Topological “In-Out” Isomerism in Perhydrogenated Fullerenes Revisited. $C_{60}H_{58}R^1R^2$ with Two $R$ Groups “In” ($R^1$, $R^2 = H, Me$)

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Molecular mechanics calculations (using MM+, MMX and AMBER force fields) of all constitutional and topological isomers of $C_{60}H_{58}R^1R^2$ with $R^1$, $R^2 = H, Me$ revealed that “in, in” isomers are always the most stable, while the corresponding “out, out” isomers have the biggest energy. Moreover, a substitution of an “in” hydrogen atom by a methyl group in the confined volume of the $C_{60}$ cage does not change, or even lowers, the steric energy. The dependence of steric energy on the distance between the “in” hydrogen atoms (or between the carbon atoms of “in” methyl groups) reveals highly irregular behaviour, for close neighbours, reflecting differences in the energies associated with considerable distortions of the fullerene skeleton.

Key words: fullerenes, in-out topological isomerism, molecular mechanics

Theoretical chemistry of organic molecules with unusual spatial structure is blooming and nowadays the calculations sometimes precede synthetic works, allowing one to predict properties of hypothetical molecules [1,2]. This is the case with the “in-out” isomerism in hydrogenated fullerenes [3]. Endohedral fullerene complexes with lanthanides, noble gases and lithium ions inside the $C_{60}$ cage, as well as nested fullerenes, have been proved experimentally [4–7] whereas the possibility, that C–H bonds in hydrogenated fullerenes point inside the $C_{60}$ cavity remains purely theoretical [3,8–11]. Up-to-date the synthesis of such an isomer is hypothetical. However, a recently executed unnoticed synthesis of the parent $C_{60}$ [12] paves the way to the synthetic realization of “in” isomers of hydrogenated fullerenes.

Recently we reported molecular mechanics, MM, calculations on fully hydrogenated fullerenes (so-called fulleranes) and their monoalkylated derivatives [11] showing that: (a) An isomer with 10 “in” hydrogen atoms seems the most stable. However, at present one cannot decide, which of the numerous configurational isomers having 10 “in” H atoms is the most stable. Our calculations yielded the highly symmetrical isomer shown in Fig. 1 as the most stable one, while Saunders [3], using a different force field and computational procedure, found that an asymmetrical isomer has the lowest steric energy. (b) Moreover, not only was the “in” isomer more stable than the “out” one for methyl-, ethyl-, $n$-propyl- and $n$-butylsubstituted fulleranes, but also for 1,51-dimethylfullerane with two methyl groups at the opposite sides

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of the \( \text{C}_{60} \) cavity (see Fig. 2 for the adopted atom numbering [13]) the “in,in” isomer was calculated to be more stable than the “in,out” one. In turn, the latter was found more stable than the “out,out” isomer. The corresponding values of steric energy were 539.3, 571.7 and 620.4 kcal/mol, respectively. (c) Considerable distortions of the \( \text{C}_{60} \) skeleton were found for the “in” isomers, but have not been analyzed in detail. (d) Topological character of the “in-out” isomerism in perhydrogenated fullerenes was recognized, leading to an extension of the concept of topological isomerism [14].

**Figure 1.** Two projections of the highly symmetrical lowest energy fullerane with 10 “in” hydrogen atoms.

**Figure 2.** The adopted atom numbering for \( \text{C}_{60} \).
Figure 3. The 23 constitutional isomers which are possible for disubstituted fullerenes and/or fulleranes, without taking into account “in-out” isomerism. Statistical weights of isomers are given in bold, the smallest number of intervening bonds in italics, whereas the substitution type is given in brackets.
(e) The results of the calculations had allowed us to rationalize the experimental data on the instability of perfluorinated fullerene, which had been proposed to be an ideal lubricant [15], on one hand, and those on the ease of formation of onion-like nested fullerenes and nanotubes [7,16], on the other. (f) The “horror vacui” concept of ancient philosophers [17] was invoked to visualize larger stability of “in” fullerene isomers.

In continuation of this work, molecular mechanics [18] calculations of the optimum geometry have been carried out for $C_{60}H_{58}R_1R_2$ with $R_1, R_2 = H, Me$, exploring all possible configurational isomers. These included both 23 constitutional isomers shown in Fig. 3 and all “in,in”, “in,out”, “out,in” and “out,out” configurations. The results of these calculations, using three different force fields, FFs, are reported.

