Stability factors among fullerene C<sub>60</sub> complete set isomers

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Various factors affecting the stability of a complete set of isomers of fullerene C<sub>60</sub> are investigated; among which, cage surface curvature, a factor that has not been paid attention much in the literature, is shown most responsible of the factors.

After successful interpretation given by π orbital axis vector (POAV) method for the cut off observed in the mass spectrum of carbon clusters C<sub>n</sub> (at n = 32) generated by laser vaporization technique<sup>2-6</sup>, a need to examine this method for explaining the relative stabilities of a complete series of isomers of a particular fullerene which is macroscopically produced is appreciated.

Study of the relative stabilities of various isomers of a given fullerene has been done by several methods, such as; isolated pentagon rule (IPR)<sup>7-14</sup>, simple Hückel resonance stability energy calculation<sup>7-16</sup>, resonance stability energy obtained by POAV<sup>1, 17-19</sup>, HOMO-LUMO energy gap calculation<sup>13-16</sup>, molecular mechanics method for small cage fullerenes with a few isomers, and ab initio and semiempirical techniques for certain restricted cases<sup>7,20-21</sup>. Except for a qualitative comparison by IPR method no other quantitative study on the correlation and comparison of these various factors on this subject is given in the literature.

In this report, we have considered the complete C<sub>60</sub> isomers set (1812 isomers)<sup>22-23</sup>, and their stability energy are calculated via simple Hückel, molecular mechanics, and POAV techniques. The degree of correlation between these stabilities and, with the amount of cage surface curvature, which is defined in the text is investigated.

Theory

The internal strains encountered in the construction of a fullerene cage is originated from two factors; the first factor which we call it “quantum strain”, is caused by a decrease in the overlap of σ and π orbitals system of the cage thereby reducing the stability of a given isomer.

Since carbon atoms of a fullerene cage have equivalent geometry, one can suggest a correlated deviation from normal hybridization angles for both σ and π systems and therefor a similar trend for changes is expected. Decrease in π - orbital system overlap is accounted for by pyramidalization angle<sup>24-28</sup> calculations using the POAV method<sup>1, 17-19</sup>. The second internal cage strain is due to a mechanical and geometrical tension within the cage structure which is raised by deviations form normal symmetries of five and six membered rings forced to fuse in the cage construction process, as well as the amount of stability gained by the Hook’s forces distribution on the cage surface.

In the POAV calculation method, these two factors are considered simultaneously. The original cage skeleton is optimized by a molecular mechanics technique which is then used as a basis for π system resonance energy stability calculations. The m factor, which is a measure of the percent decrease in overlap between the carbon atomic p<sub>z</sub> orbitals being deviated from normal hybridization angles, can be obtained by POAV method and employed for comparison.<sup>18</sup>

In this study we have regarded the deviation from perfect planar π system configuration as a geometrical factor for the cage stability<sup>24-28</sup>. For each cage vertex, this factor is defined as the difference of the angles sum on the vertex from 360 degree:

$$H_i = \sum_{j=1}^{3} \theta_{\sigma}(i, j) - 360$$  \hspace{1cm} (1)

and for a whole cage as an average over all vertices (n), we get:

$$H = \frac{1}{n} \sum_{i=1}^{n} H_i$$  \hspace{1cm} (2)
where $\theta_{oo}$ is the pyramidalization angle on a vertex which is illustrated with regard to a $p_z$ orbital in space (Figure 1).

Calculations

The complete series of isomers for C$_{60}$ (1812 isomers) were recognized in a matlab 5 software using a spyral$^{15}$ and a graphical technique. All the isomers’ geometries were optimized by molecular mechanics MM+ method. In this process, the total internal strain energy as well as van der Waals intermolecular energy was obtained for each isomer. Values for the angle $\theta_{oo}$ for all vertices of a cage were calculated; from which, and by using the R. C. Haddon$^{19}$ semiempirical results, values of m factor was obtained for each vertex. Employing the POAV method, resonance stability energy of $\pi$ system was obtained for each cage. For comparison purposes simple Hückel resonance stability energy as well as HOMO-LUMO gap energy were calculated.

Results and Discussion

Figure 2 is an illustration of the MM+ energy stability changes with that obtained by POAV method. Same result was obtained for simple Hückel calculations. No particular correlation between these factors is obvious. The stability trend is examined for intermolecular van der Waals forces obtained by MM+ and m factors used for POAV in Figure 3. A relative mild correlation is observed which means that as the m factor increases, an increase in deviation of the isomers from normal hybridization angle cause the van der
Waals energies to rise (Figure 3).

As the second factor, Figure 4 compares the deviation from planar configuration $H$ with the resonance stability energy obtained by POAV. A complete correlation between these two factors suggests that the increased cage internal strain caused by deviation from planar state shows up as a smooth decrease in the resonance stability energy. The most stable isomer, $C_{60}-I_h$, predicted by this theoretical calculation is in accord with the macroscopically generated isomer and is pointed in Figure 4. We find no correlation between $H$ with

**Figure 3** — Calculated m factors against van der Waals energy values obtained by MM+ method for the complete set of $C_{60}$ isomers (1812 isomers).

**Figure 4** — The "H" values in degrees plotted against resonance stability energies obtained by POAV for the complete set of $C_{60}$ isomers (1812 isomers).
any of the stability results obtained from MM+, simple Hückel, and HOMO-LUMO gap (Figure 5).

**Conclusion**

The trend observed for changes of resonance stability energy obtained by POAV and the degree of deviation from planar configuration $H$, for complete set of $C_{60}$ isomers, suggests a perfect logical correlation between the two stability factors. The more a configuration approaches planarity, the more stable it becomes. Therefore, the predicted most stable isomer would be the one closest to planar geometry which in the case studied is $C_{60}$-I$_0$, in agreement with highest yield isomer in the fullerenes production process.

The remarkable ability of the simple POAV method in correctly predicting the stability trend among a complete set of isomers of a given fullerene originates from the fact that this method not only considers the resonance stability due to intermolecular van der Waals forces, but at the same time, the optimized geometry obtained by molecular mechanics calculation is also taken into account.

Our results suggest that the effective forces in the caged fullerenes production process from carbon plasma are molecular mechanics forces as well as resonance stability energies.

**References**