C70 Dimers – Energetics and Topology

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All sp2 peanut-shaped dimeric fullerenes derived from $D_{5h}C_{70}$ are modeled. Construction of the isomers was monitored by a cyclic permutation of bonds in the linking zone of the two caps resulting from deleting the boundary of a face from the parent $C_{70}$ fullerene. Local curvature was calculated in terms of both angular defects and strain energy. Topological equivalence classes of the constituent substructures were evaluated by calculating the topological indices of the parent cages, their medials and duals. Detailed network transformation, starting from $C_{70}$, through sp3 dimer, peanut sp2 dimer, up to the corresponding tubulene is given. Semiempirical calculations showed a monotonic decrease in the heat of formation along the above pathway.

Key words
dimeric fullerenes
sp3 adducts
sp2 dimers
sp2 tubulene
$C_{70}$-peanut dimers
dimer topology

INTRODUCTION

The discovery of fullerenes, nanotubes and other novel allotropic forms of carbon has generated a research explosion in the fields of chemistry, physics, and materials science. The initial fascinating appeal, coming from their beautiful symmetry1–3 was later shifted to real chemistry.4–6 Carbon allotropes with finite molecular cage structures have been functionalized or inserted in supramolecular assemblies.7,8 A fullerene is an all-carbon molecule in which the atoms are arranged in a pseudospherical framework made up entirely of pentagons and hexagons. Non-classical extensions to include rings of other sizes have been considered.9,10 Multielemental cages containing pentagons and hexagons have also been studied.11

Dimeric fullerenes like $C_{120}$ and $C_{140}$ have been reported in literature as a result of a [2+2] cap-to-cap cycloaddition.12–14 In the attributed structures, the two cages are linked via a four-fold ring, consisting of sp3 hybridized carbon atoms. Linear chains of spherical monomers ($C_{60}$), formed at moderate pressure (1 GPa) and 300 °C have also been reported.12 A different molecular structure, with a peanut-shape and all sp2 carbon atoms, has been proposed as well.15–17

The present paper deals with the construction of all distinct sp2 peanut dimers of $D_{5h}C_{70}$. The topological characterization of these objects, including local curvature and subgraph equivalence classes calculation, is presented in the next section. The energy diagram of the detailed network transformation starting from the monomer, through a peanut dimer up to the corresponding tubulene, is given in terms of semiempirical data, in the third section.

sp3 ADDUCTS

Dimeric fullerenes such as $C_{120}$, $C_{140}$, and the mixed $C_{130}$ have been synthesized.18 The attributed structures involve

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sp³ hybridized carbon atoms (Figure 1) and are supposed to result from a [2+2] cycloaddition.

The most stable structure is that of a [6,6] adduct. However, in the further isomerization process (see below), the appearing pentagon pairs (pentanes units) will undesirably raise the barrier energy. In such a transformation, the sp³ [5,6]-trans adduct is prone.

**sp² DIMERS**

A tubulene is defined as a capped nanotube built up of two hemifullerene caps and a distancing tube portion. Various caps can be derived from a fullerene by deleting one or more faces. Subsequently, various tubulene-like objects can be imagined, some of them appearing as intermediates in the coalescence reaction of spherical fullerenes (see below), ending with a tubulene.

Take a fullerene face and delete the bonds forming its boundary. This results in an open structure with dangling bonds (i.e., with monovalent terminal atoms). Put two such objects face to face and join each single-connected atom of the first structure with its corresponding atom and the next atom in the second structure. In this way an all sp² peanut-shaped dimer is obtained.

There are five topologically distinct faces in C₇₀ (Figure 2a – two pentagons and three hexagons), which supply five caps (Figure 2b–f, dangling bonds are not shown).

The junction zone is tessellated by either pure heptagons (caps a and c) or heptagons and hexagons (caps b, d and e) according to the cap topology.

No mixed dimers C₆₀–C₇₀ were constructed. Figure 3 illustrates the *in silico* building of dimer C₁₄₀ef. It could appear in the coalescence of two quasi-spherical C₇₀ molecules (see below). Note that the procedure in Figure 3 is useful for straight modeling of a peanut dimer.

Construction of all possible C₇₀–peanut dimers was monitored by a cyclic permutation on the sequence of edges in the joining zone (Table I). The sequence designated by a single letter represents the fixed cap, while the others (denoted by two letters) correspond to the rotated cap. The start of the sequence is given in boldface.

Several enantiomer pairs appear among the dimers shown in Table I (Table II). Two enantiomers have the same edge sequence but a different circular visiting sense. They have identical topological and energetic parameters, thus leaving only twelve distinct dimeric structures (see the next section).

The lattice transformation of two C₇₀ fullerenes passing through the peanut dimer up to the corresponding tubulene (Figure 4) is presented in Figure 5 as geodesic projections.

