993**, *211*, 235–241. [CrossRef]
46. Vukicevic, D.; Cataldo, F.; Ori, O.; Graovac, A. Topological efficiency of C₆₆ fullerene. *Chem. Phys. Lett.* **2011**, *501*, 442–445. [CrossRef]
47. Sabirov, D.S.; Ori, O.; László, I. Isomers of the C₈₄ fullerene: A theoretical consideration within energetic, structural, and topological approaches. *Fuller. Nanotub. Carbon Nanostruct.* **2018**, *26*, 100–110. [CrossRef]
48. Dobrynin, A.A.; Ori, O.; Putz, M.V.; Vesnin, A.Y. Generalized topological efficiency – case study with C₈₄ fullerene. *Fuller. Nanotub. Carbon Nanostruct.* **2020**, *28*, 545–550. [CrossRef]
49. Chen, Q.; Robertson, A.W.; He, K.; Gong, C.; Yoon, E.; Lee, G.D.; Warner, J.H. Atomic level distributed strain within graphene divacancies from bond rotations. *ACS Nano* **2015**, *9*, 8599–8608. [CrossRef] [PubMed]
50. Haddon, R.C. Chemistry of the fullerenes: The manifestation of strain in a class of continuous aromatic molecules. *Science* **1993**, *261*, 1545–1550. [CrossRef] [PubMed]
51. Astakhova, T.Y.; Vinogradov, G.A.; Gurin, O.D.; Menon, M. Effect of local strain on the reactivity of carbon nanotubes. *Russ. Chem. Bull.* **2002**, *51*, 764–769. [CrossRef]
52. Sabirov, D.S.; Bulgakov, R.G.; Khursan, S.L. Indices of the fullerene reactivity. *ARKIVOC* **2011**, *2011*, 200–224. [CrossRef]
53. Sabirov, D.S.; Bulgakov, R.G. Reactivity of fullerene derivatives C₆₀O and C₆₀F₁₈ (C_{3v}) in terms of local curvature and polarizability. *Fuller. Nanotub. Carbon Nanostruct.* **2010**, *18*, 455–457. [CrossRef]
54. Sabirov, D.S.; Garipova, R.R. The increase in the fullerene cage volume upon its chemical functionalization. *Fuller. Nanotub. Carbon Nanostruct.* **2019**, *27*, 702–709. [CrossRef]
55. Fowler, P.W.; Manolopoulos, D.E. *An Atlas of Fullerenes*; Dover Publications Inc.: Mineola, NY, USA, 1995; pp. 1–392.

