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Homodesmotic reaction for fullerenes

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Abstract—The ASE (aromatic stabilization energy) for C_{60} and C_{70} have been evaluated by a new homodesmotic reaction and the results support the early established fact that C_{70} is more stable than C_{60}.
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1. Introduction

The homodesmotic and isodesmic reactions have been used for a long time to make estimations of the stabilization energy of aromatic systems.[1] These reactions use small molecules which retain bond types on both sides of the equation to model the intrinsic energy values due to the electronic motion of π electrons. This method has yielded good results in several cases in which the main goal was to estimate the total aromaticity of a specific compound.[2]

Homodesmotic and isodesmic reactions have been used mainly to estimate aromatic stabilization energy (ASE) of isolated rings or polyaromatic hydrocarbons (PAHs),[3] in these benzene is used as a reference giving a relative value of ASE/π (i.e., aromatic stabilization energy per π electron). Therefore, benzene presents an ASE/π value of 15 kJ/mol, thus other aromatic molecules are more or less aromatic if their value is above or below this number.

Many PAHs have been evaluated by this method[3] and only coronene and pyrene have been shown to be relatively more aromatic than benzene. However, they only present planar aromaticity and this situation can change for molecules that can have 'spherical' aromaticity, as is the case of fullerenes.

There has been an extended discussion about the spherical aromaticity of fullerenes,[4] it has been proposed that there is a correlation between the diamagnetic shielding

in the center of the icosahedral fullerenes and the aromaticity[5] and that this resembles the Hückel rule[6] such that when there are $2(N + 1)^2$ π electrons the compound has aromatic character. Following this criterium the icosahedral fullerene showed definitively aromatic character. However, there is little information about the energy involved in such a stabilization and it has been suggested that since C_{60} shows aromatic character in the six-membered ring faces and antiaromaticity in the five-membered ring faces,[7] therefore there is an equilibrium between the stable and unstable zones.

The aim of this note is to present an easy procedure to evaluate the energy associated with the spherical aromaticity in symmetrical fullerenes. This approach is based on the use of a homodesmotic reaction in which theoretical calculations have provided the needed thermodynamic data.

2. Computational method

All structures, the neutral species as well as the corresponding cations were optimized in the gas phase using the Jaguar 4.0 package.[8] A pure DFT method containing the Becke's gradient corrections[9] for exchange and Perdew–Wang's for correlation[10] were used for the energy evaluations. All calculations were performed using the 6-31G** basis set. Frequency calculations were carried out at the same level of theory to confirm that the optimized structures were at a minima of the potential surfaces. These frequencies were then used to evaluate the zero-point vibrational energy, the thermal vibrational corrections to the enthalpy and the total enthalpy values.

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3. Results and discussion

The main problem in designing homodesmotic reactions involving fullerenes is that these molecules do not contain hydrogen atoms, this problem does not affect PAHs and in this case several models have been developed.[1,2] For PAHs the source of double bonds are simple olefins such as 1,3-butadiene or propylene, however, in all cases there are hydrogen–carbon bonds. Another case in which a homodesmotic equation has been used in order to find the heat of formation[11] involves the reaction shown in Figure 1.

In this case there is a source of quaternary carbon atoms in the bay region of the corannulene molecule, therefore the new homodesmotic reaction for evaluating the ASE of these molecules should consider a reactive species containing quaternary carbon atoms. There has only been one proposition of an isodesmic reaction that evaluates ASE[12] for C_{60} and it is important to note that this proposition does not involve a source of quaternary carbon atoms; the equation is shown in Figure 2.

These authors obtained an ASE value for this procedure of 2245 kJ/mol, this is a very large value if it is taken as reference for comparison, for example the corresponding theoretical value of 418 kJ/mol for coronene,[3] which is considered as a very aromatic molecule, therefore we expect to obtain a similar value in our homodesmotic procedure.

Our proposition is the homodesmotic reaction shown in Figure 3, in this reaction the reactive molecule tetravinyl-ethylene (TVE) is included (see Fig. 4) and this is the source of quaternary carbon atoms.