Two facing pentagons rotated by π/5 (Figure 5a) are connected by two bonds, thus introducing sp³ hybridization (Figure 5b, bold lines). In order to recover the sp² network, one bond in each sphere will break (Figure 5b,
Figure 3. Construction of the C140ef dimer.

Figure 4. The C140aa peanut dimer and its corresponding tubulene.

TABLE I. Edge typing of the constructed sp² dimers

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</tr>
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<td>eg</td>
<td>67 57 67 67 57 66 66 66 67 67 57 67 66 66 66 67</td>
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TABLE II. Enantiomer pairs of the peanut dimers

<table>
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<td>cc cd dd de df</td>
</tr>
<tr>
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<td>eg</td>
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</tbody>
</table>

thick dotted lines) and undergo Stone-Wales rotation¹⁹ (Figure 5c); the linking zone now consists of two H-shaped bridges, with four heptagons and two nonagons (Figure 5d). The peanut-shaped structure will be achieved in four SW steps, performed along the circumference (Figure 5d, bold lines) while the junction zone becomes covered by heptagons (Figure 5e). This induces a negative curvature strain, but it is relaxed once the heptagons and adjacent pentagons are transformed into a hexagonal lattice (Figure 5f). For this, ten SW steps are necessary in a circumferential order (Figure 5e, bold lines).

The energy involved in the coalescence process is presented in Figure 6.

**DIMER TOPOLOGY**

**Dimer Curvature**

Let G = G(V, E) be a connected graph with the vertex set V = V(G), and edge set E = E(G). Map M is the combinatorial representation of a closed surface. If the graph G is a cycle-containing one, it can superimpose on M. Consequently, one can define F = F(G) as the set of graph faces (i.e., closed regions). Denote the cardinality of the above sets by v, e and f.

Combinatorial topology of fullerenes can be described by the Euler theorem:²⁰

\[ v - e + f = \chi(S) = 2(1 - g) \quad (1) \]

where \( \chi \) is the Euler characteristic, and g is the genus of the graph (g = 0 for a graph embedded in the sphere, and 1 in case of a torus). This formula is useful for checking the consistency of an assumed structure.

According to the Gauss-Bonnet theorem, the total Gaussian curvature \( k \) on a surface \( S \) represents a topological invariant:²¹

\[ \int_S k dA = 2\pi\chi(S) \quad (2) \]

An angular defect (or excess) at a vertex \( u \) takes into account the contributions (on average) of the surrounding
faces, keeping in mind that the sum of angles of any face (i.e., polygon) \( f_j \) is \((j - 2)\pi\):

\[
s(u) = \pi \sum_j \frac{j-2}{j}
\]

Since the total angular area surrounding a point \( u \) on a smooth surface is \(2\pi\), it is convenient to define the angular defect (a combinatorial curvature) as:

\[
ad(u) = 2 - s(u) / \pi
\]

The total angular defect for a given combinatorial surface can be calculated by:

\[
ad(P) = \sum_u ad(u)
\]

Euler’s theorem (1) can be rephrased in terms of angular defects, stating that \( ad(P) \), taken over all vertices of a polyhedron \( P \), is quite independent of the specific structure of the polyhedron: always equal to 4 if the polyhedron is embedded in the sphere, implying that enough vertices of positive angular defect must exist in any spherical polyhedron. In the case of a polyhedron embedded in the torus or in the tube, the corresponding version of Euler’s theorem states that the sum of its angular defects must always vanish (see Eqs. (1) and (2)). Further, this sum is negative for every polyhedron of a negative Euler characteristic.

In order to describe the local curvature, we selected a zone of two rows of faces each hand to the equator (i.e., the ring joining the two caps). Next, we made »longitudinal« selections (Figure 7, in bold line) within the above »parallel« selection up to complete circumscription of the structure. The local curvature was calculated (by CageVersatile v.1.1) according to Eqs. (3) to (5).

The curvature in the parallel selection is a characteristic of each of the five classes of dimers. The values are as follows: class a, 0.00; class b, 0.533; class c, 0.667; class d, 0.933 and class e, 0.80. All of them have positive signs despite the saddle-type geometry, thus being less informative. The total curvature for all constructed dimers was 4 (see above).

As mentioned above, the curvature of a selection sequence is proper for a given dimer. In the case of enantiomer pairs, the same sequence of curvature is expected but the visiting sense is opposite. Table III presents the values for these selections, the start in a circumscribing longitudinal sequence being given in boldface.

The local negative curvature is reflected in the sign of curvature values in Table III. It can be viewed as the fingerprint of a structure.