56. Sure, R.; Hansen, A.; Schwerdtfeger, P.; Grimme, S. Comprehensive theoretical study of all 1812 C₆₀ isomers. *Phys. Chem. Chem. Phys.* **2017**, *19*, 14296–14305. [\[CrossRef\]](#)
57. Klyavlina, A.I.; Rysaeva, L.K.; Murzaev, R.T. Dislocation dipole in graphene at finite temperatures. *J. Phys. Conf. Ser.* **2020**, *1435*, 012063. [\[CrossRef\]](#)
58. Sabirov, D.S. Rules of fullerene polarizability. *Fuller. Nanotub. Carbon Nanostruct.* **2020**, *28*, 71–77. [\[CrossRef\]](#)
59. Plonska-Brzezinska, M.E. Carbon nano-onions: A review of recent progress in synthesis and applications. *ChemNanoMat.* **2019**, *5*, 568–580. [\[CrossRef\]](#)
60. Bartkowski, M.; Giordani, S. Supramolecular chemistry of carbon nano-onions. *Nanoscale* **2020**, *12*, 9352–9358. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Laikov, D.N.; Ustynyuk, Y.A. PRIRODA-04: A quantum-chemical program suite. New possibilities in the study of molecular systems with the application of parallel computing. *Russ. Chem. Bull.* **2005**, *54*, 820–826. [\[CrossRef\]](#)
62. Shestakov, A.F. Reactivity of fullerene C₆₀. *Russ. J. Gen. Chem.* **2008**, *78*, 811–821. [\[CrossRef\]](#)
63. Sabirov, D.S.; Khursan, S.L.; Bulgakov, R.G. 1,3-Dipolar addition reactions to fullerenes: The role of the local curvature of carbon surface. *Russ. Chem. Bull.* **2008**, *57*, 2520–2525. [\[CrossRef\]](#)
64. Sabirov, D.S.; Zakirova, A.D.; Tukhbatullina, A.A.; Gubaydullin, I.M.; Bulgakov, R.G. Influence of the charge on the volumes of nanoscale cages (carbon and boron-nitride fullerenes, Ge₉²⁻ Zintl ions, and cubic Fe₄S₄ clusters). *RSC Adv.* **2013**, *3*, 1818–1824. [\[CrossRef\]](#)
65. Tulyabaev, A.R.; Kiryanov, I.I.; Samigullin, I.S.; Khalilov, L.M. Are there reliable DFT approaches for ¹³C NMR chemical shift predictions of fullerene C₆₀ derivatives? *Int. J. Quant. Chem.* **2017**, *117*, 7–14. [\[CrossRef\]](#)
66. Pankratyev, E.Y.; Tulyabaev, A.R.; Khalilov, L.M. How reliable are GIAO calculations of ¹H and ¹³C NMR chemical shifts? A statistical analysis and empirical corrections at DFT (PBE/3z) level? *J. Comput. Chem.* **2011**, *32*, 1993–1997. [\[CrossRef\]](#) [\[PubMed\]](#)
67. Sabirov, D.S.; Kinzyabaeva, Z.S. Sonochemical synthesis of novel C₆₀ fullerene 1,4-oxathiane derivative through the intermediate fullerene radical anion. *Ultrason. Sonochem.* **2020**, *67*, 105169. [\[CrossRef\]](#)
68. Sabirov, D.S.; Garipova, R.R.; Cataldo, F. Polarizability of isomeric and related interstellar compounds in the aspect of their abundance. *Mol. Astrophys.* **2018**, *12*, 10–12. [\[CrossRef\]](#)
69. Sabirov, D.S.; Terentyev, A.O.; Shepelevich, I.S.; Bulgakov, R.G. Inverted thermochemistry of “norbornadiene–quadricyclane” molecular system inside fullerene nanocages. *Comput. Theor. Chem.* **2014**, *1045*, 86–92. [\[CrossRef\]](#)
70. Sabirov, D.S.; Tukhbatullina, A.A.; Bulgakov, R.G. Compression of methane endofullerene CH₄@C₆₀ as a potential route to endohedral covalent fullerene derivatives: A DFT study. *Fuller. Nanotub. Carbon Nanostruct.* **2015**, *23*, 835–842. [\[CrossRef\]](#)
71. Zakirova, A.D.; Sabirov, D.S. Volume of the fullerene cages of endofullerenes and hydrogenated endofullerenes with encapsulated atoms of noble gases and nonadditivity of their polarizability. *Russ. J. Phys. Chem. A* **2020**, *94*, 963–971. [\[CrossRef\]](#)
72. Shestakov, A.F. Role of fullerene–nitrogen complexes of alkali metals in C₆₀-catalyzed nitrogen fixation. *Russ. J. Phys. Chem. A* **2020**, *94*, 919–924. [\[CrossRef\]](#)
73. Pimenova, A.S.; Kozlov, A.A.; Goryunkov, A.A.; Markov, V.Y.; Khaverl, P.A.; Avdoshenko, S.M.; Vorobiev, V.A.; Ioffe, I.N.; Sakharov, S.G.; Troyanov, S.I.; et al. Preparation and structures of [6,6]-open difluoromethylene [60]fullerenes: C₆₀(CF₂) and C₆₀(CF₂)₂. *Dalton Trans.* **2007**, 5322–5328. [\[CrossRef\]](#)
74. Ignat’eva, D.V.; Goryunkov, A.A.; Tamm, N.B.; Ioffe, I.N.; Sidorov, L.N.; Troyanov, S.I. Isolation and structural characterization of the most highly trifluoromethylated C₇₀ fullerenes: C₇₀(CF₃)₁₈ and C₇₀(CF₃)₂₀. *New J. Chem.* **2013**, *37*, 299–302. [\[CrossRef\]](#)
75. Lukonina, N.S.; Semivrazhskaya, O.O.; Apenova, M.G.; Belov, N.M.; Troyanov, S.I.; Goryunkov, A.A. CF₂-functionalized trifluoromethylated fullerene C₇₀(CF₃)₈(CF₂): Structure, electronic properties, and spontaneous oxidation at the bridgehead carbon atoms. *Asian J. Org. Chem.* **2019**, *8*, 1924–1932. [\[CrossRef\]](#)
76. Diniakhmetova, D.R.; Friesen, A.K.; Kolesov, S.V. Quantum chemical analysis of the mechanism of the participation of C₆₀ fullerene in the radical polymerization of styrene and mma initiated by benzoyl peroxide or azobisisobutyronitrile. *Russ. J. Phys. Chem. B* **2017**, *11*, 492–498. [\[CrossRef\]](#)
77. Diniakhmetova, D.R.; Friesen, A.K.; Kolesov, S.V. Quantum chemical modeling of the addition reactions of 1-*n*-phenylpropyl radicals to C₆₀ fullerene. *Int. J. Quant. Chem.* **2016**, *116*, 489–496. [\[CrossRef\]](#)

78. Diniakhmetova, D.R.; Friesen, A.K.; Yumagulova, R.K.; Kolesov, S.V. Simulation of potentially possible reactions at the initial stages of free-radical polymerization of styrene and methyl methacrylate in the presence of fullerene C₆₀. *Polymer Sci. B* **2018**, *60*, 414–420. [[CrossRef](#)]
79. Khatymov, R.V.; Muftakhov, M.V.; Tuktarov, R.F.; Raitman, O.A.; Shokurov, A.V.; Pankratyev, E.Y. Fragmentation and slow autoneutralization of isolated negative molecular ions of phthalocyanine and tetraphenylporphyrin. *J. Chem. Phys.* **2019**, *150*, 134301. [[CrossRef](#)] [[PubMed](#)]
80. Khatymov, R.V.; Shchukin, P.V.; Muftakhov, M.V.; Yakushchenko, I.K.; Yarmolenko, O.V.; Pankratyev, E.Y. A unified statistical RRKM approach to the fragmentation and autoneutralization of metastable molecular negative ions of hexaazatrinaphthylenes. *Phys. Chem. Chem. Phys.* **2020**, *22*, 3073–3088. [[CrossRef](#)] [[PubMed](#)]
81. Kuznetsov, V.V. Stereochemistry of simple molecules inside nanotubes and fullerenes: Unusual behavior of usual systems. *Molecules* **2020**, *25*, 2437. [[CrossRef](#)] [[PubMed](#)]



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