Structural symmetry analysis of possible addition/elimination and isomeric rearrangement mechanisms of fullerenes

Ying-Nan Chiu a,b,*, Xuliang Jiang a, Pavel Ganelin a, Bo-Cheng Wang c

a Center for Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, DC 20064, USA
b Institute of Chemistry, Academia Sinica, Taipei, Taiwan
' Department of Chemistry, Tamkang University, Tamsui, 25137, Taiwan

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Abstract

This work displays two-dimensional planar diagrams of three-dimensional fullerene cage clusters to clearly visualize the symmetrical arrangements of the complete number of vertices (carbon atoms), edges (bonds) and faces (carbon rings) and to search for the possible isomeric rearrangement and addition/elimination reaction mechanisms. The reactionary symmetry correlation is based on the choice of the common subgroup symmetry for the total reaction coordinate — the latter comes from the combination of multiple sets of local reaction coordinates over the periodic surface of the fullerene cage. The symmetric analysis also involves the determination of the number of symmetry-equivalent ways for such combinations to generate the total reaction coordinate. The symmetry investigation also involves the hypothetical mechanisms for the addition (and elimination) of two (diatomic) carbon atoms to (and from) the reactant fullerene cage, to be followed by subsequent cooperative cage surface rearrangements over the cyclic boundaries to reach the structural symmetry of the final-product fullerene cage.

The diagrams and isomeric rearrangement mechanisms elaborated are C 76(D 2h) + C 2 (T d) → C 90(D 5h), C 60(I h) → C 78(C 3v), and C 76(D 2 ) → C 78(C 2v, D 3h ) → C 80(D 5d ) b.

1. Introduction

We have designed [1,2] two-dimensional diagrams of fullerene [3–6] structures that display completely and symmetrically all of the vertices (carbon atoms), faces (carbon rings) and edges (carbon–carbon bonds). These two-dimensional diagrams, with resemblance to and modification of the principle of Schlegel diagrams, avoid the possible confusion caused by crossing, overlapping and eclipsing of three-dimensional figures projected and flattened on a (two-dimensional) paper. Such clarify of symmetry and structure will be used here to search for and to elaborate the rearrangement, addition/elimination mechanisms that possess the common primary symmetry of the reactants and products. Such common symmetry was used in Woodward and Hoffmann's electronic symmetry correlation of chemical reactions [7–9]. We shall use some of the known (electronic) reaction mechanisms for small, isolated...
molecular systems — such as the dyotropic reaction [10,11] of 4e$^-$ pyracylene rearrangement [12–14], for example, related to $\text{C}_{78}(\text{C}_2v - D_{3h})$ [13]. But our emphasis is on the search for new types of reaction mechanisms and the periodic combination of a number of sets of identical new local reaction coordinates, in addition to the periodic combination of known isolated molecular reaction mechanisms. This is to facilitate the hypothesis of novel reactions of cage clusters which have periodic symmetry around the whole surface. The appropriate combination of multiple sets of the same-type of local reaction coordinates is to yield the transition state with a desired common subgroup symmetry of the overall (total) reaction mechanism of the whole fullerene cage.

The isomers enumerated are just possibilities and are not necessarily the common experimental probabilities. It is based on purely symmetry analysis of basic principles which may be useful for future extraordinary high energy reactions or for future new clusters.

The clear and exact preservation of closed cages in planar diagrams automatically contain and demonstrate the mathematical rules such as the Euler's rule for the number of pentagons, hexagons and heptagons for trivalent clusters. It will also develop new rules for different valency and different polygons.

The symmetry study is mainly for the case of continuously closed cage clusters with their periodic surface reactions. The symmetry considerations yield only one necessary condition and do not necessarily contain the sufficient satisfactory conditions such as the energetic requirement which remains to be numerically calculated later.

Before energetic evaluations [15], the general symmetry approach may be firstly to find the minimum allowed symmetry of multiple sets of reactionary breaking and formation of bonds. Our various symmetry analyzed combinations will in addition promote the qualitative visualization of the various possible (excited) isomers and various possible addition/elimination of two carbon atoms. Our symmetry designed multiple sets of identical local reaction coordinates do not necessarily mean simultaneous concerted reactions with combined and (multiple-level) raised high potentials. Rather, it may lead to consecutive step-by-step 'running-wave' reactions with cooperation factors across the whole periodic surface.

![Diagram](image)

Fig. 1. Rearrangement of $\text{C}_{60}(I_h)$ to $\text{C}_{60}(D_{6h})$, with breaking (-) 12 bonds and forming (...) 12 new bonds. The combination of six sets of dyotropic 4e$^-$ pyracylene reaction coordinates results in $S_6$ symmetry. There will be only 20 equivalent combinations because there are 20 hexagons. Even though there are left and right chiral combinations of reaction coordinates for each hexagon at the center, the front (center and small) and back (outermost and largest) hexagons share the common combination. There are also 20 equivalent combinations for $D_3$ symmetry.
For example, to visualize the isomeric rearrangement from $C_{60}(I_h)$ to one kind [2,16] of $C_{60}(D_{6h})$, we first draw a planar diagram of the reactant $C_{60}(I_h)$ that displays the common subgroup of three-fold symmetry belonging to the product $C_{60}(D_{6h})$ (Fig. 1). The total reaction mechanism involves the combination of six local sets of 4e⁻ pyracylene rearrangement reaction coordinates (Fig. 2). This 4e⁻ pyracylene rearrangement guarantees the preservation of the same number of pentagons and hexagons but may be thermally unfavorable. It is therefore of interest to produce new rearrangements through the two-dimensional diagrams, to be compared energetically by later numerical calculations. The combination has the overall possible symmetry of either $C_3$, $S_6$ or $D_3$ (still the common subgroups of $I_h$ and $D_{6h}$). But, each individual (say the first) local set of the reaction produces the abutting (merging) of a pentagon with the nearest neighboring pentagon. When the nearest neighboring (say the second) set of reaction coordinate is pressured by this abutting, it may immediately or cooperatively proceed to move. Again, it produces the abutting of the next (the third) neighboring pentagon (in this case, there is also the reverse abutting too!). The total reaction is complete when the six sets of reaction coordinates proceed consecutively around and come back to the periodic boundary of the first set. Therefore, it is somewhat like the running-wave ‘resonant’ motion across the whole surface. While we have illustrated the possible symmetry and possible interaction of local reaction coordinates, the result is an unusual, widely altered and excited isomer with a large number (6 sets) of abutting pentagons of high energy. The high energy may be due to the large number of sets of nearby (local) rearrangement coordinates. From the symmetry picture of our two-dimensional diagram, we can alternatively pick a smaller number of (three) sets of 4e⁻
pyracylene rearrangement reactions with a (common) subgroup $C_3$ symmetry (Figs 3 and 4). This will result in another possible isomer with different symmetry, fewer alternation and lower energy, i.e., the chiral $C_{60}(C_3)$ (Fig. 4) which has only three sets of (two) abutting pentagons and has six left-over separated pentagons which are far away and not affected during the rearrangement.

In addition to the above symmetry analysis, we can also count the number of bond breaking and bond formation based on the detailed symmetry picture. Similarly, we can also figure out the possible equivalent ways to combine the multiple sets of local reaction coordinates. Because each set of the $4e^-$ pyracylene rearrangement involves the breaking of two bonds and formation of two bonds, the three sets of such reactions of three-fold symmetry will have six bond breaking and six-bond formation. Because the three-fold symmetry is displayed by our two-dimensional diagram with a hexagon at the center surrounded by three equal systems of neighbors, we can determine that, based on the fact that there are twenty of such equivalent hexagons in $C_{60}(I_h)$, there may be twenty equivalent ways to combine three local sets of $4e^-$ pyracylene rearrangement reaction coordinates. But the two opposite hexagons, one on the front (center of the two-dimensional diagram) and one in the back (outermost of the two-dimensional diagram) have the same combined three-fold symmetry. Therefore, there are only $20/2 = 10$ equivalencies. However, because of the left/right chiral symmetry of $C_3$, we should enumerate this two times, resulting in $2 \times 10 = 20$ equivalent ways of combination for the overall reaction mechanism! This is just a simple example for a simple rearrangement reaction. Other examples in this work will provide guidelines for other complex, new reaction symmetry analysis.

