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FULLERENES AS MULTI-ISOMERIC MIXTURES: COMPUTATIONAL STUDIES OF THE C_{70} AND C_{60} CASES

Zdeněk Slanina**, Mei-Ling Sun*, Shyi-Long Lee* and Ludwik Adamowicz*

*Department of Chemistry, National Chung-Cheng University
Ming-Hsiung, Chia-Yi 62107, Taiwan

**Department of Chemistry, The University of Arizona
Tucson, AZ 85721, USA

The computational treatment of multi-configuration fullerene systems is demonstrated on two IPR isomeric sets, viz. C_{70} and C_{60}, based on the AM1 calculations. While in the former case temperature does not change the picture, the latter set is considerably temperature sensitive.

INTRODUCTION

Although the C_{60} itself is a unique structure, other fullerene-related species frequently exhibit isomerism. In computations, the isomers emerge as different local energy minima on the potential hypersurface representing the total stoichiometry. The computational search starts with a topological reasoning and frequently is limited to the structures obeying the isolated pentagon rule (IPR). Then, a full geometry optimization is performed. The optimizations should be followed by vibrational analysis in order to check the nature of the optimized structures. However, the step is sometimes skipped owing to computational demands. As quite high temperatures are involved, their effects on the inter-isomeric relative stabilities should be treated. At present, it is done within the thermodynamic-equilibrium conditions. Higher temperatures allow for some relative stability interchanges, and this can even concern the ground-state species. In overall, a conclusion on the stability order at experimental conditions cannot in some cases be based (1.4) on the relative potential energy terms alone (or it can be misleading). Three systems were already treated from the point of view (1.4), in fact the systems which have received attention from many sides and angles - C_{70} [5-8], C_{62} [9-10], and C_{84} [16-31].

In this paper we shall illustrate the problem on two interesting fullerene systems, C_{70} and C_{60}. Since its isolation by Ettl et al. (32), C_{70} has also been

* On a leave of absence from the Academy of Sciences of the Czech Republic, Prague, to whom correspondence should be addressed at the NCCU.
given a considerable attention (33-41). On the other hand, C_{60} has not been isolated yet and thus, it has been treated only rarely, and only computationally (42-44).

CALCULATIONS

The computations were carried out with various computational-chemistry program packages, mostly at semiempirical level (though some HF ab initio results are included, too). The key tool was the standard version of the AM1 semiempirical quantum-chemical method (45-47). The geometry optimizations were mostly carried out with the SPARTAN 3.0 (Iris/Silicon Graphics XZ4000 workstation) program package (48). Supporting computations were also performed with the GAUSSIAN 92 (49) and MOPAC 5.0 (50) programs. The full geometry optimization was based on the analytical energy gradient in Cartesian coordinates. In the stationary points found, their harmonic vibrational analysis was then carried out in order to check the stationary-point type and to generate vibrational spectrum. The vibrational analysis was based on a numerical differentiation (0.01 Å step) of the analytical energy gradient. For the C_{60} IPR set the computations were repeated with the newly introduced SAM1 semiempirical method (51) implemented in the AMPAC package (52).

Relative concentrations in a set of n isomers were computed as the mole fractions \( w_i \), using the isomeric partition functions \( q_i \) based on the rigid-rotor and harmonic-oscillator approximation. In the terms of \( q_i \) and the ground-state energy changes \( \Delta H_{0,i}^* \), the mole fractions are given (53)

\[
w_i = \frac{q_i \exp(-\Delta H_{0,i}^*/(RT))}{\sum_{j=1}^{n} q_j \exp(-\Delta H_{0,j}^*/(RT))},
\]

where \( R \) is the gas constant and \( T \) the absolute temperature. The conventional heats of formation at room temperature were converted to heats of formation at the absolute zero temperature, and finally the vibrational zero-point energy was extracted. Hence, the relative potential energies \( \Delta E_{rel} \) resulted from the treatment (this quantity primarily comes from ab initio computations).