METHOD

We believe, that at present the molecular mechanics [18] is the method of choice for calculations of such large hydrocarbon molecules as fullerene isomers. To check, whether the results depend on the FF used, the calculations have been carried out for MMX (using PCMODEL 5.13 program [19]), MM+ [20] and AMBER [21] (as implemented in HyperChem 3.0 [25]) FFs using default parameter values. Several calculations, using differing starting geometries, have been performed to ensure that irregular trends in the distance dependence of steric energy presented in Fig. 4 are not artefacts.

RESULTS AND DISCUSSION

**H-“in”,H-“in”:** The minimum steric energy as a function of the distance between the “in”-hydrogen atoms for MMX, MM+ and AMBER force fields, FFs, [19–21] is shown in Fig. 4. The following conclusions can be drawn on the basis of the curves depicted there: (1) For all three FFs used, all isomers with two hydrogen atoms inside the $C_{60}$ cage have lower energies than the corresponding values for one hydrogen “in” and all-“out”, i.e. H-“in”,H-“out” and H-“out”,H-“out” isomers. Interestingly, the extra stabilization, due to the inclusion of one hydrogen atom inside the $C_{60}$ cage, equals ca. 5 kcal/mol for the least stable H-“in”,H-“in” isomer and is higher than 40 kcal/mol for the most stable H-“in”,H- “in” isomer. (2) Understandably, the MMX and MM+ FFs yield much closer energy values than the AMBER since the first two are modifications of MM2 FF [22]. (3) Above ca. 2.35 Å the curves exhibit, as expected, a regular dependence on the distance. However, there is a surprising highly irregular behaviour for the smaller distances. We believe that these irregularities are not the artefacts of the calculations (differing minimization procedures are used in the program packages applied in these calculations and the irregularities persist for different FFs and different starting geometries), but reflect differences in the energies of deformation of the carbon cage, which consists of two types of CC bonds: the ones connecting two six-membered rings and those connecting five-membered and six-membered rings. Thus, the energies associated with the deformation of these types of bonds are different. Considerable differences in the calculated steric energies (10.0, 5.5 and 6.8 kcal/mol for MM+, MMX and AMBER, respectively) for closest neighbours (1,2- and 1,31-isomers) illustrate this point, showing consistently lower
Figure 4. Minimum steric energy as a function of the distance between “in”-hydrogen atoms for three force fields used.
energies for the latter isomer involving the junction of 5- and 6-membered rings. The H...H distances (between “in” hydrogen atoms) calculated with these FFs differ slightly. The important point is, however, that MM+ and AMBER yield shorter distance for (1,31) isomer with the junction involving both 5- and 6-membered rings (by 0.008 and 0.031 Å, respectively), while MMX yielded the distance for (1,2)-isomer shorter by 0.042 Å. (4) As expected, the (1,51)-isomer, corresponding to the substitution at opposing ends of the C_{60} cage, exhibited the biggest distance between the “in” hydrogen atoms. However, it was not of the lowest-energy for the H-“in”,H-“in” isomers. The latter depended on the FF used. These were (1,36)- and (1,9)-isomers with MM+, and (1,48)-one with both MMX and AMBER. The energy differences of ca. 0.2 kcal/mol, obtained for all three FFs used, clearly lie within the limits of error of the method. However, the result that (1,51)-isomer with “in”-hydrogen atoms on the opposite site of the cage (characterized by the largest H...H distance) is not of the lowest energy, seems reliable since it does not depend on the FF used.

**H-“out”,H-“out”,H-“in”,H-“out” and Me-“in”,H-“out” substitution types:**

Each of these fullerenes has only one isomer. Their energies are collected in Table 1. An inspection of the data in Table 1 reveals, that the energy of H-“out”,H-“out” isomer, which is all-“out” one, is higher than that of H-“in”,H-“out” isomer by more than 40 kcal/mol. This result does not depend on the FF used. Approximately the same value for the energy difference between H-“in”,H-“out” and the most stable H-“in”,H-“in” isomer was discussed above. Moreover, there is a further decrease in energy, when “in” hydrogen atom is substituted by methyl group. This result is another manifestation of the “horror vacui” introduced earlier [17]. As mentioned earlier, with all FFs used the all-“out” (i.e. H-“out”,H-“out”) isomer has a higher energy than all H-“in”,H-“in” isomers of perhydrogenated fullerene.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Force Field</th>
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<tbody>
<tr>
<td></td>
<td>MMX</td>
</tr>
<tr>
<td>Me-“in”,H-“out”</td>
<td>560.2</td>
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<tr>
<td>H-“in”,H-“out”</td>
<td>561.9</td>
</tr>
<tr>
<td>H-“out”,H-“out”</td>
<td>604.8</td>
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**H-“in”,Me-“out”:** For these isomers with all FFs used, the lowest energy was obtained for (1,32)-substitution, the (1,3)-one being the next on the energy scale. The most probable interpretation is that the “in” hydrogen atom in these positions relieves most effectively nonbonded strain of the “out”-methyl group.