Instead of the possibility of open cage cluster reactions [6,17–20], our purpose is to investigate the possible reactions with closed cage cluster surface based on the symmetry. Therefore, we will investigate the symmetry factors for the addition and elimination of hypothetically possible excited states of diatomic carbons with structures such as :C=:C: (related to four-bond breaking/formation) or :C–C: (related to six-bond breaking/formation). It is different from the reaction with $\text{H}_2\text{C}=\text{CH}_2$ such as the Diels–Alder reaction with butadiene (related to two-bond formation). For this concerted pericycle Diels–Alder reaction of isolated molecules, the common symmetry for the reaction coordinate is simply the reflection symmetry $C_s(\sigma_v)$ which is a common subgroup of the two-fold symmetries $C_2\nu$ and $D_{2h}$. For the addition/elimination of two carbon atoms, the reaction coordinate may also involve two-fold symmetries, such as $C_6(\sigma_v)$ or $C_2$. $C_6(\sigma_v)$, for example, is the common subgroup of the elimination of $C_{28}(T_d)$ towards $C_{26}(D_{3h})$ or addition towards $C_{30}(D_{5h})$ (Figs. 16 and 22). Besides designing the detailed new reaction mechanism, we shall also enumerate the equivalent combinations for the overall $\sigma_v$ symmetries of the total reaction mechanism. Based on the perfect $\pi$-bond resonance and
because of $T_d$ symmetry of $C_{28}$, there will of course be six $\sigma_d$ symmetry for the $C_s$ mechanism. Our symmetry diagram finally demonstrates that there are twelve equivalent $C_s$ combination mechanisms. Simultaneously, our complete detailed symmetry and bonding diagram will also give guide to the effect of non-resonant alternating ($\pi$) bonds on the structure and the symmetry of reactants and products. The display of fixed double bond (one $\sigma$ and one $\pi$) structures will show the possibility of addition of hydrogen atoms to the carbon atoms that have no such double bonds and have only three $\sigma$ bonds plus one odd $\pi$-electron, e.g., $C_7$ to $C_7H_4$ with the four hydrogens occupying $T_d$ symmetry positions [2]. In addition, it also gives the relationship of the reaction coordinates with the total normal mode of vibration of the reactants. The exploration of different symmetries of reaction coordinates will yield different possible reaction branches and will serve as basis for future numerical calculation of relative energies of reaction branches.

After the addition/elimination of two carbon atoms, our emphasis will be on the detailed planar diagram description that will provide the subsequent step-by-step bond breaking/formation rearrangements around the whole cage cluster surface to reach the symmetry of the product. Such symmetry analysis will also show the possible intermediate states and abnormal or new reaction processes, etc.

2. Isomeric rearrangements of $C_{60}(I_h, D_{5h}, C_{3v}, C_3, D_3)$ and the common subgroup symmetry of total reaction coordinates

The $C_{60}$ Buckyball has the highest, icosahedral ($I_h$) symmetry and has twelve low-strain non-abutting (separate) pentagons. It has major subgroups such as $D_{2h}, D_{3d}, D_{5d}, S_6, D_3$, etc. The isomeric $C_{60}$ with one kind of (we name it “b” type) $D_{5h}$ symmetry has the same number of pentagons. But these twelve pentagons have six sets of higher strain double abutting, with every two abutting pentagons share one common edge [16]. The $D_{5h}$ isomer has major subgroups such as $D_{2h}, D_{3d}, D_{3h}, C_{6h}, S_6, D_3, C_6, C_3$, etc. The isomeric rearrangement from $C_{60}(I_h)$ to $C_{60}(D_{5h})b$ implies the transition state of the common three-fold subgroup symmetry ($C_3, D_3$) or $S_6$ subgroup symmetry in the reaction mechanism. The merging of two pentagons in the isomeric transformation is due to the two neighbouring $4e^-$ pyracylene rearrangement reactions (Fig. 1). The bond movements of the six sets of this rearrangement which has overall $S_6$ symmetry correspond to the antisymmetric $A_u$ vibrational normal mode of the icosahedral $I_h$ symmetry of $C_{60}$. The vibrational correlation to the non-vibrating totally symmetric $C_{60}(D_{5h})$ product is as follows:

$$I_h(A_u) \Rightarrow D_{3d}(A_{1u}) \Rightarrow S_6(A_u) \Rightarrow [C_3(A)]$$

$$= [D_3(A_1)] \leftarrow S_6(A_g) \leftarrow D_{3d}(A_{1g}) \leftarrow D_{5h}(A_{1g})$$

(1)

If the ground electronic states of the reactant and the product are both totally symmetric, the qualitative electronic correlation may be as follows:

$$I_h(A_{1g}) \Rightarrow D_{3d}(A_{1g}) \Rightarrow S_6(A_g) \Rightarrow [C_1(A)]$$

$$= [D_3(A_1)] \leftarrow S_6(A_g) \leftarrow D_{3d}(A_{1g}) \leftarrow D_{5h}(A_{1g})$$

(2)

For this cage cluster rearrangement, it should be noticed that the $4e^-$ pyracylene rearrangement here is not the same as that in the usual isolated molecular rearrangement (Fig. 2). The latter case involves eight lonely unaffected hydrogen atoms around the sides of the molecule. The cage cluster case involves eight unaffected $C-C \sigma$ bonds attached to the neighboring cluster atoms. The above mentioned six sets of dyotropic $4e^-$ pyracylene rearrangements will convert the reactant $C_{60}(I_h)$ to $C_{60}(D_{5h})b$. Afterwards, an additional three sets of these dyotropic rearrangements with overall $C_3$ symmetry can convert the product $C_{60}(D_{5h})b$ to the next higher energy isomeric product $C_{60}(C_{3v})b$. The latter has three groups of three abutting pentagons (Fig. 3). The three sets of dyotropic rearrangements with overall $C_3$ symmetry can also convert $C_{60}(I_h)$ to chiral $C_{60}(C_1)$ (Fig. 4). In all of these cases, the common subgroup $C_3$ symmetry is satisfied. The above isomerizations all involve combinations of sets of well-known $4e^-$ pyracylene rearrangements. Three sets involve six-bond breaking and six-bond formation. Six sets involve 12 bond breakage and 12 bond formation.
A much more intriguing complex reaction can involve, besides the six sets of such dyotropic reaction, six other sets of different rearrangements connected with these dyotropic reactions. This is the case of the transformation from $C_{60}(I_h)$ to an isomer of an alternative (we name it “a” type) $D_{6h}$ symmetry [16,21] and with two groups of six abutting pentagons (Fig. 5) which have much more constraint energy. There are twelve sets of local reaction coordinates involving 24 bond breakage and 24 bond formation. Among these twelve sets, a combination group of 3 sets of rearrangements maintains $C_3$ symmetry. There are four groups of such $C_3$ symmetry combination. These may not be the most realistic procedures. Nevertheless, these complete group symmetry analysis will provide the basis for future numerical analysis of the possibility of three intermediate states (each intermediate state comes from each group of $C_3$ combination) before reaching the final product state through the fourth group.

