Retrosynthetic Analysis of Fullerene C$_{60}$: Structure, Stereochemistry, and Calculated Stability of C$_{30}$ Fragments

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Abstract: The total number of possible retrosynthetic bisections of C$_{60}$ leads to nine different isometric C$_{30}$ fragments. These molecules include five chiral units, four of which derive from partitions corresponding to four distinct “Coupes du Roi”. The energies, curvatures, and homodesmic stabilization energies of the C$_{30}$ fragments are evaluated at the ab initio 6-31G level.

Bowl-shaped polyaromatic hydrocarbons, which are fragments of the fullerene structure (buckybowls, after the American architect R. Buckminster Fuller), have generated intense research activity in recent years. As far as fullerene C$_{60}$ is considered, the use of these buckybowls as synthons for some future total syntheses might also be imagined. In fact, several such C$_{30}$ fragments (2–8) have been recognized and some have been prepared. These molecules include (i) a nonisometric fragment; (ii) a chiral buckybowl (generated by a homochiral segmentation usually referred to as “La Coupe du Roi”); (iii) a chiral isomer (coming from a heterochiral segmentation); and (iv) four achiral isomers (4–7).

However, the total number of all possible isometric C$_{30}$ note that curvature induces chirality for some of these bowl-shaped hydrocarbons.

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However, the total number of all possible isometric C$_{30}$
fragments, either chiral or achiral, has not yet been methodically identified.

The general problem of fragmenting molecules into isometric segments, including the bisection of an achiral object into isometric homochiral halves (La Coupe du Roi: a way to divide an apple into two halves that have the same chirality), has been comprehensively examined by Mislow. Therefore, we decided to use this methodology to determine the total number of pairs of isometric C₃₀ fragments constituting the fullerene C₆₀.

We find nine bisections, including four chiral C₃₀ buckybowls from four different Coupes du Roi. Additional insight into this series is also provided by (i) the calculated energies and curvatures of these C₆₀ fragments and (ii) the estimated strain energies, reflected by the stabilization energies obtained from the appropriate homodesmic reactions.

Mislow and co-workers pointed out several limitations imposed on the ways in which molecules can be segmented. First, some of their assumptions will be briefly recalled before the segmentation of C₆₀ into isometric halves is considered. Thus, the cut objects (C/O) are defined as “the ensemble of isometric segments in the shape of the object with the cut in place”. The segments must be related by a symmetry operation of the C/O. Consequently, as long as achiral molecules are considered, bisecting may yield achiral, heterochiral, and homochiral segments.

Considering the icosahedral object C₆₀ (symmetry elements corresponding to a truncated regular icosahedron) and the dissections to C₃₀ segments, the connections of two isometric halves, which have to be related by a symmetry operation of the C/O, involve exclusively a C₂ axis or an inversion center. The corresponding “belts” can also be identified by applying the same two symmetry elements.

Practically, belts are obtained starting at any pair of condensed rings on the surface of C₆₀ and, with the consideration of these two symmetry elements, by achieving one turn around the fullerene. The distinct bisects, and consequently the C₃₀ segments, eventually arise from these belt structures. Excluding the nonisometric isomer 2, we presently find nine bisects to isometric C₃₀, that is, three additional bisects as compared to the previous ones (Scheme 2). The present nine C₃₀, including heterochiral fragment 3, as well as four homochiral (8–11) and four achiral segments (4–7), are shown in the Figure 1.

We have calculated at the ab initio RHF 6-31G level the relative energies of energy-minimized geometries of these nine C₃₀ segments, as well as the parameters related to their curvatures. The results involve three series of compounds (Table 1).

Interesting tendencies are displayed by these series: (i) the more stable isomers (3 and 4) correspond to the lower number of five-membered rings; (ii) within each (C₃₀H₁₀) and (C₃₀H₁₂), series the energy contents smoothly increase when the number of pentagons is increased by one, although a more abrupt variation occurs if the number of pentagons is simultaneously increased by two units (compare 4 to 5 vs 3 to 10); and (iii) the shapes of the segments differ considerably from the carbon skeletons mapped onto the C₆₀ surface prior to segmentation. This issue, involving the “curvatures” of these molecules, is now detailed.

The pyramidalization angle obtained from the τ-orbital axis vector (POAV) has been shown to provide a useful index of the “local curvature” of fullerenes. Alternatively, the present calculation of dihedral angles θ (as defined in the caption of Figure 2; θa and θmax are, respectively, average and maximum values) also yields useful local parameters to characterize the curvature of such nonplanar polyaromatic hydrocarbons. In fact, for every distinct C₃₀, there are significant variations of curvature along the structure emphasized by the (θmax−θa) differences (Table 1). For comparison, the “regularly curved” spherical fullerene C₆₀ corresponds to θmax = θa = 41.8°. These “irregular” distributions of curvature are reminiscent of the recent gas-phase molecular structure of corannulene, exhibiting a slightly flattened shape in addition, the curvature values of the distinct C₃₀ (23) Geometries were optimized and energies computed at the ab initio RHF 6-31G level using the Gaussian 98 (revision A.7) package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dauphich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malic, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Rego, E. S.; Pople, J. A. Gaussian 98, revision A.7, Gaussian, Inc.: Pittsburg, PA, 1998.