**Strain Energy Calculation**

In the POAV1 theory,\(^{23-26}\) the \(\pi\)-orbital axis vector is defined as the vector that makes equal angles \(\theta_{\sigma\pi}\) to the three \(\sigma\)-bonds of the sp\(^2\) carbon atom and the pyramidalization angle is obtained as:

\[
\theta_p = \theta_{\sigma\pi} - 90^\circ
\]

This angle is used for estimating the strain energy, induced by a pyramidalized carbon atom, by:

\[
E_s = 200 \cdot (\theta_p)^2
\]
with $\theta_p$ being measured in radians. The difference $120 - \frac{1}{3} \sum \theta_p$ gives the deviation to planarity. Data of the POA V1 analysis for $D_{5h}C_{70}$, the peanut dimer and the corresponding tubulene are given in Table IV.

The results of the POA V1 analysis are in agreement with the heat of formation values (see Figure 6). The strain energy of the sp$^3$ adduct can be approximated as twice that of $C_{70}$ (1010.388 kcal mol$^{-1}$). In the peanut structure, the vertices shared by three heptagons are only slightly deviated from planarity; however, the structure is still more strained than the corresponding tubulene. A negative value was attributed to the strain of atoms in the junction zone (level 8 and 9, Table IV) where the local curvature is negative. The tubulene is the most relaxed structure, as indicated by the lowest value of its total strain energy.

**Topological Symmetry**

Given a graph $G$ with $S = S(G)$ being the set of subgraphs of a given size and a group of automorphisms $Aut(G(S))$, the two subgraphs $S_i, S_j$ of $G$ are called equivalent if there is a group element $aut(N_{S_i}) \in Aut(G(S))$ such that $S_j aut(N_{S_i}) S_i$ (i.e., an automorphic permutation that transforms two subgraphs to each other).

The set of all subgraphs $S_j$ obeying the above equivalence relation is called the orbit (i.e., class of equivalence) of the subgraph $S_i, S_{NS_i}$. The orbits represent disjoint automorphic partitions: $S \neq \bigcup S_{NS_i}$. Our only object
here is to find the equivalence classes for the vertices, edges and faces of a fullerene cage. As an equivalence criterion, we used the topological indices of centricity \( C(LM) \) and centrocomplexity \( X(LM) \), defined on layer matrices \( LM \).27

The vertex orbits are found by simply applying the above centric index to the layer of distance sum matrix \( LDS \) of the parent graph. The edge orbits are calculable with the same index but applied to the \( LDS \) matrix of the corresponding medial graph.28

The face orbits are obtained from the dual of the parent graph,28 the criterion being the index of centrocomplexity \( X(L) \), where \( L(W) \) matrix is the layer matrix of valences. Each vertex in the dual has the valence equal to the parent face size. In this way, one can select the orbits for each face type. Data are listed in Table V.

It can be seen that highly symmetric structures have a low number of equivalence classes.

Figure 8 illustrates the medial (Figure 8a) and the dual (Figure 8b) of the \( C_{140} \) dimer.

### ENERGETICS OF \( C_{70} \)-PEANUT DIMERS

Molecular modeling was performed using the semiempirical method PM3 with the parametrization supplied by the HyperChem software (version 4.5, Hypercube, Inc.).29 Structures were optimized using the Polak-Ribier conjugate-gradient method, energy minimization was terminated at an RMS gradient \(<0.01 \text{ kcal Å}^{-1} \text{ mol}^{-1}\) for all isomers.

The lowest heat of formation was computed for isomer aa (\( D_{5d} \) symmetry), for which the lowest deviation to

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<th>Level</th>
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<th>C(_{140}) peanut</th>
<th>C(_{140}) tubulene</th>
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### Table IV. Data of the POAV1 analysis

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<th>( E_v / \text{kcal mol}^{-1} )</th>
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TABLE V. Subgroup equivalence classes in peanut C_{140} dimers

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<td>70x(2);</td>
<td>2x(1);102x(2);1x(4);</td>
<td>[5] 6(2);2(4);6(9);5(4);1(6);7(1);2(2);4(4);</td>
</tr>
<tr>
<td>c140ee</td>
<td>35x(4);</td>
<td>3x(2);45x(4);3x(8);</td>
<td>[5] 3(4);1(8);6(5);3(8);7(2);4(4);</td>
</tr>
<tr>
<td>c140ef</td>
<td>7x(4);14x(8);</td>
<td>1x(2);6x(4);23x(8);</td>
<td>[5] 1(4);2(8);6(5);3(8);7(1);8(8);</td>
</tr>
</tbody>
</table>

Figure 8. The medial (a) and the dual (b) of the C_{140}aa dimer.

planarity in the junction zone was found. Note that the enantiomer pairs have one and the same heat of formation.