Chirality contribution is to be considered with Eq. (1). There is no asymmetric carbon atom in conventional sense in the fullerene cages (with three coordinated carbon atoms), nevertheless, some of the structures are still chiral, i.e. they are not superimposable upon their mirror image. This structural dissymmetry can readily be recognized from the point group of symmetry as presence of no reflection symmetry, i.e. absence of rotation-reflection axes \( S_n \) except only the \( C_n, D_n, T, O, \) and \( I \) groups obey the requirement. For an enantiomeric pair its partition function \( q_i \) in Eq. (1) has to be doubled (if we assume the presence of both optical isomers, which seems natural under fullerene synthesis conditions).
Table I. The AM1 Energies of the $D_2$ and $D_{2d}$ Structures of C$_{76}$

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$\Delta H^*_{298}$ (kcal/mol)</th>
<th>$\Delta H^*_{298,r}$ (kl/mol)</th>
<th>$\Delta E_r$ (kl/mol)</th>
<th>ZPE* (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_2$</td>
<td>1122</td>
<td>0.0</td>
<td>0.0</td>
<td>1408</td>
</tr>
<tr>
<td>$D_{2d}$</td>
<td>1147</td>
<td>103.1</td>
<td>108.4</td>
<td>1403</td>
</tr>
</tbody>
</table>

* The vibrational zero-point energy.

Table II. The AM1 Computed Rotational and Vibrational Characteristics of the C$_{76}$ Isomers

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$A$ (cm$^{-1}$)</th>
<th>$B$ (cm$^{-1}$)</th>
<th>$C$ (cm$^{-1}$)</th>
<th>$\omega_n$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_2$</td>
<td>0.00194</td>
<td>0.00171</td>
<td>0.00156</td>
<td>221/1344/41/1607/79</td>
</tr>
<tr>
<td></td>
<td>1683/96</td>
<td>1723/41</td>
<td>1764/62</td>
<td>1846</td>
</tr>
<tr>
<td>$D_{2d}$</td>
<td>0.00174</td>
<td>0.00173</td>
<td>0.00173</td>
<td>243/909/85/1289/81</td>
</tr>
<tr>
<td></td>
<td>1335/86</td>
<td>1365/75</td>
<td>1431/71</td>
<td>1841</td>
</tr>
<tr>
<td></td>
<td>1516/72</td>
<td>1832/100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Only the lowest, the highest, and seven IR most intense vibrational wavenumbers $\omega_n$ are given (the most intense wavenumbers are followed by their relative IR intensities in arbitrary units).

Table III. The AM1 Temperature Dependency of the Equilibrium Mole Fractions $w_i$ of the C$_{76}$ Isomers

<table>
<thead>
<tr>
<th>Isomer</th>
<th>500 K</th>
<th>1000 K</th>
<th>1500 K</th>
<th>2000 K</th>
<th>2500 K</th>
<th>3000 K</th>
<th>4000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_2$</td>
<td>100.0</td>
<td>100.0</td>
<td>99.98</td>
<td>99.80</td>
<td>99.29</td>
<td>98.34</td>
<td>95.29</td>
</tr>
<tr>
<td>$D_{2d}$</td>
<td>1x10$^{-9}$</td>
<td>3x10$^{-4}$</td>
<td>0.02</td>
<td>0.20</td>
<td>0.71</td>
<td>1.06</td>
<td>4.71</td>
</tr>
</tbody>
</table>
Fig. 1. The AM1 optimized IPR structures of C_{36}.
Table IV. The AM1 Structures and Energetics* of the IPR Structures of C_{80}

<table>
<thead>
<tr>
<th>Species</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
<th>( \Delta H_{f,298,rel}^\circ )</th>
<th>( \Delta E_{rel} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
</tr>
<tr>
<td>A</td>
<td>0.00179</td>
<td>0.00150</td>
<td>0.00142</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td>B</td>
<td>0.00157</td>
<td>0.00156</td>
<td>0.00155</td>
<td>273</td>
<td>301</td>
</tr>
<tr>
<td>C</td>
<td>0.00188</td>
<td>0.00142</td>
<td>0.00142</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>0.00157</td>
<td>0.00156</td>
<td>0.00155</td>
<td>132</td>
<td>144</td>
</tr>
<tr>
<td>E</td>
<td>0.00167</td>
<td>0.00156</td>
<td>0.00146</td>
<td>73</td>
<td>77</td>
</tr>
<tr>
<td>F</td>
<td>0.00166</td>
<td>0.00156</td>
<td>0.00140</td>
<td>132</td>
<td>137</td>
</tr>
<tr>
<td>G</td>
<td>0.00163</td>
<td>0.00156</td>
<td>0.00151</td>
<td>104</td>
<td>110</td>
</tr>
</tbody>
</table>

* Relative heats of formation at room temperature (\( \Delta H_{f,298,rel}^\circ \)) or relative potential energies (\( \Delta E_{rel} \)).