(24) The relative energies of these fragments have also been computed at the semiempirical AM1 level, and very similar trends to the ab initio results are obtained.


within each series are also highly dissimilar\(^2\)\(^2\) [see the unlike mean values (\(\bar{\theta}_{\text{a}}\)) and disparate (\(\theta_{\text{max}}\) – \(\bar{\theta}_{\text{a}}\)) differences (Table 1)]. Moreover, the shapes of the C\(_{30}\) are, on the average, much more flattened compared to the substructures on the C\(_{60}\) surface before bisections (significantly lower values of \(\bar{\theta}_{\text{a}}\) as compared to 41.8° for C\(_{60}\)). This effect possibly reflects some release of strain upon fragmentation. However, the main effect remains the number of five-membered rings, as shown by the more stable although less flattened (higher \(\bar{\theta}_{\text{a}}\)) fragments (3 and 4) containing the lower number of pentagons.

The relative stabilization energies (SE) of this series of C\(_{30}\) hydrocarbons at the ab initio RHF 6-31G level are illustrated in eq 1. For the individual energy contents calculated at the ab initio RHF 6-31G level see ref 22.

### Table 1. Ab initio Calculated Energies (\(\Delta E\)) and Curvatures\(^\text{a}\) \(\theta_{\text{a}}\) (average) and \(\theta_{\text{max}}\) (maximum value) of Distinct Isometrical C\(_{30}\) Segments

<table>
<thead>
<tr>
<th>C(_{30})</th>
<th>(\Delta E)</th>
<th>(\theta_{\text{max}})</th>
<th>(\bar{\theta}_{\text{a}})</th>
<th>(\theta_{\text{max}} - \bar{\theta}_{\text{a}})</th>
<th>total number of five-membered rings</th>
<th>total number of six-membered rings(^\text{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C(<em>{30})H(</em>{10}))</td>
<td>4</td>
<td>0</td>
<td>45.5</td>
<td>34.5</td>
<td>11.0</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.67</td>
<td>45.5</td>
<td>33.1</td>
<td>12.4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>7.22</td>
<td>39.6</td>
<td>33.3</td>
<td>10.2</td>
<td>5</td>
</tr>
<tr>
<td>(C(<em>{30})H(</em>{12}))</td>
<td>3</td>
<td>0</td>
<td>38.1</td>
<td>27.0</td>
<td>11.1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>87.90</td>
<td>39.0</td>
<td>19.6</td>
<td>19.4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>89.18</td>
<td>39.4</td>
<td>18.2</td>
<td>21.2</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>106.78</td>
<td>36.7</td>
<td>19.0</td>
<td>17.7</td>
<td>6</td>
</tr>
<tr>
<td>(C(<em>{30})H(</em>{14}))</td>
<td>5</td>
<td>4.67</td>
<td>41.8</td>
<td>41.8</td>
<td>0</td>
<td>12</td>
</tr>
</tbody>
</table>

\(\text{a}\) Zero energies (in kcal/mol) correspond, in each series of compounds, to the most stable energy-minimized C\(_{30}\) (\(\Delta E\) in kcal/mol); for the individual energy contents see ref 22. \(\text{b}\) Angles \(\theta\) (in degrees) as parameters for the C\(_{30}\) curvatures are determined as \(\theta = \pi - \angle \text{d}\), with the dihedral angles \(\angle \text{d}\) being \(\angle (1,2,3);(2,3,4)\).

As a delicate balance between \(\pi\)-conjugation stabilization and curvature-related strain destabilization, the calculated SE values (Table 2) involve surprisingly a limited range of 10 kcal/mol (around 65 kcal/mol) for most of the compounds. Two remarkable exceptions (the highly stabilized compound 3 and the more destabilized compound 4) must be emphasized. More qualitatively, it is interesting to mention that the number of benzenoid hexagons, the so-called Fries number, which has been proposed as a \(\pi\)-system’s relative-stability criterion,\(^2\)\(^7\) is also significantly higher for 3 than 7 (seven and one, respectively). It is also worth noting that the more stable fragment 3 is presently the only member of this series that has yet been synthesized.\(^1\)\(^3\)\(^1\)\(^4\)

In summary, we have identified all of the possible ways to bisect fullerene C\(_{60}\) into isometric C\(_{30}\) segments, most of which (five out of nine) are chiral molecules. The shapes of most of these C\(_{60}\) substructures are found to be far from perfect “geodesic” half spheres, and the associated energy values are highly dependent on the considered structures. The evaluation of the relative stabilization energies highlights the more stable, already isolated C\(_{30}\) 3. However, besides their strain contents, the stereochemistry of these synthons will ultimately have to be considered for future “dimerizations” in the direction of a total synthesis of C\(_{60}\).

### Supporting Information Available

Dihedral angles, Cartesian coordinates, ab initio and AM1 calculated electronic energy contents, and the structures of belts corresponding to the nine distinct C\(_{30}\) fragments. This material is available free of charge via the Internet at http://pubs.acs.org.

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\(\text{Notes}\)