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

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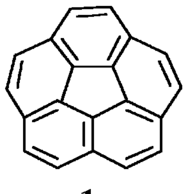
Abstract: The total number of possible retrosynthetic bisections of C_{60} leads to nine different isometric C_{30} fragments. These molecules include five chiral units, four of which derive from partitions corresponding to four distinct "Coupes du Roi". The energies, curvatures, and homodesmotic stabilization 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.[1−3] Most of such curved hydrocarbons have been synthesized in the recent years, although the recently improved[4] syntheses of the smallest of these curved fragments, corannulene **1** (Scheme 1), was first described long before[5] the discovery of fullerenes.

The interest in these curved buckybowls, involving two distinct (concave and convex) surfaces, includes various aspects related to properties such as, e.g., reactivity[1,6] or endo- vs exohedral metal complexation ability,[7] as well as other theoretical aspects of these interesting conjugated and strained structures.[8] It is also interesting to note that curvature induces chirality for some of these bowl-shaped hydrocarbons.

Scheme 1



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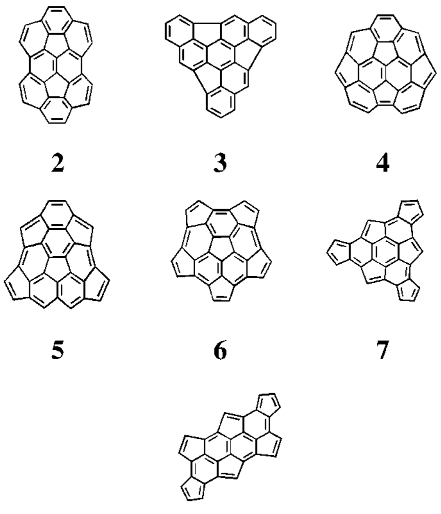
Scheme 2



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[2,3,9−11] (Scheme 2), and some have been prepared: **2**[12] and **3**.[13,14]

These molecules include (i) a nonisometric[15] fragment **2**; (ii) a chiral buckybowl **8** (generated by a homochiral[16] segmentation usually referred to as "La Coupe du Roi");[17,18] (iii) a chiral isomer **3** (coming from a heterochiral[16] bisection); and (iv) four achiral isomers (**4**−**7**).

However, the total number of all possible isometric C_{30}

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(15) Two molecules are isometric if the atoms and their connectivity are the same. Thus, the *nonisometric* buckybowl **2** (Scheme 2) "...is not an exact half of C_{60} since when buckminsterfullerene is 'taken apart' to produce the carbon framework that leads to it, the remaining carbon fragment is not identical with it....", as stated in ref 2.

(16) A brief and interesting glossary of stereochemical terminology is found in the ref 17.

(17) For a nice historical account of the trick to divide an apple into two homochiral halves by "La Coupe du Roi" and for the use of this story in chemistry, see: Mislow, K. *Bull. Soc. Chim. Fr.* **1994**, *131,* 534.

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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),[16] has been comprehensively examined by Mislow.[17] Therefore, we decided to use this methodology[17,18] to determine the total number of pairs of isometric C_{30} fragments constituting the fullerene C_{60}.

We find *nine* bisections, including four chiral C_{30} buckybowls from four different Coupes du Roi. Additional insight into this series is also provided by (i) the calculated[19] energies and curvatures of these C_{60} fragments and (ii) the estimated strain energies, reflected by the stabilization energies obtained from the appropriate homodesmotic reactions.

Mislow and co-workers[17] 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 C_{60} 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, bisections may yield achiral, heterochiral, and homochiral segments.

Considering the icosahedral object C_{60} (symmetry elements corresponding to a truncated regular icosahedron) and the dissections[20] to C_{30} segments, the connections of *two isometric halves*, which have to be related by a symmetry operation of the C/O, *involve exclusively a C_2 axis or an inversion center*. The corresponding “belts”[21] 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 C_{60} and, with the consideration of these two symmetry elements, by achieving one turn around the fullerene.[22] The distinct dissections, and consequently the C_{30} segments, eventually arise from these belt structures.

Excluding the nonisometric isomer **2**, we presently find nine bisections to isometric C_{30}, that is, three additional bisections as compared to the previous ones (Scheme 2). The present nine C_{30}, 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[23] the relative energies of energy-minimized geometries of these nine C_{30} segments,[24] as well as the parameters related to their curvatures.[22] The results involve three series of compounds (Table 1).

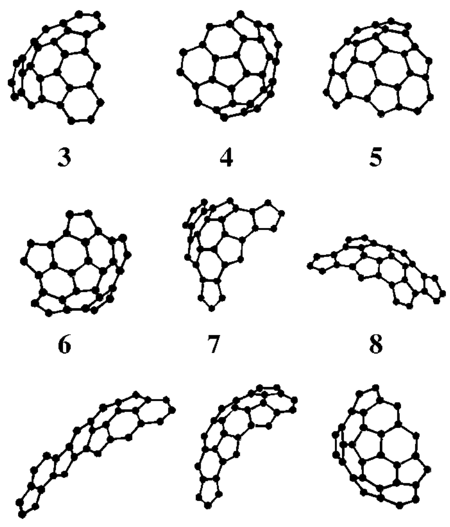

Figure 1. Nine isometric C_{30} energy-minimized structures. Fragments **3** (resulting from a heterochiral cut) and **8**−**11** are chiral.