In the above cases, even with the shifts and
inter-conversions of hexagons and pentagons, the $C_{60}$ isomers with 60 vertices ($V$) still contain 12 pentagons and 20 hexagons,

$$V = \frac{1}{3} \sum nF_n; \quad V = 60 = \frac{1}{3}(5 \times 12 + 6 \times 20)$$

where $F_n$ stands for the number of $n$-vertex polygons ($n$-edge carbon ring structure). We shall use symmetry analysis based on our two-dimensional diagrams to investigate the production of different numbers of polygons by new reaction mechanisms. The mechanisms may continue to maintain the possession of trivalent three $\sigma$ bonds and one $\pi$ bond for each carbon atom. And the breakage of two bonds will be compensated by the formation of two bonds either within the set of the local reacting system or connected with the neighbor. As an example, we shall convert the latest isomer of Fig. 5, $C_{60}(D_{6h})_h$ into another $C_{60}(C_{3v})_h$ (Fig. 6), but with a different dyotropic rearrangement [22] for the formation of a heptagon next to the pentagon similar to an azulene (Fig. 7). But it is a new cage cluster surface rearrangement mechanism different from the isomeric conversion of an isolated naphthalene $C_{10}H_8$ into azulene. In this isolated molecular case, there are two atoms that interchange from three $\sigma$ bonding to two $\sigma$ bonding. As a result, the carbon atom that previously has two $\sigma$ bonds, now transfers its hydrogen to the new two-sigma bonding carbon atom. At the same time, there is also $\pi$-bond resonance transfer. In contrast, the polyhedron $C_{60}(D_{6h})_h$ rearrangement to $C_{60}(C_{3v})_h$ can involve no $\pi$-bond resonance transfer and no exterior (side) bonding displacement (Fig. 7). The changes in the number of polygonal faces result in 15 pentagons (from the initial 12), 3 heptagons (from the initial zero) and a decrease of six hexagons (from the initial 20) resulting in only 14 left-over hexagons. This means the equal number of increase of pentagons and heptagons via the hexagons. Because the decrease of the vertex from hexagon to pentagon is compensated by the identical increase of vertex from hexagon to heptagon, the number of vertices is the same after such isomerization. The carbon vertices ($V$) are now (for $C_{60}(C_{3v})_h$) evaluated as follows:

$$V = 60 = \frac{1}{3}(5 \times 15 + 6 \times 14 + 7 \times 3)$$

This is because each trivalent vertex is still shared by three polygonal faces (carbon rings) as well as shared by three edges (bonds). The final numbers of pentagons ($F_5$) minus the newly increased number of heptagons ($F_7$) is $F_5 - F_7 = 12$, which was the
initial number of pentagons. Because the total increase of pentagons and heptagons (= 2F7) is at the expense of hexagons, the final number of hexagons (Fe) can be obtained as follows:

\[ V = \frac{1}{2} \left[ 5 \times F_5 + 6 \times F_6 + 7 \times F_7 \right] \]

\[ = \frac{1}{2} \left[ 5 \times (12 + F_7) + 6 \times F_6 + 7 \times F_7 \right] \]

\[ F_6 = \frac{1}{2} \left( V - \frac{5 \times 12}{3} \right) - (5 + 7) \times F_7 \]

\[ = \frac{1}{2} \left( V - 20 \right) - 2 \times F_7 \]  

(4b)

From (4a) or (4b), we get:

\[ 14 = \frac{1}{2} (60 - 20) - 2 \times 3 \]  

(4c)

This means that our exact and clear two-dimensional diagrams enable us to continuously obtain the correct closed cage cluster structures of fullerenes that automatically contain and satisfy the Euler’s rule. As an extreme case based only on symmetry, the intermediate state for \( C_{60}(I_h) \) rearrangement to \( C_{60}(D_{6h}) \) may even contain nine-vertex carbon rings (nonagons) besides heptagons, and the whole cage cluster possesses the common subgroup \( D_3 \) symmetry (Fig. 8). The unusual aspect of this case is that some of the vertices have two and not three \( \sigma \) bonds and have two rather than one \( \pi \) bond, which also satisfy a different Euler’s rule of \( V + \sum_a F_a = e + 2 \) where \( e \) is the number of edges (bonds) (see caption of Fig. 8 and Eq. (6e) below).

In the above-mentioned rearrangements of \( C_{60}(I_h)\), because the reaction mechanism and the product have common three-fold symmetry (or \( S_6 \) symmetry), therefore, we draw \( C_{60}(I_h) \) in a planar diagram with three-fold symmetry of a central hexagon surrounded by three equivalent neighboring rings. In case we want to have rearrangements to a chiral isomer with \( D_5 \) symmetry, then we should rather draw the \( C_{60}(I_h) \) in a two-dimensional planar diagram with a (central) pentagon showing the five-fold symmetry of \( I_h \). The combination of five sets of 4e- pyracylene rearrangements with the common subgroup \( C_5 \) symmetry will then lead to the \( C_{60}(D_2) \) isomer (Fig. 9). This is again the advantage of the completely displayed fullerenes on planar diagrams for symmetry analysis.

3. Isomeric rearrangement of \( C_{76}(T_d, D_2, C_3) \), \( C_{84}(T_d, C_3, C_{3v}) \) and the number of equivalent ways to generate the combinations for common subgroup reaction coordinates

We had derived [2] the \( C_{76} \) structure with \( T_d \) symmetry (along with different stylistic \( T_d \) structures of \( C_{25}, C_{40}, C_{56}, C_{68}, C_{84}, C_{92}, C_{112}, C_{164}, \) etc.). The known chiral structure of \( C_{76} \) is of \( D_2 \) symmetry [23,24]. Because \( D_2 \) is already a
Fig. 7. Contrast of the rearrangement mechanisms from $C_{60}(D_{5h})_a$ to $C_{60}(C_{3v})_a$ (Fig. 6) and from naphthalene to azulene. The upper part shows the special set of local rearrangement in the reaction from $C_{60}(D_{5h})_a$ to $C_{60}(C_{3v})_a$ whereas the bottom part shows the rearrangement in the reaction from naphthalene to azulene. All atoms in the former reaction maintain three $\sigma$ and one $\pi$ bonds, and there is no motion of double bonds. In the latter reaction, however, two atoms interchange one $\sigma$ bond and a hydrogen atom shifts from one carbon to another carbon, and there is movement of double bonds. This local rearrangement from $D_{5h}$ to $C_{3v}$ involves the same formation and breakage of two bonds as the 4e$^-$ pyracylene rearrangements. But it causes the change of [3 hexagons + 1 pentagon] to [1 hexagon + 2 pentagons + 1 heptagon]. The sum of equal number of increase of pentagons and heptagons is equal to the total decrease of hexagons. It also satisfies the Euler’s rule of Eq. (4b).

subgroup of $T_d$, to convert $T_d$ into a chiral $D_2$ symmetry isomer we need only to find the total reaction coordinates that correlate with the "A" irreducible representation of $D_2$. The irreducible representation correlations are:

$$
T_d(A_2) = D_{2d}(B_1) = D_2(A);
$$
$$
T_d(E) = D_{2d}(A_1 + B_1) = D_2(A + A);
$$
(5)

