On applicability of the Wiener index to estimate relative stabilities of the higher-fullerene IPR isomers

ZDENĚK SLANINA*, MIN-CHU CHAO†, SHYI-LONG LEE* and IVAN GUTMAN‡

‡Department of Chemistry, National Chung-Cheng University Ming-Hsiung, Chia-Yi 62117, Taiwan and
*Faculty of Science, University of Kragujevac, P.O. Box 60, YU-34000 Kragujevac, Yugoslavia

(Received 16 August 1996)

The Wiener index is tested as a possible measure of the relative-stability order for the isolated-pentagon-rule (IPR) isomers of higher fullerenes. The quotient works very well for the C_{60} IPR set (and is superior to the topological HOMO-LUMO gap). The Harary index produces a comparable correlation. The Wiener index, however, does not produce a good stability correlation for the IPR sets of C_{34} and C_{36}.

Keywords: Wiener index, higher fullerenes, IPR structures, relative stabilities.

The apparent stability of C_{60} and some higher fullerenes represents a challenging theoretical problem. According to Taylor, C_{60} is the most accessible but not necessarily the most stable fullerene. Chemical theory has not yet suggested a practical stability quotient in order to measure the stabilities of fullerenes of different dimensions. Designing such a quotient is not an easy task, as the stabilities of two different fullerenes depend on both temperature and pressure. Most probably, the formation of fullerenes is controlled by a complicated kinetics, with relevant processes not only in gas but also in the condensed phase.

The fullerene stability problem can, however, be considerably delineated if we select one particular fullerene, C_{m}, keep the carbon contents n constant, and treat the relative stabilities of various fullerene isomers with the composition C_{n}. In fact, experimental knowledge on higher fullerenes is rather extensive – about twenty stable species have been reported with n from 60 to 90. The actual number of all isomeric cages built from pentagons and hexagons is rather high – for example C_{60} allows for 1812 fullerene isomers (3532 if enantiomeric pairs are considered as two distinct fullerenes). This amount of structures can be drastically reduced using the so-called isolated-pentagon-rule (IPR). This empirical rule claims that higher fullerene cages, with all 12 pentagons exclusively surrounded by hexagons, are especially stable. The IPR concept has been computationally tested on the C_{76} family. The rule has widely been accepted in both experimental and theoretical studies of higher fullerenes. The smallest possible IPR species is the celebrated buckminsterfullerene, and together with C_{70} is a unique structure. The smallest fullerene with more than one IPR structure is C_{76}; however, thereafter the number of IPR isomers increases quite rapidly as demonstrated in enumerations with the spiral algorithm. For n = 100 we already encounter

* Corresponding author. On a leave of absence from the Academy of Sciences of the Czech Republic, Prague.
450 IPR isomers (862 if enantiomers are respected). This isomeric set could hardly be handled by quantitative quantum-chemical methods. Clearly, much simpler and more transparent approaches are needed.

Observations have frequently indicated the coexistence of several isomers for higher fullerenes.\(^4\) In fact, there are three fullerene-isomeric mixtures with considerable experimental-theoretical agreement: \(C_{78}\) (e.g., Refs. 7-10), \(C_{82}\) (e.g., Refs. 11-15), and \(C_{84}\) (e.g., Refs. 16-20). Very recently, computations\(^{21-26}\) on \(C_{80}\) have been experimentally confirmed.\(^{27}\) At present, we have continued our studies with still higher fullerenes, in particular\(^{28}\) the \(C_{86}\) isomeric set. Thus, we have created a bank of quantum-chemical fullerene data, and we can try to search for quotients correlated with them, and then use them in reliable predictions for \(n\) well beyond 100.