Table V. The AM1 Equilibrium Relative Concentrations (%) of the IPR Structures of C_{80}

<table>
<thead>
<tr>
<th>T (K)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3.20</td>
<td>4x10^{-24}</td>
<td>96.8</td>
<td>5x10^{-11}</td>
<td>3x10^{-5}</td>
<td>2x10^{-11}</td>
<td>4x10^{-8}</td>
</tr>
<tr>
<td>1000</td>
<td>30.0</td>
<td>1x10^{-9}</td>
<td>69.8</td>
<td>5x10^{-4}</td>
<td>0.17</td>
<td>1x10^{-4}</td>
<td>0.01</td>
</tr>
<tr>
<td>1485</td>
<td>48.6</td>
<td>9x10^{-5}</td>
<td>48.6</td>
<td>0.08</td>
<td>2.19</td>
<td>0.02</td>
<td>0.46</td>
</tr>
<tr>
<td>2000</td>
<td>53.9</td>
<td>0.03</td>
<td>34.3</td>
<td>1.00</td>
<td>7.48</td>
<td>0.23</td>
<td>3.06</td>
</tr>
<tr>
<td>3000</td>
<td>39.8</td>
<td>4.82</td>
<td>16.4</td>
<td>8.19</td>
<td>16.4</td>
<td>1.66</td>
<td>12.8</td>
</tr>
<tr>
<td>3345</td>
<td>31.9</td>
<td>12.0</td>
<td>12.0</td>
<td>10.8</td>
<td>16.4</td>
<td>2.14</td>
<td>14.7</td>
</tr>
<tr>
<td>3711</td>
<td>23.7</td>
<td>23.7</td>
<td>8.28</td>
<td>12.3</td>
<td>14.8</td>
<td>2.38</td>
<td>14.9</td>
</tr>
</tbody>
</table>

* Two-structure equimolarity point.

Table VI. The Separation Energy between the Two Lowest IPR Isomers (A-C) of C_{80} (kJ/mol)

<table>
<thead>
<tr>
<th>AM1</th>
<th>SAM1</th>
<th>HF/STO-3G</th>
<th>HF/3-21G</th>
<th>HF/4-31G</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>17</td>
<td>23</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

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RESULTS AND DISCUSSION

C_{76} is the smallest fullerene which allows \( \text{(54)} \) for two different IPR structures. Their topological symmetries are \( D_2 \) and \( T_6 \). However, the latter structure exhibits degenerate, partially filled frontier orbitals and thus, it has to undergo a Jahn-Teller lowering of symmetry and energy. It turns out in our AM1 computations that this process ends in a \( D_{2d} \) symmetry. The \( D_{2d} \) isomer is located about 108 kJ/mol above the ground state in the AM1 potential energy (Table I). The geometrical distortion is quite small as can be seen from the almost identical rotational constants of the structure (Table II). All computed vibrational frequencies are real; hence we really deal with local energy minima.

The \( D_2 \) structure is in a convenient situation as it is lower in energy, it is enhanced by its chirality factor, and its low vibrational frequencies are lower than those of the \( D_{2d} \) isomer. Owing to this coincidence it must be prevailing even at elevated temperatures, and this can be indeed seen in Table III. Even at 4000 K the ground-state structure represents more than 95 % of the two-isomer equilibrium mixture. Hence, the \( D_{2d} \) \( C_{76} \) species can hardly be observed.

The \( C_{60} \) system allows \( \text{(54)} \) for seven different IPR structures (Figure 1). The isomers are coded by A-G which correspond to the letters used in Ref. 44. Of the seven IPR \( C_{60} \) structures, the species B is especially interesting. Its topological symmetry is \( I_h \), i.e., the same as in the icosahedral \( C_{60} \). However, according to the concept of the Goldberg polyhedra based on topological duals (55) it has to be an open shell and it has to undergo a Jahn-Teller distortion towards lower energy and lower symmetry. We can see in Table IV on the rotational constants that the distortions are again quite small. This is in agreement with the findings for charged \( C_{60} \) species (56-58) where the Jahn-Teller geometry distortions are of the order of \( 10^{-3} \) Å only.

