

BIS-AZAHOMOFULLERENES: REGIOSELECTIVE SYNTHESIS AND MECHANISM OF REACTIONS

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Introduction

Reactions of organic cycloaddition to fullerene C_{60} can hypothetically lead to formation of variety of adducts. However a choice of experimentally isolated structures is not so wide. [6,6]-closed regioisomers dominate over [5,6]-open isomers at the syntheses of bis-cycloadducts [1,2]. Earlier [3,4] high selectivity of reactions of fullerene C_{60} with azides has been found out. We used HF and DFT methods with BLYP, B3LYP and PBE [5,6] functionals and basis sets 6-311G** and TZ2P to investigate isomers of $C_{60}NH$ and have found the good consent between the results of these different methods [7]. We also used DFT/PBE/TZ2P [5,6] computations to investigate influence of the nature of the substituents R on stability of regioisomers of mono- and bis-adducts of $C_{60}(NR)_2$ and have found an agreement of experimental and theoretical results [7-9], which essentially differ from the data obtained by AM1 method [10, 11].

Here we present the results of DFT/PBE/TZ2P research of both stable and unstable mono- and bis-cycloadducts of fullerene C_{60} , as well as correlations between molecular parameters (bond lengths) and stability of adducts; mechanisms and selectivity of reactions C_{60} with azides are revealed too.

Results and discussion

According to DFT/PBE/TZ2P calculations mono-cycloadducts of fullerene C_{60} , containing 4-, 5- or 6-membered exohedral cycles, are shown to be exclusively [6,6]-closed isomers. [5,6]-closed structures are 15-18 kcal/mol less stable than the [6,6]-closed isomers; the [6,6] and [5,6]-open isomers do not correspond to local minima. On the contrary, both [6,6]-closed and [5,6]-open isomers of adducts with 3-membered exohedral cycles are stable.

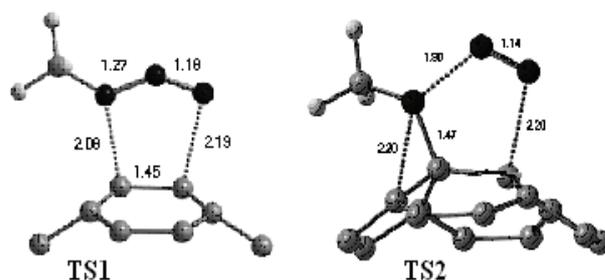
The interrelation between stability of mono- and bis-cycloadducts, the mechanism and selectivity of reactions of C_{60} with azides is considered in detail.

By DFT/PBE/TZ2P method we explored the relative total energies of [5,6]-open bis-cycloadducts of $C_{60}(NH)_2$ and [5,6] - open and [6,6]-closed bis-cycloadducts of $C_{60}(NH)(N_3H)$

and have found, that the relative energies of [5,6]- open regioisomers (1,6; m, n) $C_{60}(NH)_2$, obtained at the fixed of (1,6) NH bridges and a variation of places of localization of the second NH-group, single bonds of m-n monoadduct 1,6- $C_{60}NR$, monotonously decrease with contraction of broken link m-n. In contrast to $C_{60}(NH)_2$ series, relative stability of (1,6; m, n) - isomers of $C_{60}(NH)(N_3H)$ increases with reduction of lengths of m, n links. The bonds m, n in all regioisomers of $C_{60}(NH)(N_3H)$ are not broken.

It is shown, that free energy dispersion of experimentally produced regioisomers of bis-cycloadducts reaches ~17 kcal/mol. In contrast to mono-adduct $C_{60}NH$, which has a local minimum only for the 1,6-open structure, both 1,6- open, and the 1,6-closed structures are possible for $C_{60}(NH)_2$ and $C_{60}(NH)(N_3H)$ bisisomers. Probably we predict for the first time possibility of formation of 1,6- closed aziridines.