THE WIENER INDEX AND RELATED CALCULATIONS

The Wiener index (labelled \(W\)-index in the tabular and graphical materials) is a rather natural choice for the correlation tests. The carbon atoms in fullerenes are always distorted from an ideal \(sp^2\) hybridization; this distortion can be measured by the surface curvature. Buckminsterfullerene itself exhibits a constant curvature. Other stable fullerenes exhibit quasispheroidal shapes. On the other hand, structures with abrupt changes of curvature (which happens, for example, if two pentagons are connected) are likely to have high energy, \(i.e.,\) low stability. The abrupt changes in curvature cause an elongated rather than spheroidal shape. Instead of treating terms of curvature or quasi-spheroidality, we can use a measure of the structural compactness, and the Wiener index in particular.

The Wiener index is defined\(^{29,30}\) as the sum of topological distances between all pairs of vertices in a molecular graph. Traditionally, it has been evaluated from the adjacency matrix of the corresponding graph. The adjacency matrix itself can readily be deduced from the Cartesian coordinates of the atoms resulting from a quantum chemical geometry optimization. The quality of the optimized geometry is not important (unless the connectivity pattern is changed during the optimization) as the Wiener index is a topological invariant. The energetics used in our correlations with the Wiener index originated in our previous semiempirical quantum chemical-calculations. The semiempirical methods primarily yield the heat of formation at room temperature, and the term could be directly used. We, however, prefer to keep consistency with the related \(ab\ initio\) calculations we performed as checks of the semiempirical treatments. Hence, the semiempirical data were reduced to the absolute zero temperature and the vibrational zero-point energy was extracted, yielding the terms of potential energy (\(i.e.,\) the primary output of \(ab\ initio\) calculations).

As always with topological indices, we cannot say \textit{a priori} whether one kind of correlation with a physico-chemical property will work well. It has to be tested, and possibly adjusted. In any case, with higher fullerenes there is a strong need for a simple tool to predict isomeric stabilities.

RESULTS AND DISCUSSION

Let us start with the IPR isomers of \(C_{90}\) – they are seven and their symmetries are rather diversified (Table I). The relative potential-energy changes are derived from our recent SAM1 (Semi-Ab-Initio Model 1) calculations.\(^{26}\) The ground state structure has a \(D_{5d}\) symmetry and is closely followed by a structure with a \(D_2\) symmetry. Table I shows that the
computed relative concentrations at a temperature of 1000 K correspond to the potential-energy order. Although the HOMO-LUMO gap has sometimes been suggested as a possible stability measure for fullerenes, there are numerous examples where this term fails. This is also documented by the correlation between the SAM1 relative potential energies and the topological, Hückel HOMO-LUMO gaps in the C_{80} IPR set presented in Fig. 1. The correlation coefficient reads 0.574 in this case.

**TABLE 1. Selected characteristics of the IPR isomers of C_{80}**

<table>
<thead>
<tr>
<th>Species</th>
<th>Symmetry</th>
<th>$W$-index</th>
<th>$\Delta E_{rel}$ (kJ/mol)</th>
<th>$\chi^{1000}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2</td>
<td>$D_{2}$</td>
<td>17352</td>
<td>17</td>
<td>42.6</td>
</tr>
<tr>
<td>B 7</td>
<td>$D_{2}$</td>
<td>17600</td>
<td>314</td>
<td>$6\times10^{11}$</td>
</tr>
<tr>
<td>C 1</td>
<td>$D_{5d}$</td>
<td>17340</td>
<td>0</td>
<td>57.1</td>
</tr>
<tr>
<td>D 6</td>
<td>$C_{2v}$</td>
<td>17500</td>
<td>154</td>
<td>$1\times10^{3}$</td>
</tr>
<tr>
<td>E 3</td>
<td>$C_{2v}$</td>
<td>17412</td>
<td>75</td>
<td>$3\times10^{1}$</td>
</tr>
<tr>
<td>F 4</td>
<td>$C_{2}$</td>
<td>17368</td>
<td>138</td>
<td>$6\times10^{3}$</td>
</tr>
<tr>
<td>G 5</td>
<td>$C_{s}$</td>
<td>17454</td>
<td>115</td>
<td>$3\times10^{2}$</td>
</tr>
</tbody>
</table>

*The letter and number code are taken from Refs. 25 and 1, respectively. bThe SAM1 relative potential energy. cThe SAM1 mole fraction at 1000 K.