The vibration of $T_d$ symmetry system (such as the CH$_4$ molecule system [25]) has $\nu(E)$ in which the bending vibration $\nu(E_{b1}) = \nu(E_{\pi})$ will yield $A_2$ of $D_{2d}$. Only the twisting vibration of $\nu(E_{s1}) = \nu(E_{\sigma})$ will yield the $B_1$ motion of $D_{2d}$ that continues to distort the $D_{2d}$ structure into a subgroup $D_2$ chiral structure. For the conversion into a two-fold symmetry of $D_2$, we choose to draw the $D_{2d}$ subgroup aspect of the $C_{76}(T_d)$ structure in a two-dimensional planar diagram. The combined bond-breakage and bond-formation reaction coordinates related to the twisting vibration $\nu(E_s)$, which has two-fold $C_2$ symmetry, then rearrange $C_{76}(T_d)$ into $C_{76}(D_2)$ (Fig. 10). Our two-dimensional diagram shows an alternative position to generate another $C_2$ reaction coordinate (factor of 2) on the same ‘plane’ with the same $C_2$ axis. In addition, the point group of $C_{76}(T_d)$ has three equivalent $C_2$ axes belonging to the same class (factor of 3). Therefore, based on these factors, there will be a total of $2 \times 3 - 6$ equivalent ways to generate the $C_2$ common subgroup rearrangement reaction coordinates. However, even though the overall rearrangement symmetry is correct, the mechanism is very complicated — involving 25 bond breakages and 25 bond formations. A simpler mechanism that yields another chiral isomeric structure $C_{76}(C_3)_a$
Fig. 8. $C_{60}(D_3)$: a possible unusual intermediate state from $C_{60}(I_h)$ transformation resulting in 12 pentagons, two hexagons, six heptagons (VII) and six nonagons (IX). Each heptagon (VII) has an unusual carbon with only two $\sigma$ bonds, and each nonagon (IX) has three unusual carbons of which each has only two $\sigma$ bonds. The counting of total vertices is: $V = 60 = 1/3 \times (5 \times 12 + 6 \times 2 + 7 \times 6 + 9 \times 6) + (1/2 - 1/3) \times [1 \times 6 + 3 \times 6]$. This also satisfies the Euler's rule (of Equation 6e): $V + \sum F_a = e + 2$, because $60 + (12 + 2 + 6 + 6) = 84 + 2$. The number of edges/bonds ($e$) can be counted exactly from the planar diagram or obtained from $e = \frac{1}{2} \sum nF_a = 84$. The combination reaction coordinate has $D_3$ symmetry and involve breakage of 18 bonds and formation of 12 bonds. There will be 20 equivalent ways for the combination of six sets of local reaction mechanisms.

needs the common subgroup 3-fold $C_3$ symmetry. Therefore we start by drawing the 3-fold $C_{3v}$ (instead of the two-fold $D_{2d}$) planar diagram of $C_{76}(T_d)$ (Fig. 11). We found it to be still a fairly complex new mechanism with 12 bond breakages and 12 bond formations coming from three sets of local rearrangement coordinates. Each set has four bond breakage and four bond formation and each

Fig. 9. The isomeric rearrangement from $C_{60}(I_h)$ to $C_{60}(D_3)$. The alternative drawing of $C_{60}(I_h)$ in a two-dimensional diagram shows the five-fold symmetry. The overall (combined) reaction coordinate has $C_5$ symmetry and there are twelve equivalent ways to combine five sets of 4e$^-$ pyracylene rearrangements.
Fig. 10. The isomeric rearrangement from $C_{76}(T_d)$ to $C_{76}(D_2)$. The overall reaction coordinate symmetry is $C_2$. There are six equivalent ways for the overall reaction. Each involves the breakage of 25 bonds and the formation of 25 new bonds. Both the reactant and the product have 12 pentagons and 28 hexagons.
The isomeric transformation from C_{76}(T_d) to C_{76}(C_3). The overall combined reaction-coordinate symmetry is C_3. There are eight equivalent ways to combine the three sets of local reaction mechanisms. Eight is equal to 4 tetrahedral corners multiplied by two (reflection of bond formation and breakage). The total number of breakage of bonds is twelve and the formation of new bonds is also twelve. The counting of vertices for the reactant and product is as follows:

\[ V = \frac{1}{3} \sum_{n} nF_n = \frac{1}{3} (5 \times 12 + 6 \times 28) = \frac{1}{3} (5 \times 15 + 6 \times 22 + 7 \times 3) = 76. \]

The final number of hexagons \( F_6 = 22 = 1/2(76 - 20) - 2 \times 3 = 1/2(V - 20) - 2F_7 \) (see Eq. (4)). It agrees with Euler’s rule.

set converts one hexagon to heptagon and one hexagon to pentagon (Fig. 12) with a total of three new heptagons and three more pentagons (the total becomes 15) and a loss of six hexagons resulting in 22 left-over hexagons. Therefore, the number of polygons \( \sum F_n \) is the same for these isomers. The summations for the vertices are:

\[ V = 76 = \frac{1}{3} (5 \times 12 + 6 \times 28) = \frac{1}{3} \sum_{n} nF_n \]

for \( C_{76}(T_d) \) and \( C_{76}(D_2) \) \( (6a) \)

\[ V = 76 = \frac{1}{3} (5 \times 15 + 6 \times 22 + 7 \times 3) = \frac{1}{3} \sum_{n} nF_n \]

for \( C_{76}(C_3) \) \( (6b) \)

\[ F_6 = 22 = \frac{1}{2} (76 - 20) - 2 \times 3 \]

\( (6c) \)

Because both are still closed cage clusters, each edge (bond) is shared by two polygons. The number of edges \( (e) \) is the same for these isomers (of (6a) and (6b)).

\[ e = \frac{1}{2} \sum_{n} nF_n = \frac{1}{2} (5 \times F_5 + 6 \times F_6 + 7 \times F_7) \]

\[ = \frac{1}{2} \times 228 = 114 \]

(6d)

The number of vertices (76) is also the same because of the isomeric reaction mechanism. Our structural confirmations automatically satisfy the Euler’s rules for both cases.

\[ V + \sum F_n = e + 2 \]

\[ 76 + 40 = 114 + 2 \]

(6e)

This is interesting because of the new cage cluster surface rearrangement mechanisms (Fig. 12) due to the consecutive cooperative reaction with next neighbors. Our two-dimensional diagram shows that there are two equal ways to generate \( C_3 \) symmetry combination coordinates on a given plane with the same \( C_3 \) axes. In addition the point group \( T_d \) has four \( C_3 \) symmetry axes in the same class. Therefore, there will be \( 2 \times 4 = 8 \) equivalent ways to generate the combination of local reaction

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\[ 76 + 40 = 114 + 2 \] (6e)

This is interesting because of the new cage cluster surface rearrangement mechanisms (Fig. 12) due to the consecutive cooperative reaction with next neighbors. Our two-dimensional diagram shows that there are two equal ways to generate \( C_3 \) symmetry combination coordinates on a given plane with the same \( C_3 \) axes. In addition the point group \( T_d \) has four \( C_3 \) symmetry axes in the same class. Therefore, there will be \( 2 \times 4 = 8 \) equivalent ways to generate the combination of local reaction
Fig. 12. (a) The one (out of three) special set (top line plus bottom line) of the interconnected local reaction mechanism for the rearrangement from $C_76(T_d)$ to $C_76(C_3)_2$. If we add (dotted lines) the crucial hexagons then the reaction from [one pentagon + three hexagons] to [two pentagons + one hexagon + one heptagon] is the same as Fig. 7. However, because of the connection with the next neighboring reaction, the newly produced crucial pentagon (64, 65, 66, 75, 74) on the top line will react further and change back to the original crucial hexagon. Similarly, the newly produced crucial heptagon (55, 56, 36, 37, 38, 58, 57) on the bottom line will also react further and change back to the original crucial hexagon. Therefore, these two (top and bottom) crucial hexagons are not counted. The overall changes (top plus bottom) is from [2 pentagons + 4 hexagons] to [3 pentagons + 2 hexagons + 1 heptagon]. The increase of (one) pentagon is the same as the increase of (one) heptagon, and the decrease of (two) hexagons is the sum of the increase of pentagon plus hexagon. Such increase and decrease of two connected mechanisms are the same as the one set in Fig. 7, but the periodic cooperation of reaction is unique and different although it looks like that it should be a double set of Fig. 7. (b) The combination of the above two mechanisms. We will name this as 8e− penta–hexa–hepta rearrangement.
coordinates with overall $C_3$ common subgroup symmetry. Due to the clear display of symmetry in the $C_{76}(T_d)$ planar diagram, we found that even with three sets of the conventional 4e$^-$ pyracylene rearrangement we can also get a chiral $C_{76}(C_3)_b$ isomer (Fig. 13). It has the same number of (12) pentagons and (20) hexagons, except that there are three groups of abutting double pentagons (Fig. 13). Similarly, we found that we can use three sets of 4e$^-$ pyracylene rearrangements.
to transform $C_{84}(T_d) [2]$ into a chiral $C_{84}(C_3)$ (Fig. 14) and also transform $C_{84}(D_{6h}) [2]$ into a subgroup symmetry of $C_{84}(C_{3v})$ (Fig. 15). Because $C_{84}$ is a large structure (with 32 hexagons), our two-dimensional diagram of $C_{84}(T_d)$ shows that there are two equivalent ways (factor of 2) to place the pyracylene bond formation lines on the hexagons. Such double placement is not expressed by the pure mathematical group character table. Furthermore, the $C_3$ symmetry combination of pyracylene rearrangements can have left versus right (factor of 2) chirality (only in this case it can be compared with the $C_{3}^{\pm}$ and $C_{3}^{-}$ operations in the group character table). In addition, there are four $C_3$ axes in $T_d$ (factor of 4). Therefore there are a total of $2 \times 2 \times 4 = 16$ equivalent ways for the $C_3$ symmetry combination of three $4e^-$ pyracylene rearrangements for the isomeric transformation from $C_{84}(T_d)$ to $C_{84}(C_3)$. Because of the large structure and the separation of pentagons in $C_{84}(T_d)$, there will be no neighboring cooperations between the three $4e^-$ pyracylene rearrangements.

