

# COMPARATIVE STUDY OF FULLERENES DOPED WITH BORON AND NITROGEN

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Closed molecular structures made of carbon have been intensively studied in the last years, especially after the discovery of the fullerenes [1] and carbon nanotubes [2]. These structures are very attractive due to their outstanding structural and electronic properties. Several applications, including molecular actuators, transistors and rectifiers have recently been proposed in which some closed molecular form plays an active role in the electronic device. The control and manipulation of the molecular electronic properties are done in a variety of ways, for example through functionalization or doping.

The doping of fullerenes and nanotubes has been reported by several authors. The most common doping agents are boron and nitrogen, since the former has one electron less and the latter has one electron in excess compared to carbon. Varying the relative concentrations of C, B, and N in the molecular species allows the control of the number of  $\pi$  electrons and the strength of the chemical bond in certain regions of the molecule, especially the curved and stressed regions.

In the present work the structure and stability of heterofullerenes  $C_{n-x}B_x$  and  $C_{n-x}N_x$  ( $40 \leq n \leq 50$ ) were theoretically investigated through PM3 [3] semi-empirical quantum chemical calculations. The package SPARTAN [4] was used. For comparison purposes, calculations on  $C_{60}$  were also carried out. The evolution of structure and stability of  $C_{60}$  under boron and nitrogen substitution were theoretically investigated by Xie and collaborators [5]. These authors used density functional theory with B3LYP functional combined with the 6-31G\* basis set. Our PM3 calculations reproduced the B3LYP/6-31G\* molecular geometries on doped  $C_{60}$  and gave essentially the same results concerning the molecular stability. The calculated heats of formation indicate that the structure of small fullerenes stabilize upon boron and nitrogen substitution. This is one major advantage of small fullerenes over  $C_{60}$ , which is very stable in the pure form and the introduction of heteroatoms usually destroys its symmetry and increases the heat of formation. The existence of  $C_{n-x}N_x$  molecular cages has already been established [6] and the comparison between boron and nitrogen doped molecules suggests that the boron substituted species should be experimentally obtained as well. Two  $C_{50}$  isomers appear as the most stable substituted small fullerenes, with heats of formation per atom approaching that of  $C_{60}$ . Calculations at the BLYP/6-31G\* [7] level of theory were carried out to assess the electronic structure of B and N doped  $C_{50}$  isomers. Results are consistent with the most stable substituted molecules forming suitable donor/acceptor pairs that could be used to build molecular rectifiers. [FAPESP, CNPQ]

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