The Wiener numbers do correlate much better with the SAM1 relative energies for the C_{80} IPR family (Fig. 2). The correlation coefficient is now 0.911. In agreement with our qualitative reasoning on structural compactness, the two isomers low in energy also show relatively small values of the Wiener index. The Wiener index is clearly superior to the Hückel HOMO-LUMO gap. An equally good correlation (the correlation coefficient is 0.917) is seen with the Harary index (Fig. 3, $H$-index – a reciprocal analogy of the Wiener index).

C_{84} already allows for 24 IPR isomers. In an NMR observation Kikuchi et al. concluded that C_{84} should have two major isomers of $D_{2}$ and $D_{5d}$ symmetries in a ratio of 2:1. The relative potential energies used in this report are derived by the MNDO semi-
Fig. 2. Plot of the relative potential energies against the Wiener numbers for the IPR set of C₈₀.

Fig. 3. Plot of the relative potential energies against the Harary numbers for the IPR set of C₈₀.

empirical method. The predicted global minimum of $D_{2d}$ symmetry remains the most stable species in the equilibrium isomeric mixture only till 276 K, and is replaced by a $D_2$ species beyond that point. The calculated composition²⁰ around the temperature of 1000 K is consistent with the NMR observations. However, if we now plot in Fig. 4 the MNDO relative potential energies against the Wiener index for all 24 IPR isomers of C₈₄, the degree of correlation is low (the correlation coefficient is only 0.566). Moreover, the fitted straight line is decreasing, not increasing (i.e., contrary to the finding in Fig. 2).

C₈₆ is the third fullerene system we selected for our prospector study. There are nineteen topologically different C₈₆ IPR structures¹. Achiba et al. concluded⁴ from $^{13}$C-NMR spectra the presence of two $C_2$ isomers in their C₈₆ sample (the abundance of the isomers was about 4:1). The temperature of their sample production is not known. Our SAM1 computations²⁸ around 1500 K basically agree with their observation, though at higher
temperatures the coexistence of more than two isomers would be predicted. There is, however, a problem because one of the two particularly stable species has a $C_5$, not $C_2$ symmetry. Fig. 5 presents the correlation of the SAM1 relative potential energies with the Wiener numbers for the $C_{86}$ family. Although the correlation is not particularly good (the correlation coefficient is 0.520), the fitted straight line has the same orientation as found in Fig. 2.

This first-ever attempt to correlate fullerene stabilities with the Wiener indices is rather encouraging. There are several points which should be further clarified. Although we have used the computed relative potential energies, we could also use the Gibbs free energies at some selected high temperature. The choice of the representative temperature is still unclear at present (and it also may not be uniform). On the other hand, all the available experience suggests that thermodynamics rather than kinetics is responsible for the relative concentra-
ИЗВОД

О ПРИМЕНЉИВОСТИ ВИНЕРОВОГ ИНДЕКСА ЗА ПРОЦЕНУ РЕЛАТИВНЕ СТАБИЛНОСТИ ИЗОМЕРА ВИШИХ ФУЛЕРЕНА КОЈИ ЗАДОВОЉАВАЈУ ПРАВИЛО ИЗОЛОВАНИХ ПЕНТАГОНА

ЗДЕЊЕК СЛАНИНА,1 MIN-ЧУ ЧАО,1 ШАЈ-ЛОНГ ЛИ1 И ИВАН ГУТМАН2

1 Одељење хемије, Национално Училиште Обрни, Џенге, Тайван и 2 Природно-математички факултет, Универзитет у Краљевцу

Винеров индекс је тестиран као могућа мера релативне стабилности изомера виших фулерена који задовољавају правило изолованих пентагона (IPR). Индекс даје врло добре резултате за Sω и Sω IPR-изомере (и бољи је од томополске НОМО-ЛУМО сепарације). Характеристике и незначајне резултате. У случају Sω и Sω+ IPR-изомера између Винеровог индекса и стабилности не постоји добри корелација.

(Примљено 16. августа 1996)

REFERENCES