4. **Symmetry analysis of possible fullerene surface addition/elimination reaction mechanisms and subsequent boundary rearrangements**: $C_{78}(D_3) \rightarrow C_{78}(C_{2v}, D_{3h}) \rightarrow C_{90}(D_{5d})$; $C_{26}(D_{3h}) \rightarrow C_{28}(T_d) \rightarrow C_{30}(D_{5h})$; $C_{60}(I_h) \rightarrow C_{58}(C_{3v})$

We are not investigating the addition and elimination of two carbon atoms for the growth and shrinkage of open carbon clusters [6,17–20] — clusters which close up later as cage fullerenes. Instead, we consider the possible symmetry aspects of addition/elimination of two carbon atoms on the fullerene ‘ball’ surface, resulting in different sizes and different symmetries of fullerenes. This is not the simple reaction of isolated molecules at functional positions only. It also involves the subsequent cooperative rearrangements of many neighboring periodic cluster surface structures following addition/elimination. It therefore deals with postulates of new macromolecular polyhedron reaction mechanism that have the common subgroup symmetry (of the intermediate and final structures) of reactants and products. It can be relevant to the electronic symmetry correlation of chemical reactions that involve the frontier electron in orbitals of the same irreducible representation of the same common subgroup of reactants and products.

Because the diatomic carbon $C_2$ reactant has planar reflection ($\sigma_v$) and two-fold rotation ($C_2$ for $180^\circ$) symmetry, it is necessary that the complete reaction mechanism must contain the subsequent rearrangements (bond breakage and formation) that also have this symmetry as the common subgroup symmetry of reactants and products. For example, the growth of $C_{28}(T_d)$ to $C_{30}(D_{5h})$ [16,26] involves the reactant symmetry $T_d$ which has high-level subgroups of $C_{3v}$, $D_{2d}$ and $T$ and the product symmetry $D_{5h}$ which has high-level subgroups of $C_{2v}$, $D_{5}$, $C_{5h}$ and $C_{3v}$. The common minimum symmetry is the $C_3(\sigma_v)$ of :C=C:C: which can produce four new bonds on the surface of the $C_{28}(T_d)$ (Fig. 16). According to
Fig. 16. Addition of two carbon atoms (29–30) to \( C_{2s}(T_d) \) to become \( C_{3g}(D_{5h}) \) and the reverse process of elimination of two carbon atoms. There is no change on double bonds. The combination of two sets of reaction coordinates results in overall \( \sigma_v \) symmetry of the reaction mechanism for the resonant structure. There will be twelve equivalent ways of such combinations of reactions, corresponding to twelve edges of the cube that contain \( T_d \) symmetry. There will be a breakage of six bonds and formation of eight new bonds in the addition. The reverse elimination involves breakage of eight bonds and formation of six new bonds. Both the reactant and the product have 12 pentagons. \( C_{2s}(T_d) \) has four hexagons and \( C_{3g}(D_{5h}) \) has one more, i.e., 5 hexagons.

Feyereisen et al., the \( C_{2s}(T_d) \) ground state is \(^5\)A\(_{2}\). It therefore has four free (radical) electrons. Therefore, it is perhaps not very surprising that it can combine with the four electrons in :C=C:. The subsequent rearrangement coordinate of the \( C_{2s}(T_d) \) atoms must also maintain this \( \sigma_v \) symmetry in order to transform to \( C_{3g}(D_{5h}) \). The interesting point is that the addition of two carbon atoms change the 3-fold subgroup symmetry of \( T_d \) into the 5-fold symmetry of \( D_{5h} \). In detail, it changes the 3-fold symmetry of 3 sets of equivalent double pentagons into the 5-fold symmetry of five pentagons. Because of this change from three-fold to five-fold symmetry, we started by drawing the reactant \( T_d \) structure in a two-dimensional diagram showing the subgroup \( C_{3v} \) with three-fold symmetry. The principal new reaction mechanism involves formation of eight new bonds and

Fig. 17. The mechanism of addition of two carbon atoms (29–30) into \( C_{2s}(T_d) \) to become \( C_{3g}(D_{5h}) \) (and the reverse mechanism of elimination). It involves 'periodic' rearrangement of pentagons and hexagons with only one net increase of hexagon.
breakage of six bonds (Fig. 17). These are beyond the four-bond formation of the addition of :C=C: because of the necessity of the subsequent rearrangement of the closed cage cluster (surface). The diatomic C_2 can approach the C_{58}(T_d) in twelve equivalent ways (six \sigma_d of T_d multiplied by two) of maintaining C_6(\sigma_v) symmetry, and producing the addition reaction. In detail, this is similar to the approach to the 12 edges of the cube that contains the T_d symmetry. The latter has six

---

**Fig. 18.** The addition of two carbon atoms (77–78) to C_{76}(D_2) resulting in C_{78}(C_{2v}). The overall reaction-coordinate has C_3 symmetry. The reaction involves the breakage of 15 bonds and formation of 15 bonds (not counting the one-bond breakage of the added diatomic carbon atoms). Both the reactant and the product have 12 pentagons. C_{76}(D_2) has 28 hexagons and C_{78}(C_{2v}) has one more, i.e., 29 hexagons.
“equivalent” \( \sigma_d \) operations of the same class. Each of the \( \sigma_d \) plane can have two equivalent addition reaction mechanisms — one on each of the two ends of the plane. These ends of the plane and the edges of the \((O_b)\) cube which contains the \(T_d\) subgroup (the other two ends of the plane are on the two faces of the cube). This is far different from the Diels–Alder reaction of ethylene with butadiene that involves only one way of formation of two bonds by the two carbon atoms of ethylene. This Diels–Alder reaction needs little subsequent (\( \sigma \)-bond breaking and forming) rearrangements except only one \( \pi \) bond movement to the center of butadiene.

As an alternative way of adding two carbon atoms to the surface of a fullerene cluster, we consider the growth of \( \sigma_v \) to \( \sigma_v \) \( \left[13\right] \) (Fig. 18). Because of the common two-fold symmetry, we start by drawing the reactant \( C_{76}(D_2) \) in a planar diagram with \( C_v \) symmetry which is shared by the product \( C_{78}(D_{2v}) \) as well as by the approaching fellow (addition) reactant which we consider to be \( :C=C:\) (instead of the previous \( :C=C:\) ). This fellow reactant will form six bonds with \( C_{76}(D_2) \) and maintain two-fold \( C_2 \) symmetry (Fig. 19). Although \( D_2 \) symmetry has three two-fold \( C_2 \) operations, yet these \( C_2 \)'s are of different classes.