**Me-“in”,H-“in”:** The lowest steric energy obtained were 517.6, 509.6 and 462.4 kcal/mol for MMX, MM+ and AMBER FFs, respectively, for the isomer with the opposite (1,51)-substitution. The highest C(Me)...H distances were obtained for all FFs used for this isomer. Interestingly, the values calculated with MMX and AMBER FFs for the Me-“in”,H-“in” isomer are by ca. 1 kcal/mol smaller than the correspond-
ing values for H-“in”,H-“in” isomers, while an opposite trend is observed with MM+ FF. In any case, this is not what one would expect substituting a hydrogen atom by a methyl group in the restricted volume within the C_{60} cage.

**Me-“in”,Me-“in”**: Similar trends to those observed for H-“in”,H-“in” were obtained for Me-“in”,Me-“in” isomer with larger irregularities for small distances between the carbon atoms of the methyl groups. For all FFs used, the lowest-energy isomer was the “opposite” (1,51)-one, while the closest C(Me)...C(Me) distance was obtained for (1,48)-isomer. As discussed in detail earlier [11], for the most stable (1,51)-dimethylfulleranes Me-“in”,Me-“in” isomer is the most stable one. It is followed by the Me-“in”,Me-“out” isomer, which in turn, is more stable than the Me-“out”,Me-“out” one.

Three points have to be mentioned in addition to the numerical results discussed here. First, it should be stressed that the bigger stability of “in” fullerane isomers, in comparison to the “out” ones, is due mainly to a higher stress in the latter. Nevertheless, the “horror vacui” concept seems of some value here, since it correctly describes comparable or even higher stability of fulleranes with “in” methyl group(s), in comparison to those with “in” hydrogen atom(s). Secondly, it should be stressed that we do not accept Saunders’ proposal on the way of obtaining the “in” fullerane isomers [3]. Heating advocated by him seems unacceptable in view of the high barrier between the corresponding “in” and “out” fullerane isomers. A similar view, advocating inversion on carbon atoms during formation of hydrogenated fullerenes, was expressed by Yoshida et al. [10]. We believe that a directed synthesis is the only plausible way of obtaining the “in” isomers of perhydrogenated fullerenes. Third, it is worth noting, that the work on “in-out” isomerism of perhydrogenated fullerenes prompted us to extend the definition of topological isomers to include the barrier of interconversion between the isomers to the criteria involved [14], departing from the usual one-dimensional topology as applied, among others, by Walba [23] and Chambron, Dietrich-Buchecker and Sauvage [24].

An extension of the idea of topological isomerism to include in-out fullerene isomers and rotaxanes have been recently published [14].

**CONCLUSIONS**

MM calculations of all possible constitutional and “in”,“out” isomers of fullerenes with one or two hydrogen atoms or methyl groups inside the C_{60} cage indicate the “in, in”, “in, out” and “out, out” order of their stability. Moreover, in spite of the limited volume of the cage, a substitution of an “in” hydrogen atom by a methyl group does not result in the steric energy increase. Highly irregular steric energy dependence on the distance between the “in” hydrogen atoms (or that between carbon atoms of the “in” methyl groups) reflects mainly energy-costs of the distortion of the fullerene skeleton. The (1,51)-isomer with two methyl groups “in” at opposite sites of the molecule is the most stable, while for two hydrogen atoms “in” the energy of this isomer was by ca. 0.2 kcal/mol higher than that of the most stable one. The latter value clearly lies within the error of the calculations. However, it seems reliable, since it does not depend on the FF used.
Acknowledgments

Enumeration of all constitutional isomers of disubstituted fulleranes by Mr. G. Łach is gratefully acknowledged.

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