

STRUCTURAL AND FUNCTIONAL ASPECTS OF ZWITTERIONIC *Nido-7-NH₃-7,9-C₂B₉H₁₂*

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Carborane derivatives are of great importance for as boron-10 carriers for boron neutron capture therapy (BNCT), as organometallic reagents, and as source for semiconductor devices. This wide range of applications derives from their physicochemical properties including high stability, lipophilicity, and synthetic versatility. Carboranes exist in form of three geometrical isomers (*o*-, *m*- and *p*-carborane) based on the position of two carbon atoms in cage scaffold and can be isolated either as neutral *closo* carborane (C₂B₁₀H₁₂) or anionic species *nido* carborane (C₂B₉H₁₂⁻) species.

Removal of the most electrophilic boron atom in lipophilic neutral *closo* carboranes generates hydrophilic anionic *nido* carboranes. However, low water solubility of *closo* carboranes and low lipid solubility of *nido* carboranes have been limitations in their biological applications. Very recently, our group has shown that zwitterionic NH₃⁺-substituted *nido m*-carborane containing thymidines have unique hydrophilicity/hydrophobicity properties that were between those of lipophilic *closo* carborane and hydrophilic *nido* carborane thymidine derivatives.¹ The basis of these unique physicochemical properties of zwitterionic *nido* carborane is the intramolecular charge compensation between positively charged NH₃⁺ group and the negatively charged carborane cage.

A novel zwitterionic ammonium substituted *nido m*-carborane, 7-NH₃-7,9-C₂B₉H₁₂ (**I**), was synthesized and analyzed using 1D-NMR, 2D-NMR, IR, and HRMS. The experimentally obtained ¹¹B-chemical shifts for this novel system were compared with theoretical data calculated at Hartree-Fock theory (HF/6-31G* and HF/6-31G**) and density functional theory (B3LYP/6-31G* and B3LYP/6-31G**) levels. GIAO/¹¹B-NMR chemical shifts calculated at the B3LYP/6-31G* or B3LYP/6-31G** levels showed strong correlation with experimentally obtained values (r²=0.9957). Treatment of *nido-7-NH₃-7,9-C₂B₉H₁₂* (**I**) with ketone-containing compounds (acetone, cyclohexanone) without acid catalyst at room temperature provided the corresponding UV-active carboranyl iminium compounds, indicating the potential of compound **I** to serve as a novel type of protective groups for carbonyl functions in organic molecules. The unique chemical properties of the compound **I** and the mechanism of its transformation into the carboranyl iminium compound will be presented.

1. Byun, Y. et al. (2005) J Med Chem. 48(4), 1188-1198.

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