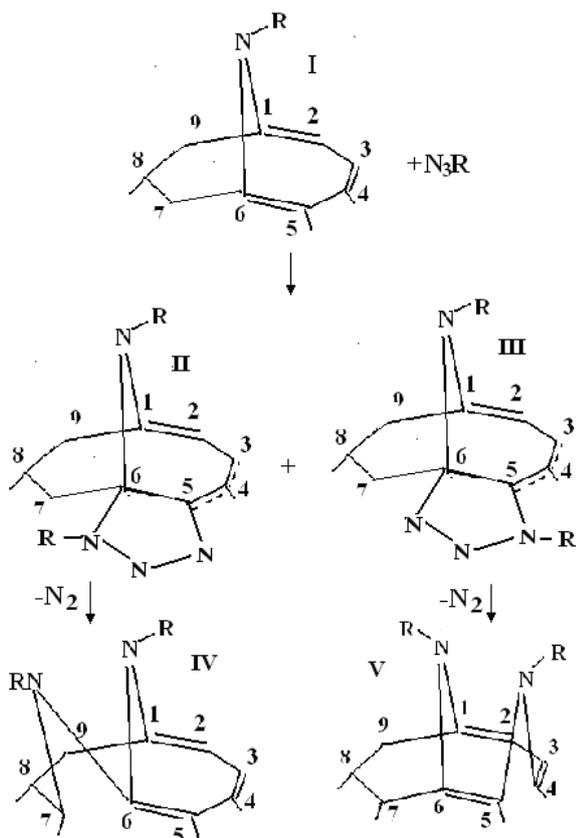
As the changes of the relative energies of [5,6]-bisadducts (40 kcal/mol) are essentially larger the changes of the relative energies of $C_{60}(CH)_2$ and $C_{60}(NH)_2$ [6,6]-bisadducts (5-8 kcal/mol), studied by us earlier [7], higher selectivity [5,6]- cycloaddition on single bonds in comparison with - [6,6]- cycloaddition on double



bonds may be supposed.

It is established, that the concerted mechanism of bond formation and bond rupture seems to be an optimal path of cyclo-addition reaction of azides N_3R to C_{60} and elimination of N_2 from $C_{60}N_3R$, which leads to formation of [6,6]-closed fullerotriazolines $C_{60}(N_3R)$ and [5,6]-open monoadduct $C_{60}NR$ and subsequent elimination of N_2 from $C_{60}(N_3R)$. Total energies of activation of these reactions TS1 and TS2 amount to 15 and

27 kcal/mole, and free energies of activation – to 28 and 39 kcal/mole (R=Me). In the first reaction azide is associated preferentially on C₆₀ double bond and the most stable [6,6]-closed adduct C₆₀N₃R is formed. [5,6]-closed adduct C₆₀N₃R is less stable and, unlike [6,6] - adduct, has not been obtained [1-4]. The differences of total and free energies of [5,6] and [6,6]-closed adducts are equal to 15.1 and 14.8 kcal/mol. Second reaction-elimination of N₂ from [6,6]-adducts C₆₀N₃R result in stereospecific formation of [5,6]-open isomers C₆₀NR. Both reactions are exothermic.



The subsequent formation of the bis-adducts is dominated by adding of N₃R on the equivalent bonds 5=6 and 1=2 of monoadduct I. Theoretical quantity of change of a free energy of this stage of reaction is almost zero. Earlier it was reported about the two-stage mechanism of elimination N₂ through intermediate with opening of bond NN (method AM1) [10], but according to our results synchronous eliminating of N₂ is by 15 kcal/mol more preferable than a two-stage route.

At addition of N₃R a formation of two types of more stable regioisomers II and III is possible. Eliminating of nitrogen from II and III determines final structure of adducts IV and V with an open structure of sphere which are isolated [3,4]. We will note, that intermediate products II and, possibly, III are also obtained [4].

According to [4] at ambient temperature intermediate compounds II and III sluggishly transfer in IV and as it is supposed, in V which are formed in the ratio 6:1, that is in the full conformity with the theoretical data gained by us.

The total energy and free energy values are used as stability estimate.

Conclusions

Predicted stable and unstable mono- and bis-cycloadducts of fullerene C₆₀, presents correlations between molecular parameters (bond lengths) and stability of adducts; mechanisms and selectivity of reactions C₆₀ with azides are revealed too.

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