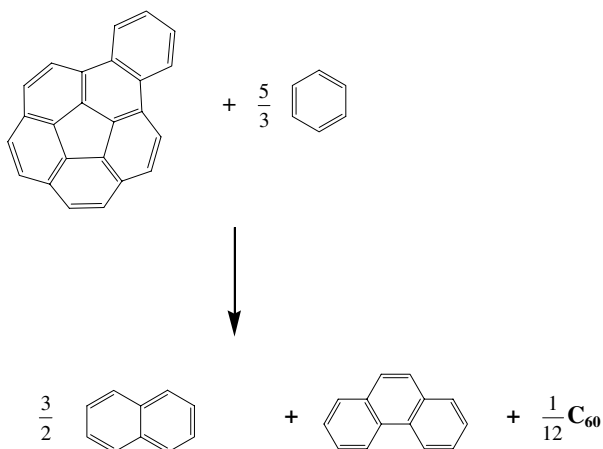TVE has been used in the schemes of homodesmotic and isodesmic reactions by George[1] with excellent results.

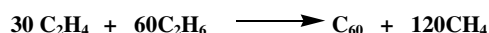**Figure 1.** Homodesmotic reaction suggested by Green and co-workers.[11]

$$30\ C_2H_4\ +\ 60C_2H_6\ \longrightarrow\ C_{60}\ +\ 120CH_4$$

Figure 2. Isodesmic reaction proposed by Fowler et al.[12]
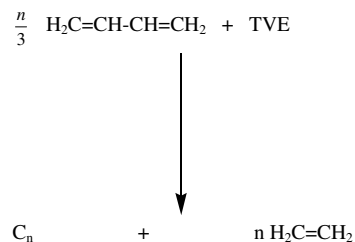

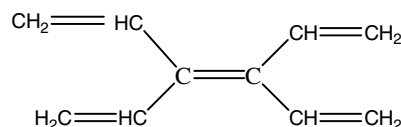**Figure 3.** Homodesmotic reaction for evaluating the ASE of fullerenes.

Figure 4. Tetravinyl-ethylene (TVE).

The fullerenes that were analyzed were C_{60} and C_{70}, the homodesmotic reaction is also useful to analyse other large spherical molecules but the Density Functional calculations become very expensive and complicated with the increase in the molecular weight.

The ASE values obtained with our model are 2345.88 kJ/mol for C_{60} and 2993.98 kJ/mol for C_{70}. These values can be compared with the average obtained for the same molecules by Slayden and Liebman[3] (2509 kJ/mol $\pm$ 55 kJ/mol for C_{60} from seven reports and 2713 kJ/mol $\pm$ 111 kJ/mol for C_{70} from three reports) and the result is acceptable. Furthermore, the ASE/π index shows a very interesting result. The heat of formation of fullerenes has been theoretically[11] and experimentally found[13,14] and it has been suggested[13] that C_{70} is more stable that fullerene C_{60} on the basis of those thermodynamical results. It seems that this proposition is correct, indeed in our case the ASE/π of C_{60} is 39.08 kJ/mol whereas the same value of the index for C_{70} is 42.77 kJ/mol, therefore C_{70} effectively is more aromatic than C_{60} and it is expected always the ASE of larger fullerenes will be larger of that of the small. However, the same index for benzene is 15 kJ/mol[3], and this probably shows that spherical aromaticity should be evaluated and considered in different ways than that of PAHs.

One of our referees has suggested that the election of TVE is problematic because its intrinsic tension may produce an artificial stabilization on the calculation and lead to masked results in the homodesmic procedure. He has suggested other way to validate our results by using DVE (divinyl-ethylene) instead of TVE and the implementation of the new homodesmic reaction is shown in Figure 5.

The use of this new scheme yields better results for C_{70} although not as good as the average reported values. On the other context, the obtained value for C_{60} is worse than the first one obtained. The new ASE for C_{60} is 2290.113 kJ/mol with an ASE/π of 38.17 kJ/mol whereas the same for C_{70} is 2895.93 kJ/mol with an ASE/π index of 41.37 kJ/mol. These results show the

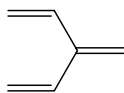$$n(CH_2=CH)_2C=CH_2 \rightarrow C_n + nCH_2CHCH=CH_2 + \frac{n}{2} CH_2=CH_2$$
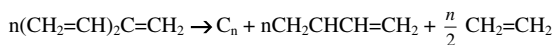

Figure 5. Divinyl-ethylene (DVE).

fullerene molecules are very strained species in which the uncertainty is large and difficult to predict.

References and notes

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