

# 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.

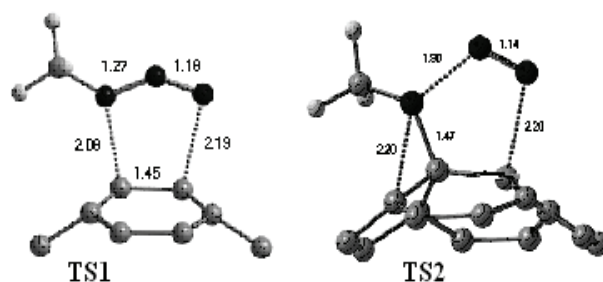
The interrelation between stability of mono- and bis-cycloadducts, the mechanism and selectivity of reactions of  $C_{60}$  with azides is considered in detail.

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.

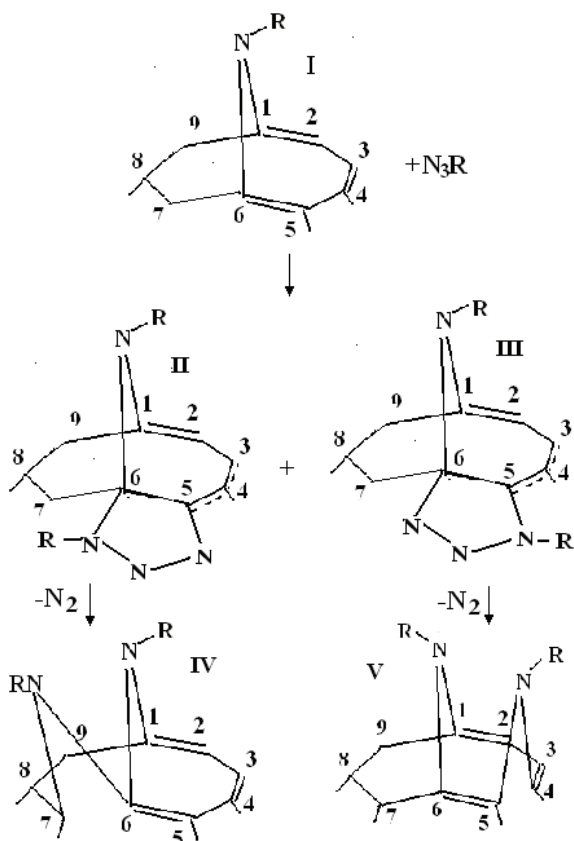
As the changes of the relative energies of [5,6]-bisadducts (40 kcal/mol) are essentially larger the changes of the relative energies of  $C_{60}(CH)_2$  and  $C_{60}(NH)_2$  [6,6]-bisadducts (5-8 kcal/mol), studied by us earlier [7], higher selectivity [5,6]- cycloaddition on single bonds in comparison 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 C<sub>60</sub> double bond and the most stable [6,6]-closed adduct C<sub>60</sub>N<sub>3</sub>R is formed. [5,6]-closed adduct C<sub>60</sub>N<sub>3</sub>R 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 N<sub>2</sub> from [6,6]-adducts C<sub>60</sub>N<sub>3</sub>R result in stereospecific formation of [5,6]-open isomers C<sub>60</sub>NR. Both reactions are exothermic.



The subsequent formation of the bis-adducts is dominated by adding of N<sub>3</sub>R 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 N<sub>2</sub> through intermediate with opening of bond NN (method AM1) [10], but according to our results synchronous eliminating of N<sub>2</sub> is by 15 kcal/mol more preferable than a two-stage route.

At addition of N<sub>3</sub>R 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 C<sub>60</sub>, presents correlations between molecular parameters (bond lengths) and stability of adducts; mechanisms and selectivity of reactions C<sub>60</sub> with azides are revealed too.

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