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 $(C_{30}H_{10})$ and $(C_{30}H_{12})$, 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 C_{60} surface prior to segmentation. This issue, involving the “curvatures” of these molecules, is now detailed.

The pyramidalization angle obtained from the π-orbital axis vector (POAV) has been shown to provide a useful index of the “local curvature” of fullerenes.[25] Alternatively, the present calculation of dihedral angles θ (as defined in the caption of Figure 2; θ_a and θ_{max} 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 C_{30}, there are significant variations of curvature along the structure,[22] emphasized by the $(\theta_{max}) - (\theta_a)$ differences (Table 1). For comparison, the “regularly curved” spherical fullerene C_{60} corresponds to $\theta_{max} = \theta_a = 41.8°$. These “irregular” distributions of curvature are reminiscent of the recent gas-phase molecular structure of corannulene, exhibiting a slightly flattened shape.[26] In addition, the curvature values of the distinct C_{30}

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(19) See also: Alvarez, S.; Serratosa, F. *J. Am. Chem. Soc.* **1992**, *114*, 2623

(20) The “cuts” corresponding to various bisections involve homolytic bond splitting. The C_{30} segments are obtained by attachment of hydrogen atoms to the resulting “dangling” carbon bonds.

(21) Sequences of five- and/or six-membered condensed rings on the C_{60} surface outline the “belts”,[22] assembled from the end-carbons of the C_{30} segments. To outline exclusively C_{30} fragments originating from condensed rings, the corresponding belt should only involve two-ring junctions. The “cuts”, defining the split bonds of C_{60}, cross through the junctions of the “belts”.

(22) See Supporting Information.

(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.; Dapprich, 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.; Malick, 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.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, 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.[22]

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Table 1. Ab initio Calculated Energies (ΔE)[a] and Curvatures[b] θ_a (average) and θ_{max} (maximum value) of Distinct Isometrical C_{30} Segments

C_{30}	ΔE	θ_{max}	θ_a	$\theta_{max}-\theta_a$	total number of five-membered rings	total number of six-membered rings[c]
($C_{30}H_{10}$)						
4	0	45.5	34.5	11.0	4	7
↓	4.67	45.5	33.1	12.4	5	6
5	5.91	43.5	33.3	10.2	5	6
↓	7.22	39.6	31.5	8.1	6	5
11						
↓						
6						
($C_{30}H_{12}$)						
3	0	38.1	27.0	11.1	3	7
↓	87.90	39.0	19.6	19.4	5	5
10	89.18	39.4	18.2	21.2	6	4
↓	106.78	36.7	19.0	17.7	6	4
8						
↓						
7						
($C_{30}H_{14}$)						
9		25.3	10.2	15.1	4	5
fullerene						
C_{60}		41.8	41.8	0	12	20

[a] Zero energies (in kcal/mol) correspond, in each series of compounds, to the most stable energy-minimized C_{30} (ΔE in kcal/mol); for the individual energy contents see ref 22. [b] Angles θ (in degrees) as parameters for the C_{30} curvatures are defined in the Figure 2 caption (see also ref 22 for all calculated values). [c] This number of six-membered rings does not reflect the number of *benzenoid* hexagons (Fries number), vide infra.

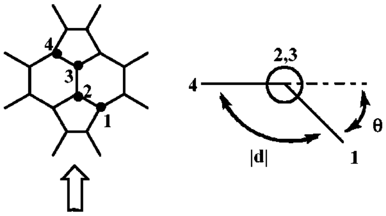

Figure 2. "Curvature" angles θ are determined as $\theta = \pi - |d|$, with the dihedral angles d being $\angle(1,2,3);(2,3,4)$.

Table 2. Stabilization Energies for Distinct Isometrical C_{30} Segments[a]

C_{30} + **a** $C_2H_6 \rightarrow$ **b** C_4H_8 + **c** C_5H_{10} + **d** C_6H_{12}	(a)	(b)	(c)	(d)	SE
3	24	3	6	6	−144.58
6	25	5	0	10	−70.15
4	25	3	4	8	−69.23
9	23	2	10	3	−65.86
5	25	3	4	8	−64.57
11	25	3	4	8	−63.32
8	24	4	4	7	−59.47
10	24	2	8	5	−52.60
7	24	3	6	6	−37.80

[a] Stabilization energy SE = $E_{C_{30}} + a.E_{C_2H_6} - b.E_{C_4H_8} - c.E_{C_5H_{10}} - d.E_{C_6H_{12}}$ in kcal/mol, using homodesmotic reactions of the type illustrated in eq 1. For the individual energy contents calculated at the ab initio RHF 6-31G level see ref 22.

within each series are also highly dissimilar[22] [see the unlike mean values (θ_a) and disparate (θ_{max}) − (θ_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 θ_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 θ_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 compared by means of homodesmotic bond separation reactions of the type illustrated in eq 1.

$$C_{30} + \mathbf{a}\ C_2H_6\ \text{(ethane)} \rightarrow \mathbf{b}\ C_4H_8\ \text{(cis 2-butene)} + \mathbf{c}\ C_5H_{10}\ \text{(2-methyl 2-butene)} + \mathbf{d}\ C_6H_{12}\ \text{(2,3-dimethyl 2-butene)} \quad (1)$$

As a delicate balance between π-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 π-system's relative-stability criterion,[27] 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.[13,14]

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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(27) See, for example: Austin, S. J.; Fowler, P. W.; Manopoulos, D. E.; Zheng, M. *Chem. Phys. Lett.* **1994**, *228*, 478 and references therein.