

STABILITY OF REGIOISOMERS OF ADDUCTS IN FULLERENES WITH $C_{60}X_k$ COMPOSITION

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Abstract. The relative stability of isomers for a series of $C_{60}X_k$ fullerenes with different simple and coordination addends is studied theoretically. Isomers can differ in the relative position of addends on the surface of fullerenes. The conclusions on the stability of regioisomers are based on the calculated values of total energy. It is shown that there are two main contributions into the total energy. These are the electronic energy and the energy of the reconstruction of the carbon cluster due to the modification of fullerenes. The experimental data on the structure of fullerenes with simple monoatomic addends and for compounds like $[(R_3P)_2M]_2(C_{60})$ with transition metals are treated. The experimentally detected 6–6 addition of addends in the compounds $[(t\text{-Bu}C_5H_4N)_2OsO_4](C_{60})$, $[C_6H_4(CH_2)_2]C_{60}$, and $[(R_3P)_2M](C_{60})$ ($M = Pt, Pd, Ni$) is justified in terms of the electron-conformational picture. The NMR data on the regioisomers of $[OsO_4(py)_2]C_{60}$ are treated.

Key words: fullerenes, isomerism, electron-conformational interaction.

INTRODUCTION

After the discovering of the fullerene and the developing of efficient methods for its synthesis, the interest of researchers has shifted to the preparing of fullerene derivatives and the investigating of their properties. The products of gradual additions of hydrogen, halogens, oxygen, organic radicals, and complexes of transition metals $[(R_3P)_2M]_n(\eta^2-C_{60})$, where $M = Pt, Pd, Ir$, and $1 \leq n \leq 6$, have been obtained [1–11]. For such fullerene derivatives a wide range of isomers is possible. These isomers differ in the position of the attached groups and, therefore, in energy. Thus, the theoretical study of the relative stability of regioisomers of the fullerene derivatives X_nC_{60} with various groups X is rather a pressing problem for fullerene chemistry.

As is evident from the currently available structural data [3-7], the position of addends on the C_{60} surface is independent of the nature of the groups X. This allows one to believe that the regioisomerism of such systems is mainly determined by interactions within the carbon cluster and, to a less degree, by the properties of coordinated species.

METHOD OF CALCULATION

Let us examine, using the perturbation theory, the relative stability of the isomers formed by the molecules $C_{60}X_2$, taking the starting fullerene C_{60} in its equilibrium geometry Q_0 as the zeroth approximation. The Hamiltonian of the chemically modified molecules can then obviously be represented as

$$\mathcal{H}_1(q, Q) = \mathcal{H}_0(q, Q_0) + \mathcal{H}_S(q, Q_0) + V(q, Q), \quad (1)$$

$$V(q, Q) = \sum_v \frac{\partial V}{\partial Q_v} Q_v + \dots \quad (2)$$

Here \mathcal{H}_0 is the Hamiltonian of the starting molecule; \mathcal{H}_S denotes the "substitution operator" [12, 13], describing the perturbation due to the chemical modification of the molecule C_{60} in the starting geometry Q_0 ; $V(q, Q)$ is the well-known operator of the electronic-vibrational interaction. By using the second-order perturbation theory and Hamiltonian (1, 2) both the geometry (Q_v^f) of the chemically modified system and its energy (E_S) can be obtained [12, 13]:

$$Q_v^f = \frac{2}{K_v} \sum_j \frac{S_j A_j^v}{\omega_j}, \quad (3)$$

$$E_S = S_0 - \sum_j \frac{S_j^2}{\omega_j} - 2 \sum_v K_v (Q_v^f)^2. \quad (4)$$

Here K_v , A_j^v , and ω_j are force constants, linear vibronic coupling constants, and electronic excitation energies, respectively; $S_j = \langle \Psi_0 | \mathcal{H}_S | \Psi_j \rangle$ are the matrix elements of the substitution operator.

There are two contributions of different character to the total energy E_S of the chemically modified system. The first and the second terms determine the total energy change due to a chemical modification of the starting system without its geometry variation. The third term determines the total energy change due to the geometry reconstruction [12, 13]. These equations have been used previously in the analysis of the structure and the *cis-trans* isomerism of mixed-ligand coordination compounds [12, 13].

The immediate application of the equations to the isomerism problems of fullerene derivatives is aggravated by the large number of modes and electronic excitations in the starting C_{60} system. However, in this case it is also reasonable to calculate two contributions to the total energy of the modified system: the electronic energy for the starting interatomic distances and the variation of energy due to the geometry reconstruction.

The fullerene is a conjugated system. Therefore, we have calculated the influence of π electron factors on the stability of regioisomers, using the simple Huckel method [14], which has proved to be efficient for predicting the stability and the properties of the fullerene itself [15-17]. According to this method, the introducing of the addends X decreases the dimensions of a conjugated system and changes the number of π electrons in it. The total π electron energy of a chemically modified but not reconstructed system is calculated as the sum of one-electron energies.