The symmetry of the B structure is lowered to \( D_3 \), but still the species possesses the highest energy in the set. It is interesting to note that a Jahn-Teller effect in fact influences three factors important in stability evaluations. It lowers energy, but this is usually not significant enough comparing to other isomers. It reduces symmetry and thus the symmetry number, which effectively increases the rotational partition function. Finally, it may be associated with somewhat lower vibrational frequencies owing to less rigid character of the hypersurface. The last mentioned factor increases the vibrational partition function. In other words, a local energy minimum which originates in a Jahn-Teller distortion cannot be automatically ruled out as having no significance (though it is the case in \( C_{76} \)), as it can be enhanced by temperature/entropy factors.
The determination of the symmetry deserves a comment. The computations were performed in the Cartesian coordinates, hence, the coordinates of the symmetry-related atoms can be subject to a numerical inaccuracy. If we want to extract the related symmetry group, we have to allow for some threshold variation in the coordinates when we judge symmetry relationships. For very low value (e.g., \(10^{-5}\) Å) of such a threshold we can find simply \(C_1\) symmetry and only after its increase (say to \(10^{-4}\) or \(10^{-3}\) Å) a correct symmetry appears (and a further increase, e.g., to \(10^{-2}\) Å, may produce an artificially high symmetry). Apparently, the threshold choice should be related to the precision with which the coordinates themselves are computed. It should also be realized that a usage of internal coordinates with the strict symmetry requirements may not necessarily help as a possible imaginary frequency may be quite small (HF/STO-3G calculations) for \(B\) lead to \(D_{3d}\) symmetry, however, without vibrational analysis. Using such threshold variation we determined the symmetries presented in Table IV. The results were consistent with exception of the \(E\) and \(G\) cases where reoptimization of already optimized structure sometimes resulted in a symmetry change which, however, was not permanent. Apparently, numerical precision available was not sufficient to resolve the problem and therefore we list two alternatives of symmetry for the two particular cases. However, we preferred the lower symmetry for them in the relative-stability calculations.

The computations (both at room and at absolute zero temperature) point out the \(C\) isomer (\(D_{3d}\) symmetry) as the system ground state, being followed by the \(A\) species of a \(D_2\) symmetry. This is in agreement with density functional computations. We also computed the HOMO-LUMO gaps of the species and found the values 4.0, 4.02, 4.14, 4.15, 4.31, 4.72, and 4.95 eV for the \(D, F, B, G, E, C\), and \(A\) isomers. Hence, the stability order deduced from the HOMO-LUMO gaps is not identical with the potential-energy order.

The vibrational calculations confirmed that all the seven localized stationary points are local energy minima as there was no imaginary frequency. It is interesting to note that the isomers are vibrationally different. In particular, the most intense line is located in different spectral regions for various structures. Of the seven isomers only the \(C\) species exhibits symmetry-conditioned degeneracies. It has been well known that quantum-chemical vibrational frequencies are somewhat overestimated comparing to experiment, and thus, scaling down (by a factor of about 0.9) is important for spectral predictions. But in fact, such a uniform scaling has a negligible effect for Eq. (1). Therefore, no scaling of the computed vibrational frequencies was applied in this study. Needless to add, IR intensity (or Raman activity) has spectral but no thermodynamic significance - in Eq. (1) all vibrational modes must be considered with equal significance. Although lower frequencies are generally more important for thermodynamic functions, it is the
overall interplay of all the 234 modes which affect all matters for the relative isomeric concentrations.

