

Quantum-Chemical ab initio Calculations on the Three Isomers of Diborabenzene (C₄H₄B₂)

Jaswinder Singh^a, Yuekui Wang^b, and Gerhard Raabe^a

^a Institut für Organische Chemie, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany

^b Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan, Shanxi 030006, P.R. China

Reprint requests to G. R.; Fax: +49 241 80 92385; E-mail: gerd.raabe@thc.rwth-aachen.de

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Dedicated to Professor Dr. Jörg Fleischhauer on the occasion of his 70th birthday

Quantum-chemical ab initio calculations up to the ZPE+CCSD(T)/aug-cc-pVTZ//MP2/6-311++G** level were performed on three possible structural isomers of diborabenzene (C₄H₄B₂). All three molecules were found to be local minima on the C₄H₄B₂ energy surface and to have closed shell singlet ground states. While the ground states of the 1,3- and 1,4-isomer are planar and of C_{2v} and D_{2h} symmetry, respectively, 1,2-diborabenzene is non-planar with a C₂ axis passing through the center of the BB bond and the middle of the opposite carbon-carbon bond as the only symmetry element. The energetically most favourable 1,3-diborabenzene was found to be about 19 and 36 kcal/mol lower in energy than the 1,2- and the 1,4-isomer. Planar 1,3- and 1,4-diborabenzene have three doubly occupied π orbitals while non-planar 1,2-diborabenzene has also three doubly occupied orbitals which can be derived from the π orbitals of its 3.7 kcal/mol energetically less favourable planar form (“π-like” orbitals). The lowest unoccupied orbitals of all three isomers have σ symmetry with large coefficients at the two boron atoms. These orbitals are lower in energy than the lowest unoccupied molecular orbitals (LUMOs) of e. g. benzene and pyridine and might cause pronounced acceptor properties which could be one of the reasons for the elusiveness of the title compounds. The results of bond separation reactions show that cyclic conjugation stabilizes all three diborabenzenes relative to their isolated fragments. The most effective stabilization energy of about 24 kcal/mol was found for the energetically lowest 1,3-isomer. This value amounts to approximately one third of the experimental value for the bond separation energy of pyridine. In all cases the energetically lowest triplet states are significantly (16–24 kcal/mol) higher in energy than the singlet ground states. Also among the triplets the 1,3-isomer is the energetically most favourable species.

Key words: Diborabenzenes; Calculations; Singlet-Triplet Splitting; Relative Stabilities; Bond Separation Reactions.