Therefore, they do not provide the equivalent ways of the addition reaction mechanisms. After \( C_{78}(C_{2v}) \) has been produced, another \( 4e^- \) pyracylene rearrangement \( \left[13\right] \) can change it to \( C_{78}(D_{3h}) \) (Fig. 20). For further isomeric rearrangement to go to the chiral \( C_{78}(D_3) \) \( \left[13\right] \), we would rather draw the planar diagram of \( C_{78}(D_3) \) \( \left[13\right] \) in such a way that it shows the common \( C_3 \) symmetry between \( D_{3h} \) and \( D_3 \) (Fig. 21). Combination of three sets of \( 4e^- \) pyracylene rearrangements with overall \( C_3 \) symmetry will be the total reaction coordinate of this isomeric transformation.

As a reversal, next we will explore the possible ways of the elimination of two carbon atoms from the fullerene cage cluster. For one of the new mechanisms, consider the shrinkage of \( C_{78}(T_d) \) to \( C_{28}(D_{3h}) \) \( \left[26,27\right] \) (Fig. 22). The product symmetry of \( D_{3h} \) has high level subgroups such as \( D_3, C_{3h}, C_3, \) and \( C_{2v} \). Although it shares a common \( C_{3v} \) subgroup with the reactant \( C_{28}(T_d) \), the other fellow (elimination) product of a diatomic carbon has a two-fold (reflection) symmetry. Therefore, we found a reaction mechanism with an overall \( C_\oplus (\sigma_v) \) common subgroup symmetry (Fig. 22). The two carbon atoms eliminated are considered to be \( :C=C:\) with four bonds broken from \( C_{28}(T_d) \) fullerene surface (Fig. 23). The reverse reaction of
Fig. 20. The $C_{78}(D_{3h})$ formed from $C_{18}(C_{2v})$ through one 4e- pyracylene rearrangement of $C_2$ symmetry. The indication of breakage of two bonds and formation of two bonds is the reverse 4e- pyracylene rearrangement to return to $C_{18}(C_{2v})$. One two-dimensional diagram shows the $C_2$ symmetry of $D_{3h}$, and the other of the same $C_{78}(D_{3h})$ shows clearly the 5-fold symmetries.
Fig. 21. The isomeric rearrangement from $C_{60}(f_{5})$ to $C_{60}(D_{5})$. The alternative drawing of $C_{60}(f_{5})$ in a two-dimensional diagram shows the five-fold symmetry. The overall reaction coordinate has $C_{5}$ symmetry and there are twelve equivalent ways to combine five sets of 4e- pyracylene rearrangements.

Fig. 22. Elimination of two carbon atoms (27–28) from $C_{26}(T_{d})$ to $C_{26}(D_{3h})$. There are no changes of double bonds. The equivalent ways of the combination for the overall elimination coordinates are twelve, due to four tetrahedral corners multiplied by 3 edges. Total number of breakage of bonds is twelve and total number of formation of new bonds is ten. The dotted lines on $C_{26}(D_{3h})$ represent bonds from the bottom carbon No. 17 to carbon atoms No. 20, 22 and 24 forming three pentagons underneath. Both the reactant and the product have 12 pentagons. While $C_{26}(T_{d})$ has 4 hexagons, $C_{26}(D_{3h})$ has one less, i.e., 3 hexagons.
addition from $C_{26}(D_{3h})$ to $C_{28}(T_d)$ may be compared with the addition reaction of from $C_{28}(T_d)$ to $C_{30}(D_{5h})$ which also involves $:C\equiv C:$ (Fig. 16).

This $\sigma_v$ symmetry elimination reaction from $C_{28}(T_d)$ will have twelve equivalent ways. This again is due to the fact that the reactant of $T_d$ symmetry has six $\sigma_d$ operations of the same class. And each $\sigma_d$ plane again has two ends at the edges of the $(O_h)$ cube that contains the $T_d$ subgroup. Each of the twelve edges has an equivalent way of the elimination reaction. For another different new mechanism of elimination, we consider the shrinkage from $C_{60}(I_h)$ to $C_{58}(C_{3v})$ (Fig. 24).

Because the product of three-fold $C_{3v}$ symmetry is already the subgroup of the reactant $I_h$, we purposely propose a special and simple three-fold $C_3$ symmetry reaction coordinate which involves the breakage of two carbon atom in three ‘degenerate’ reaction directions (Fig. 25). The elimination involves two nearby (meta-) carbon atoms of a hexagon. Each has broken three bonds from $C_{60}(I_h)$ and the two meta-neighbors yet may form a bond mutually to become a $:C\equiv C:$ type diatomic carbon. It is the same diatomic carbon as the previously shown forward and backward reaction of $C_{76}(D_2)$ and $C_{78}(C_{2v})$ (Figs. 18 and 19), although...
the latter reaction involves two para-carbon atoms instead of two meta-carbon atoms form a hexagon. The special interest of the elimination of two meta-carbon atoms from a hexagon in \( \text{C}_{60}(I_h) \) is that there will be equivalent elimination reactions from the 20 hexagons. Each hexagon has three degenerate reaction ways (Fig. 25) and each also has two, left and right, \( C_3 \) chiral reaction directions. The total number of equivalent reaction mechanisms is \( 3 \times 20 \times 2 = 120 \). A large number indeed for our proposed special simple reaction!

Our hypothesis is an alternative of the elimination of two ortho-carbon atoms from the sharing edge of two abutting pentagons proposed by O’Brien et al. [28]. We are not limited to the starting reactant structure with exactly two abutting pentagons sharing one edge (e.g., our next \( \text{C}_{80} \rightarrow \text{C}_{78} \) involves two ortho-carbon atoms from the sharing edge of two abutting hexagons of \( \text{C}_{80} \)). Furthermore, our hypothesis must involve the subsequent symmetry rearrangement of the nearby cage surface after addition/elimination. Of course,

Fig. 25. The three-fold equivalence of the elimination of two meta-carbon atoms (●) in the central hexagons of the reaction from \( \text{C}_{60}(I_h) \) to \( \text{C}_{59}(C_{3v}) \). There are three more equivalent ways with opposite chiral \( C_3 \) symmetry of the three surrounding bond formations (○) at the three surrounding hexagons.

Fig. 26. The elimination of two carbon atoms (79–80) from \( \text{C}_{80}(D_{5d})_b \) to result in \( \text{C}_{78}(C_{2v}) \). It involves fourteen bonds broken and twelve bonds formed. The overall reaction symmetry is \( C_1(\sigma_v) \). There will be ten equivalent ways for the combination of this \( C_1(\sigma_v) \) symmetry of the overall reaction coordinate. Both the reactant and the product have 12 pentagons. While \( \text{C}_{80}(D_{5d})_b \) has 30 hexagons and \( \text{C}_{78}(C_{2v}) \) has one less, i.e., 29 hexagons.
the relative favorableness remains to be energetically estimated by numerical calculations.