Compared to the sp^3 dimers, the majority of sp^2 peanut dimers show a lower heat of formation (i.e., a more relaxed structure) and only two distinct structures (Table VI, entries 9–11) are energetically higher than the most stable sp^3 structure. However, the HOMO-LUMO gap (a measure of kinetic stability) is higher for the sp^3 structures (the gap for the [6,6] adduct is 5.873 eV). Which, the heat of formation or the gap, will be dominant in the balance of factors that lead to one or another structure, remains a question.

CONCLUSIONS

All the sp^2 peanut dimers of D_{5h}C_{70} have been constructed and characterized as topology and energetics.

The topology of the isomers was monitored by a cyclical permutation bond table. Semiempirical calculations supplied the same heat of formation for the enantiomer pairs. The classes of equivalence for the vertices, edges and faces of the studied peanut dimers were calculated by using two topological indices (as equivalence criteria) derived on the layer matrices of the associated graphs. They were calculated for the parent fullerenes, their medials and duals.

TABLE VI. Heat of formation, the band gap and point group symmetry for the C_{140} isomers

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF/kcal mol^{-1}</th>
<th>Band gap/eV</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>aa</td>
<td>11.768</td>
<td>5.136</td>
</tr>
<tr>
<td>2</td>
<td>bb</td>
<td>11.882</td>
<td>4.446</td>
</tr>
<tr>
<td>3</td>
<td>bf</td>
<td>11.882</td>
<td>4.446</td>
</tr>
<tr>
<td>4</td>
<td>bc</td>
<td>11.938</td>
<td>4.083</td>
</tr>
<tr>
<td>5</td>
<td>bg</td>
<td>11.938</td>
<td>4.082</td>
</tr>
<tr>
<td>6</td>
<td>be</td>
<td>11.976</td>
<td>3.978</td>
</tr>
<tr>
<td>7</td>
<td>bd</td>
<td>11.976</td>
<td>3.978</td>
</tr>
<tr>
<td>8</td>
<td>dd</td>
<td>12.021</td>
<td>4.682</td>
</tr>
<tr>
<td>9</td>
<td>di</td>
<td>12.021</td>
<td>4.682</td>
</tr>
<tr>
<td>10</td>
<td>ce</td>
<td>12.082</td>
<td>5.747</td>
</tr>
<tr>
<td>11</td>
<td>cf</td>
<td>12.082</td>
<td>5.752</td>
</tr>
<tr>
<td>12</td>
<td>cd</td>
<td>12.082</td>
<td>5.752</td>
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</tr>
<tr>
<td>14</td>
<td>cg</td>
<td>12.084</td>
<td>5.739</td>
</tr>
<tr>
<td>15</td>
<td>dh</td>
<td>12.092</td>
<td>4.671</td>
</tr>
<tr>
<td>16</td>
<td>de</td>
<td>12.092</td>
<td>4.671</td>
</tr>
<tr>
<td>17</td>
<td>df</td>
<td>12.100</td>
<td>4.624</td>
</tr>
<tr>
<td>18</td>
<td>dg</td>
<td>12.100</td>
<td>4.624</td>
</tr>
<tr>
<td>19</td>
<td>eg</td>
<td>12.705</td>
<td>4.512</td>
</tr>
<tr>
<td>20</td>
<td>ee</td>
<td>12.705</td>
<td>4.512</td>
</tr>
<tr>
<td>21</td>
<td>ef</td>
<td>12.924</td>
<td>2.119</td>
</tr>
</tbody>
</table>
The dimerization reaction of fullerenes clearly involves more than one dimeric species: sp$^2$ adduct, sp$^2$ peanut and sp$^2$ tubulene. Semiempirical calculations showed a decrease in the heat of formation along the presented reaction pathway. With the above results in mind, revisiting of the experimental data appears to be a real demand.

REFERENCES


SAŽETAK

C$_{70}$ dimeri – energetika i topologija

Csaba L. Nagy, Monica Stefu, Mircea V. Diudea, Andreas Dress i Achim Müller

Studirani su svi sp$^2$ dimeri fulereni kikirikijevoga oblika koji su izvedeni iz C$_{70}$ fulerena simerije D$_{5h}$. Konstrukcija ovih izomera praćena je cikličkom permutacijom veza u zoni povezivanja dviju kapa koje su nastale uklanjanjem poligona iz C$_{70}$ fulerena. Lokalna zakrivljenost je izračunana pomoću kutnih defekata i energije napetosti. Topologijske ekivalencijeske klase konstitutivnih podstrukturna su numerički izražene pomoću topologijskoga indeksa izvornih kavez, njihovih medijala i duala. Prikazana je u detalju transformacija od C$_{70}$, preko sp$^3$ dimera, sp$^2$ dimera kikirikijevoga oblika do odgovarajućeg tubulena. Semiempirijski računi su pokazali da toplina formacije raste monotono duž spomenute transformacije.