There are two kinds of C-C bonds in the fullerene molecule. The bonds lying on the frontiers of the two hexagons (6-6 bonds) are shorter than in benzene. These are formally double bonds [14]. The C-C bonds lying on the frontier of the pentagon and hexagon (6-5 bonds) are longer than in benzene. These are formally single bonds [14]. Thus, $|\beta_{\pi}(6-6)| > |\beta_{\pi}(C_6H_6)|$ and $|\beta_{\pi}(6-5)| < |\beta_{\pi}(C_6H_6)|$. It is known from thermochemistry that $\beta_{\pi}(C_6H_6) = -84$ kJ/mol [14]. Using the Streitwieser method [14], we assumed that β_{π} is 10% less for formally double C-C bonds and 10% larger for formally single C-C bonds than the magnitude of β_{π} for benzene $\{\beta_{\pi}(6-6) = -92.4$ and $\beta_{\pi}(6-5) = -75.6$ kJ/mol}. The origin of the energy was adopted so that $\alpha_{\pi} = 0$.

The fullerene is a strained system. In order to take into account the energy of the geometry reconstruction (steric interaction), we used molecular mechanics [18]. According to this method, the energy of the steric interactions E_{ster} is the sum of the distortion energies of bonds and angles including torsion and van der Waals interactions. The values of the corresponding parameters are presented in [18].

RESULTS

The regioisomer with two addends in the *ortho* position on a 6-6 bond (*ortho*-6,6- X_2C_{60}) is the most stable (Table). The next in stability, *para*-6,6- X_2C_{60} , is less stable by 26 kJ/mol. As is evident from the Table, steric and electron factors are favourable for stabilizing different isomers. Steric factors conduce to the most distant disposition of addends from each other, and electron factors favour the *ortho*-6,6 position. As the numerical values show, the contribution of steric interaction energy to the stabilizing of the main isomer is less than that from electron interaction.

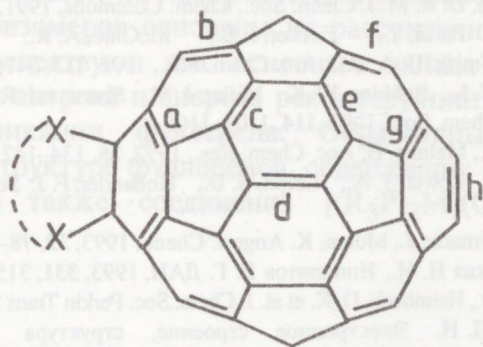
Isomer	E_{el}	E_{ster}^*	$E_{el} + E_{ster}^*$
C_{60}	-7688.5	2118.4	-5570.1
XC_{60}	-7456.8	2020.2	-5436.6
X_2C_{60}			
<i>ortho</i> -6,6- X_2C_{60}	-7361.0	1967.4	-5393.6
<i>ortho</i> -6,5- X_2C_{60}	-7297.3	1960.1	-5337.2
<i>meta</i> -6,6- X_2C_{60}	-7235.4	1925.8	-5309.6
<i>meta</i> -6,5- X_2C_{60}	-7232.2	1930.2	-5302.0
<i>para</i> -6,6- X_2C_{60}	-7290.2	1922.3	-5367.9
ω - X_2C_{60}	-7238.5	1922.0	-5316.5
$(2X_2)C_{60}$			
<i>ia</i>	-7073.5	1871.2	-5202.3
<i>ib</i>	-7027.1	1825.9	-5201.2
<i>ic</i>	-7028.2	1821.8	-5206.4
<i>id</i>	-7034.2	1818.6	-5215.6
<i>if</i>	-7033.4	1815.4	-5218.0
<i>ie</i>	-7033.0	1814.6	-5218.4
<i>ig</i>	-7033.1	1816.1	-5217.0
<i>ih</i>	-7033.2	1816.4	-5216.8

* The energy of steric interactions for fullerene derivatives with X = F and *exo* configuration of C-X bonds.

Experimental data [11] show that the predicted *ortho*-6,6 and *para*-6,6 isomers are formed in H_2C_{60} and $H(t-Bu)C_{60}$, the concentrations of *ortho*-6,6 isomers being larger. In $[(t-Bu-C_5H_4N)_2OsO_4]C_{60}$, studied by X-ray methods [8], the osmium complex is connected with the carbon cluster through two oxygen atoms. These atoms are added to a 6-6 bond, i.e. only the regioisomer most stable according to the theory occurs. It should be noted that the interatomic distance O-O (about 2.4 Å) in the osmium complex is much larger than is the 6-6 bond length. From merely steric considerations, the addition should be accomplished in the *meta* position of the hexagon or the pentagon (the C-C distance is just 2.4 Å). For this reason, the experimentally observed addition of the Ph_2C group to the shortest 6-6 bond of the fullerene with the formation of the *ortho*-6,6 regioisomer $(Ph_2C)C_{60}$ can be explained by electron factors only [1]. On the basis of NMR spectroscopic data [9], the *ortho*-quinodimethane $o-(CH_2)_2C_6H_4$ is added to the fullerene 6-6 bond, which gives the adduct $[C_6H_4(CH_2)_2]C_{60}$. For the bidentate oxygen atom with a forced *ortho* coordination in the OC_{60} cluster, two isomers, *ortho*-6,6 and *ortho*-6,5, are possible, the *ortho*-6,6 isomer being theoretically more stable of the two. This is the isomer that has been observed experimentally [6]. This *ortho*