As another illustration of symmetry consideration, we shall investigate the possibility of symmetry discrepancy. For example, let us consider the elimination reaction from \( C_{80} \) to \( C_{78}(C_{2v} \text{ or } D_{3h}) \), we have derived [2] the two-dimensional diagrams for symmetries of \( C_{80} \) isomers as \( I_{h}, D_{3d}, (D_{5d})_{a}, (D_{5d})_{b}, (D_{5d})_{c} \) and \( (D_{5d})_{d} \). To be different from the symmetries already considered we take the reactant \( C_{80}(D_{5d})_{b} \) which has twelve non-abutting pentagons that are close by for possible dyotropic \( 4e^- \) pyracylene rearrangements. Although \( D_{5d} \) has the common subgroups of \( C_{2} \) and \( C_{6}(\sigma_{v}) \) for \( D_{3d} \), the coordinates have discrepancy with that of \( D_{3d} \). Only the \( C_{6}(\sigma_{v}) \) of \( C_{80}(D_{5d})_{b} \) symmetry can match with that of \( C_{2v} \) of \( C_{78}(C_{2v}) \). Therefore, we found a reaction mechanism with \( \sigma_{v} \) symmetry from \( C_{80}(D_{5d})_{b} \) to \( C_{78}(C_{2v}) \) (Fig. 26). The eliminated diatomic carbon from four broken bonds is \( \equiv C=C: \) similar to the diatomic carbon involved in \( C_{28}(T_{d}) \rightarrow C_{26}(D_{3h}) \) (Fig. 22). But, in the latter case, the reactant \( T_{d} \) symmetry has the common \( C_{2} \) and \( \sigma_{v} \) subgroup with the same coordinates as the product of \( D_{3h} \) symmetry. The \( C_{28}(T_{d}) \rightarrow C_{26}(D_{3h}) \) reaction has twelve (equal to six \( \sigma_{d} \)’s multiplied by two) equivalent ways. The \( C_{80}(D_{5d}) \rightarrow C_{78}(C_{2v}) \) reaction has ten (equal to five equivalent \( \sigma_{d} \)’s of the same class multiplied by two) equivalent ways. To go to \( C_{78}(D_{3h}) \) we need [13] only to apply another \( 4e^- \) pyracylene rearrangement (Fig. 20) which has rotational \( C_{2} \) symmetry that is different from the previously applied \( \sigma_{v} \) symmetry.

5. Summary and discussion

Using the detailed two-dimensional diagrams of symmetry structure, we have applied the well-known dyotropic \( 4e^- \) pyracylene rearrangements for the isomeric transformation of fullerenes and for the subsequent rearrangements after addition/elimination on the fullerene cage surfaces. Some of the new aspects are: (1) the proper periodic and symmetrical combinations of multiple sets of such local rearrangements, (2) the visualization of the number of equivalent ways for such combinations and (3) the possible cooperative step-by-step resonant-type progress of the local equivalent rearrangements over the periodic boundaries. Another part of the new aspect is the search for the need of different types of new rearrangement mechanisms, other than the \( 4e^- \) pyracylene rearrangement, that satisfy the specialized cage to cage symmetry requirements besides the requirements of the number of vertices, edges, and polygons — requirements for the periodic mechanistic progress from the fullerene cage cluster surface of reactants to those of the different cage cluster products.

The well-known \( 4e^- \) pyracylene rearrangements involve the back-and-forth transformation of two hexagons to two pentagons and two pentagons to two hexagons (Fig. 2). We have found complicate rearrangement coordinates for specific cases, e.g., \( C_{60}(I_{h}) \) to \( C_{60}(D_{5h})_{a} \) (Fig. 5). But we have also found some simpler and general rearrangement mechanisms that will satisfy the symmetry needs when they are properly combined periodically. For example, we found a rearrangement mechanism that transforms [three hexagons plus one pentagon] to [one hexagon, two pentagons and one heptagon] (Fig. 7 to \( C_{60}(D_{6h}) \) to \( C_{60}(C_{3v}) \)). We also found a mechanism that involves the transformation similar to the case from acenaphthylene to as-Indacene plus the transformation of [two hexagons plus one pentagon] to [one hexagon, one pentagon and one heptagon] (Fig. 12 for \( C_{76}(T_{d}) \) to \( C_{76}(C_{3}) \)). The production of heptagons merged with pentagons in this cage cluster surface reaction is different from the transformation of isolated naphthalene to azulene. All of these simple and complex mechanism may be used to help detect the possible isomers [27–29] and to help the subsequent rearrangement of cage cluster surface after addition/elimination. For the symmetry satisfaction of addition/elimination of two carbon atoms, we found that the diatomic carbon can be visualized as \( \equiv C=C: \) with the formation or breakage of four bonds or \( \cdot C=C. \) with the formation and breakage of six bonds (plus its own \( C-C \) \( \sigma \) bond) — followed by subsequent rearrangements of the neighboring structures to return to the periodic surface. We have also enumerated the number of equivalent ways of such overall rearrangement and the addition/
**Table 1**

**Summary of symmetry analysis of cage cluster fullerene reaction mechanisms**

<table>
<thead>
<tr>
<th>Fullerene reactant (point group symmetry)</th>
<th>Another reactant (+) product (−) (postulated structure)</th>
<th>Fullerene product (point group symmetry)</th>
<th>Some individual sets of local reaction mechanisms</th>
<th>Total symmetry of combined local reaction sets</th>
<th>Alternative symmetry of combined local reaction sets</th>
<th>Number of equivalent ways of combinations of reaction sets</th>
<th>Total number of bond breakage/formation</th>
<th>Figure number</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}(T_d)</td>
<td>−:C=C:</td>
<td>C_{60}(D_{3h})</td>
<td>two special sets</td>
<td>C_5(σ_v)</td>
<td>C_3</td>
<td>12</td>
<td>12/10</td>
<td>22, 23</td>
</tr>
<tr>
<td>C_{60}(T_d)</td>
<td>+:C=C:</td>
<td>C_{30}(D_{3h})</td>
<td>two special sets</td>
<td>C_5(σ_v)</td>
<td>C_3</td>
<td>12</td>
<td>6/8</td>
<td>16, 17</td>
</tr>
<tr>
<td>C_{40}(T_h)</td>
<td>−:−:C−C− (meta)</td>
<td>C_{30}(C_{3v})</td>
<td>(4 hexagons + 3 pentagons) → (3 hexagons + 3 pentagons)</td>
<td>C_1</td>
<td></td>
<td>120</td>
<td>7/4</td>
<td>24, 25</td>
</tr>
<tr>
<td>C_{60}(T_d)</td>
<td>0</td>
<td>C_{60}(D_{6h})</td>
<td>6 sets of dyotropic 4e− pyracylene rearrangements</td>
<td>S_6</td>
<td>D_3, C_3</td>
<td>20</td>
<td>12/12</td>
<td>1, 2</td>
</tr>
<tr>
<td>C_{60}(D_{6h})b</td>
<td>0</td>
<td>C_{60}(C_{3v})b</td>
<td>3 sets of 4e− pyracylene rearrangements</td>
<td>C_3</td>
<td></td>
<td>4</td>
<td>6/6</td>
<td>3</td>
</tr>
<tr>
<td>C_{60}(T_d)</td>
<td>0</td>
<td>C_{60}(C_{3})</td>
<td>3 sets of 4e− pyracylene rearrangements</td>
<td>C_3</td>
<td></td>
<td>80</td>
<td>6/6</td>
<td>4</td>
</tr>
<tr>
<td>C_{60}(T_d)</td>
<td>0</td>
<td>C_{60}(D_{6h})a</td>
<td>6 sets of two types of dyotropic 4e− rearrangements</td>
<td>D_3</td>
<td>S_6, C_3</td>
<td>20</td>
<td>24/24</td>
<td>5</td>
</tr>
<tr>
<td>C_{60}(D_{6h})b</td>
<td>0</td>
<td>C_{60}(C_{3v})a</td>
<td>3 sets of (3 hexagons + 1 pentagons) → (1 hexagon + 1 heptagon + 2 pentagons)</td>
<td>C_3</td>
<td></td>
<td>8</td>
<td>6/6</td>
<td>6, 7</td>
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</tbody>
</table>