Table V reports the temperature evolution of the AM1 computed relative concentrations, \( w_c \), for the seven-membered mixture under the thermodynamic-equilibrium conditions. At very low temperatures the ground-state structure, C, has to be prevailing, and the relative concentrations of other structures have to obey the \( \Delta H^\text{f, std} \) order. But at higher temperatures pre-exponential factors in Eq. (1) become important (while importance of the exponential part is gradually decreased). At a temperature of 1485 K the A species reaches equimolarity with the C species, and beyond that point is always more populated. Nevertheless, at considerably high temperatures (above 3700 K) actually the B species becomes the most populated one (though the temperatures are probably already too high from a practical point of view). This surprising high-temperature importance of the B isomer originates in an interplay of terms we already mentioned above in discussing the ways how the Jahn-Teller distortion contributes to stabilization of a species. Indeed, with the B structure we can notice that it has the lowest low-frequency terms, though the chirality enhancement is relevant, too. Other four structures (D-G) are less important though not entirely negligible. It is of interest to note that the two structures with somewhat unclear symmetries, E and F, in fact do not change the overall picture even if their alternative (higher) symmetries are considered instead.

We also checked the computed separation energies and relative concentrations by the newly introduced SAM1 semiempirical method (51). The results are pretty similar to those produced by the AM1 method. However, there were no difficulties in determination of the symmetries of the structures. The C isomer is again the ground state and it reaches its equimolarity point with the A species already at a temperature of 1180 K. This can be related to the lower separation energy between the A and C structures in the SAM1 method. In order to have a wider perspective, we also computed the particular separation energy at three \textit{ab initio} levels - HF/STO-3G, HF/3-21G, and HF/4-31G (Table VI). The \textit{ab initio} computations were performed in the optimized SAM1 geometries, i.e., as a single point calculation without any further geometry optimization. The results basically agree with the AM1 and SAM1 predictions. Although there is a decrease with the basis set increase, we can hardly expect this feature to be a generally valid trend. The agreement between various types of computations supports reliability of the predicted relative concentrations, though the really final critical test is to be done by a future observation.

In both discussed cases, \( C_{16} \) and \( C_{20} \), chirality contribution played some role. Still more instructive example is however supplied by the \( C_{34} \) system. In our recent study (59) the complete set of 24 IPR isomers of \( C_{34} \) was treated with a particular respect to their chirality properties. The results turn out to
be considerably different with and without the inclusion of the chirality contributions. In fact, out of the 24 isomers only two are significantly populated at low temperatures. Moreover, they interchange their relative stabilities close to room temperature. This equilibrium point is considerably increased if the chirality contribution is neglected. At high temperatures, however, other structures become the most populated species. The structural interplay is also reflected in the overall heat capacity, which is substantially higher than that of the global minimum (by about 16 J K⁻¹ mol⁻¹), but it is not particularly sensitive to the chirality neglect. Although we prefer in our treatment to include pairs of optical isomers, in principle, a stereo-selective generation of only one of them could take place under specific conditions. It is also of interest that even in such a large isomeric system as C₆₀, various quantum-chemical approaches (29), both semiempirical and ab initio, produce essentially the same separation energies. This has also been observed (60) with a new parametrization of the MNDO method suitable for large carbon clusters. Although it perfectly reproduces the absolute values of heats of formation available from experiment, the separation energetics of isomeric fullerenes is modified only a little bit by the new procedure. Apparently, there are some fortunate cancellations in play when we deal with the relative energies (and only the relative terms matter for the relative concentrations).

The reported considerable thermal effects on the relative isomeric stabilities in the C₆₀ case result from an interplay between rotational, vibrational, potential-energy terms, and chirality factors. The whole scheme however refers to a thermodynamic equilibrium, though only to the inter-isomeric equilibrium. We can hardly say anything on the degree to which this presumption is satisfied in a future experiment. After all, fullerene synthesis is probably controlled by kinetics rather than by thermodynamics and it may explain why the C₆₀ has not yet been isolated. Other explanation could be based on a different polarity of the molecules (and, consequently, different solubility or adsorption properties). However, the most positive and most negative charge in the A and C structures is about comparable with the AM1 values for C₆₀ (though the spatial distribution of charges matters, too). In overall, computations predict that under the supposed fullerene-synthesis conditions the species A and C should primarily be produced (and the former one in a larger amount), and possibly other isomers in less significant concentrations. The proportions are however quite temperature sensitive and thus, the particular temperature regime must be known. The differences in temperature history of various samples could explain variations in isomeric composition for some higher fullerenes. The fact that in all higher fullerene isomeric systems treated by now an agreement has been achieved between observations and computations can suggest that the experiments are after all reasonably close to a partial thermodynamic equilibrium.
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