isomer has also been detected in the compounds $[(R_3P)_2M]-\eta^2-C_{60}$ (where $M = Pt$ and Pd [7]), in which two carbon atoms are coordinated by transition metals.

We will now discuss the relative stability of regioisomers of disubstituted complexes of the $[OsO_4(py)_2]_2C_{60}$ type. Five regioisomers of this complex were detected by the NMR method in [3], but it failed to establish their structure. To assign the structure of the most stable regioisomers, we calculated the total energy of various isomers with the *ortho* attachment of two bidentate substituents in the 6-6 and 6-5 positions. As the calculations show, the 6,5-6,6 regioisomers are more stable than the 6,5-6,5 isomers by 26 to 72 kJ/mol. The 6,6-6,6 isomers are more stable than the 6,6-6,5 isomers by 58.5 to 97.6 kJ/mol. Thus, similar to the former complex, the addition of the second complex must occur at the 6,6-bond. According to geometric considerations, up to eight 6,6-6,6 regioisomers can exist. It is convenient to use the following structural formula for their designation:



Five isomers – *id*, *if*, *ie*, *ig*, and *ih*, have an equal total energy with the accuracy of ± 1.5 kJ/mol. Relative to these, the isomers *ia*, *ic*, and *ib* are destabilized by 10–15 kJ/mol. Hence, the five isomers observed in experiment [3] are *id*, *if*, *ie*, *ig*, and *ih*, which have practically equal energy.

The signals of three isomers have been detected by the NMR method in solutions of the complex $[(Et_3P)_2Pt]_2C_{60}$ [7]. One of the isomers is *ih*, but the structure of the other ones has not yet been determined uniquely. A preliminary assignment of the spectra indicates that two other isomers are *ic*, *ie*, *if*, or *ig* [7]. In this series, the *ic* and *id* isomers are less stable (see the Table).

According to X-ray data [7], the compound $C_{60}[Ir(CO)Cl(PMe_2Ph)_2]_2$ has the *ih* structure in the solid state. The addition product of two *ortho*-quinodimethane molecules to the fullerene $C_{60}[(CH_2)_2C_6H_4]_2$ has the same structure [9].

To sum up, the energetics of the fullerene derivatives depends primarily on the electron-vibrational interactions within carbon clusters. The isomerism of fullerene derivatives is determined by the joint action of

two factors: the π electron and steric interactions. Analogous results have been obtained for the derivatives of C_{70} [19].

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ADUKTIDE REGIOISOMEERIDE STABIILSUS $C_{60}X_k$ -KOOSTISEGA FULLEREENIDES

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Teoreetilisel on uuritud isomeeride suhtelist stabiilsust fullereenide $C_{60}X_k$ reas erinevate lihtsate ja koordinatsioonilisandite puhul. Isomeerid võivad erineda lisandite suhtelise positsiooni poolest fullereenide pinnal. Järeldused regioisomeeride stabiilsuse kohta põhinevad arvutatud koguenergia väärtusel. Eksisteerib kaks põhilist panust koguenergiasse:

elektronenergia ja süsinikklastri rekonstruktsioonienergia fullereeni modifitseerumisel. On käsitletud eksperimentaalandmeid lihtsate monoatomi-
liste lisanditega ja siirdemetalle sisaldavate ühenditega $[(R_3P)_2M]_2(C_{60})$
fullereenide struktuuri kohta.

СТАБИЛЬНОСТЬ РЕГИОИЗОМЕРОВ АДДУКТОВ В ФУЛЛЕРЕНАХ С $C_{60}X_k$ -СОСТАВОМ

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ИППОЛИТОВ

Теоретически исследована относительная стабильность изомеров в серии фуллеренов $C_{60}X_k$ с различными простыми и координационными примесями. Изомеры могут различаться относительной позицией примесей на поверхности фуллеренов. Выводы о стабильности региоизомеров основаны на рассчитанных значениях полной энергии. Существуют два основных вклада в полную энергию: электронная энергия и энергия реконструкции углеродного кластера при модификации фуллерена. Обработаны экспериментальные данные по структуре фуллеренов, содержащих простые одноатомные примеси, а также соединения $[(R_3P)_2M](C_{60})$ с переходными металлами.