- **Note:** The table details various fullerene reactants and their corresponding reaction mechanisms, including symmetries, reaction sets, and the number of equivalent ways of combinations, along with figure numbers for reference.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Species</th>
<th>Generation</th>
<th>Special Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{60}(I_h))</td>
<td>0</td>
<td>(C_{60}(D_3))</td>
<td>6 sets of special dyotropic 4c(^-) rearrangements</td>
</tr>
<tr>
<td>(C_{60}(I_h))</td>
<td>0</td>
<td>(C_{60}(D_2))</td>
<td>5 sets of 4e(^-) pyracylene rearrangements</td>
</tr>
<tr>
<td>(C_{78}(T_d))</td>
<td>0</td>
<td>(C_{78}(D_2))</td>
<td>two sets of special complex mechanism</td>
</tr>
<tr>
<td>(C_{78}(T_d))</td>
<td>0</td>
<td>(C_{78}(C_1))</td>
<td>3 sets of (4 hexagons + 2 pentagons) → (2 hexagons + 1 heptagon + 3 pentagons)</td>
</tr>
<tr>
<td>(C_{78}(T_d))</td>
<td>0</td>
<td>(C_{78}(C_3))</td>
<td>3 sets of 4e(^-) pyracylene rearrangements</td>
</tr>
<tr>
<td>(C_{78}(D_2))</td>
<td>+C=C: (para)</td>
<td>(C_{78}(C_2))</td>
<td>two sets of 4e(^-) pyracylene plus addition of two carbons to (para) positions</td>
</tr>
<tr>
<td>(C_{78}(C_2))</td>
<td>0</td>
<td>(C_{78}(D_{3h}))</td>
<td>one set of 4e(^-) pyracylene</td>
</tr>
<tr>
<td>(C_{78}(D_{3h}))</td>
<td>0</td>
<td>(C_{78}(D_1))</td>
<td>3 sets of 4e(^-) pyracylene rearrangements</td>
</tr>
<tr>
<td>(C_{84}(D_{4h}))</td>
<td>−C=C:</td>
<td>(C_{84}(C_3))</td>
<td>two sets of special mechanisms</td>
</tr>
<tr>
<td>(C_{84}(T_d))</td>
<td>0</td>
<td>(C_{84}(C_1))</td>
<td>3 sets of 4e(^-) pyracylene rearrangements</td>
</tr>
<tr>
<td>(C_{84}(D_{2h}))</td>
<td>0</td>
<td>(C_{84}(C_3))</td>
<td>3 sets of 4e(^-) pyracylene rearrangements</td>
</tr>
</tbody>
</table>
elimination mechanism. For example, the number of $C_3$ (left and right chiral), $C_2$ and $\sigma_v(\sigma_d)$ reaction coordinates will depend on the number of such equivalent operations in the same point-group class. But we also found other structural factors such as the equivalence of front end versus the back end of the $\sigma_v(\sigma_d)$ reflection mirror (Figs. 16 and 22). All of these results are summarized in Table 1.

Our structural symmetry analysis is just one of the minimum requirements. Energies and other considerations [30–32], such as electronic [33] and related symmetry considerations of isolated systems [34–38], are also important for these clusters. Because of these, there may also be other specific electronic, vibrational (even rotational) symmetry requirements for state-to-state reactions [39]. In the consideration of structural symmetry, we have not elaborated on the detailed electronic and vibrational and rotational symmetry of the reactants and products [40,41], especially the excited states. For $C_{60}(I_h)$ rearrangement to $C_{60}(D_{5h})$ via $C_3$ (or $S_6$ or $D_3$) reaction coordinates, it is assumed that both the reactant and the product are electronically and vibrationally totally symmetric so that $I_h(A_g) = C_3(A) = S_6(A_g) = D_3(A_1) = D_{5h}(A_{1g})$. If the product $C_{60}(D_{5h})$ has vibronic symmetry of $\Gamma_{1B_{1g}}$ or $\Gamma_{1B_{2g}}$, the symmetry correlation of the reaction coordinate is still satisfactory because

$$I_h(A_g) = C_3(A) = S_6(A_g) = D_{5h}(A_{2g}, B_{1g}, B_{2g})$$

But, if the $C_{60}(D_{5h})$ product is vibrationally excited to $^1E_{2g}, ^1E_{1u}, ^1E_{2u}$ state, then the reaction coordinate has to be changed to $C_2$ or $S_4$ to be satisfactory, for example:

$$I_h(A_g) = C_2(A) = C_4(A') \Leftrightarrow C_2(A + B) \text{ and}$$

$$C_4(A' + A'') = D_{5h}(E_{2g})$$

The vibrational effect of surface resonances should also be interesting to be investigated because of the periodic boundary of cage clusters. Similarly the periodic running wave of a set of 'excited' rearrangement reaction (bond breakage plus formation) across the boundary is also worth investigation.

The relative energetic probability of these new symmetry allowed reaction mechanisms should be investigated numerically next. Similarly the energetic comparison of the complicated specific reaction coordinates (e.g. Fig. 5) versus the combination of simpler reaction coordinates (Figs. 6 and 11) should also be looked into. As an improvement over the three-dimensional picture for the identification of all sets of local reactions, our two-dimensional diagrams with complete detail clarity of bonds (edges), atoms (vertices) and carbon rings (faces) have helped. They will be useful in additional future works under progress, such as:

1. Draw clearly localized $\pi$-bonds for alternative bonding structure instead of completely delocalized resonant conjugate structure. The drawing of $\pi$-bonds will allow the finding of the free radical electrons that occurs without (double) $\pi$-bonding. It will help to determine the addition of hydrogen atoms to the radical sites and to analyze the reaction of such free radicals with $C_4$ and $C_6$ considered by O’Brien et al. [28] besides $C_2$ and metal ions.

2. Use the two-dimensional diagrams to analyze the symmetry requirements of fullerene reactions [19,20] with compounds such as $C_{18}$, $C_{24}$, $C_{30}$.

3. Besides the $C_2$ reactivity of $:C=C:$ and $:C-C:$, search for the special reaction with $:C=C:$ involving only 2 bond breakage (or formation).

4. Continue to search for alternative reaction mechanisms that satisfy the same subgroup symmetry and compare their energetic advantages numerically. Emphasis should also be on the subsequent rearrangements after addition/elimination and the consecutive local reactions around periodic cage surface.

Our symmetry-allowed methodology and proposed mechanisms hopefully will promote further explanation of possible reaction mechanisms of experimentally observed products.

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Postscript


Appendix. Registry numbers

\[
\begin{align*}
C_{26}, & \quad 144636-53-3; \\
C_{28}, & \quad 144636-55-5; \\
C_{30}, & \quad 144636-66-8; \\
\text{Fullerene-C}_{58}, & \quad 137232-07-6; \\
\text{Fullerene-C}_{60}, & \quad 135105-52-1; \\
[5,6]-\text{Fullerene-C}_{60}-I_6, & \quad 99685-96-8; \\
[5,6]-\text{Fullerene-C}_{60}-D_{6h}, & \quad 112303-18-1; \\
[5,6]-\text{Fullerene-C}_{60}-D_3, & \quad 139703-75-6; \\
\text{Fullerene-C}_{76}, & \quad 135113-15-4; \\
[5,6]-\text{Fullerene-C}_{76}-D_{2d}, & \quad 142136-39-8; \\
\text{Fullerene-C}_{78}, & \quad 136316-32-0; \\
[5,6]-\text{Fullerene-C}_{78}-D_{2d}, & \quad 139707-96-3; \\
& \quad 143974-29-2; \\
[5,6]-\text{Fullerene-C}_{78}-D_3, & \quad 139707-95-2; \\
[5,6]-\text{Fullerene-C}_{80}-D_{5d}, & \quad 134109-59-4; \\
\text{Fullerene-C}_{84}, & \quad 135113-16-5; \\
[5,6]-\text{Fullerene-C}_{84}-D_{2d}, & \quad 138015-77-7; \\
& \quad 145226-11-5; \\
[5,6]-\text{Fullerene-C}_{84}-D_{6h}, & \quad 144438-79-9; \\
& \quad 134847-09-9; \\
[5,6]-\text{Fullerene-C}_{84}-T_d, & \quad 134847-08-8.
\end{align*}
\]

References