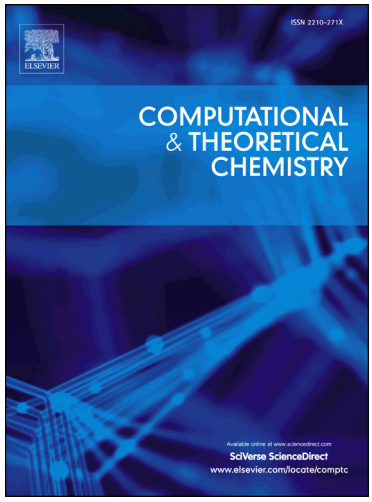

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Theoretical study of protonation of the $B_{12}H_{12}^{2-}$ anion and subsequent hydrogen loss from the $B_{12}H_{13}^{-}$: effect of the medium.

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Abstract

Protonation of $B_{12}H_{12}^{2-}$ in the presence of acetonitrile molecules has been studied using density functional theory on the B3LYP/6-31+G* and more flexible B3LYP/6-311++G** levels. The $B_{12}H_{12}^{2-}$ anion has been surrounded with twelve acetonitrile molecules according to the "supermolecular" approach and H^+ was added to the system. Protonation of $B_{12}H_{12}^{2-}$ is considered as a proton H^* transfer from a nitrogen atom of protonated acetonitrile $CH_3CN{\cdot}H^+$ to a facet BBB of a boron cluster. Calculated Proton Affinity (PA) of $B_{12}H_{12}^{2-}$ in the presence of solvent molecules is ~0.4 kcal/mol. This is much lower than that reported previously for bare $B_{12}H_{12}^{2-}$ and is within the error of B3LYP calculation. Removal of H_2 from the previously formed $B_{12}H_{13}^{-}{\cdot}12CH_3CN$ has been studied. The estimated value of the energy barrier for hydrogen removal is ~11.1 kcal/mol. BH_2-isomer of $B_{12}H_{13}^{-}{\cdot}12CH_3CN$ is in the ground state and is the starting reagent for calculating the elementary reaction of H_2 removal. Both $B_{12}H_{13}^{-}{\cdot}12CH_3CN$ systems either with BH_2-form of $B_{12}H_{13}^{-}$ or with an additional H^* located on the triangular facet BBB have similar energies with the preference (~5.2 kcal/mol) of the BH_2-form. Total energy needed for hydrogen removal and generation of the $B_{12}H_{11}^{-}$ anion with a vacant "hole" is moderate. Once the energy barrier has been overcome, the reaction becomes endothermic. IR spectra for a solvated $B_{12}H_{12}^{2-}$ anion in the presence of H^+ (either close to one of CH_3CN molecules or as a part of $B_{12}H_{13}^{-}$) have been calculated and compared with IR spectra of $[(CH_2Naph)Ph_3P]_2B_{12}H_{12}$ and $(Bu_4N)_2B_{12}H_{12}$ in acetonitrile and/or CF_3COOH solutions. Splitting of ν(B–H) band of the $B_{12}H_{12}^{2-}$ anion is treated by a solvate model.

Keywords: dodecahydro-*closo*-dodecaborate; Protonation; Solvation; IR spectra