



Theoretical study of protonation of the $B_{10}H_{10}^{2-}$ anion and subsequent hydrogen removal due to substitution reaction in acidic medium



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ABSTRACT

The protonation of $B_{10}H_{10}^{2-}$ in the presence of acetonitrile molecules has been studied using the Density Functional Theory on the B3LYP/6-31G* and more flexible B3LYP/6-311++G** levels. The $B_{10}H_{10}^{2-}$ anion was surrounded by twenty acetonitrile molecules CH_3CN to complete the first sphere of solvation, and H^+ was added to the system. The protonation of $B_{10}H_{10}^{2-}$ is regarded as a proton H^+ transfer from a nitrogen atom of protonated acetonitrile $CH_3CN\cdot H^+$ to a facet of a boron cluster, accompanied by overcoming a small activation barrier of ca. 4.9 kcal/mol. The proton affinity (PA) of $B_{10}H_{10}^{2-}$ in the presence of solvent molecules is ca. 8.7 kcal/mol, which is much lower than that of the “bare” $B_{10}H_{10}^{2-}$. The effect of a solvent presence upon the isomerism of $B_{10}H_{11}^-$ was studied, and it was shown that the local configuration of acetonitrile molecules facilitates the existence of BH_2 -isomers for $B_{10}H_{11}^-$. The removal of H_2 from the formed $B_{10}H_{11}^- \cdot 20CH_3CN$ species was also investigated. In contrast to the “bare” $B_{10}H_{11}^-$ that features different activation barriers for H_2 removal from vertices with initial coordination number 6 or 5, the solvation facilitates this process only for the coordination number 6, while the other leads to the deprotonation of $B_{10}H_{11}^-$ back to $B_{10}H_{10}^{2-}$. Estimated energy barrier value for hydrogen removal is ca. 23.6 kcal/mol, which equals to boiling conditions in the case of actual experiment. One of the nearest CH_3CN molecules substitutes instead of H_2 giving $B_{10}H_9(NCCH_3)^-$. This reaction shows an exothermic effect of ca. 16.1 kcal/mol.

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1. Introduction

Boron compounds based on electron-deficient cluster anions $B_nH_n^{2-}$ ($n = 6-12$) can be used as fuels components [1,2], pharmaceuticals [3], and other materials [4]. $K_2[B_{10}H_{10}]$, $K_2[B_{12}H_{12}]$ and Cs $[B_{10}H_{11}]$ compounds can be considered as complex hydrides, which is associated with the unique protonation reactions of $B_nH_n^{2-}$ anions which result in more electron-deficient particles $B_nH_{n+1}^-$. The existence of the protonated $B_{12}H_{13}^-$ as an individual compound [5] was originally believed based on the very high value of gas-phase proton affinity for $B_{12}H_{12}^{2-}$. Up to now, however, no information can be found in the literature concerning the isolation of this species. In our previous work [6] we studied the influence of solvation on properties of $B_{12}H_{12}^{2-}$ anion in an acetonitrile solution. It turned out that the addition of only twelve acetonitrile molecules (CH_3CN) resulted in the near-zero (within the limits of B3LYP error) proton affinity of $B_{12}H_{12}^{2-}$. In this case, both possible $B_{12}H_{13}^-$ isomers (the one with a BH_2 -group and the facet isomer where H^+ is located over the triangular face BBB) switch places on the

energy scale during solvation; as a result, the activation barrier for the H_2 removal leading to the formation of $B_{12}H_{11}^-$ intermediate has a moderate value. These calculations also quite accurately reproduce the observed splitting of $\nu(BH)$ band in the IR spectrum attributed to interaction of hydrogen atoms of $B_{12}H_{12}^{2-}$ anion with protons of the solvent (CH_3CN). The substantial impact of small number of CH_3CN molecules on the properties of $B_{12}H_{12}^{2-}$ is reflected in the term “long-range interaction” for which the distances between H atoms of $B_{12}H_{12}^{2-}$ and those of the nearest CH_3CN molecules exceed the doubled value of the van der Waals radius (~ 2.2 Å) of hydrogen. Such interactions are discussed in the literature [7] in terms of homopolar dihydrogen bonding in main group hydrides. The analysis of crystallographic data using QTAIM (Quantum Theory of Atoms in Molecules) indicates the presence of a considerable amount of charge density (up to $\sim 0.2-0.3 e$) between hydrogen atoms sufficiently separated from each other.

The release of H_2 from an acidic solution can also be observed for $B_{10}H_{10}^{2-}$, in particular, during *exo*-polyhedral substitution reactions [8]. In [6,9,10], elementary reactions of H_2 removal from $B_nH_{n+1}^-$ were studied for all series within the range $n = 6-12$. In all cases (except $B_{10}H_{11}^-$ and $B_{12}H_{13}^-$) such reactions require overcoming high activation barriers (>30 kcal/mol). The initial estimate

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(ca. 4.8 kcal/mol) of the activation barrier of H₂ removal for “bare” B₁₂H₁₃⁻ was further corrected [6] up to ca. 11.1 kcal/mol by surrounding the B₁₂H₁₃⁻ anion by the CH₃CN molecules. Thus, only the influence of solvation on the properties of B₁₀H₁₀²⁻ remains to be examined. For other B_nH_n²⁻ anions (n = 6–9, 11) the reasonable approach is to study the electrophilic substitution accompanied by the removal of H⁺ in basic medium rather than a nucleophilic mechanism (*exo*-polyhedral substitution accompanied by the removal of H₂ in acidic medium). In the case of B₆H₆²⁻ it was thoroughly studied in [11].

The present paper deals with the results of a theoretical study of B₁₀H₁₀²⁻ protonation with the formation of B₁₀H₁₁⁻ anion and subsequent removal of H₂, described using the solvation model {B₁₀H₁₀²⁻·H⁺·20CH₃CN} (**1**) (see Fig. 1). An examination of the properties of solvated B₁₀H₁₀²⁻ can be also useful for compounds containing heteroatoms, for example, carboranes CB₉H₁₀, C₂B₈H₁₀, or thioboranes B₈S₂H₈. In addition, such calculations on B₁₀H₁₀²⁻ would provide more accurate data as compared to those obtained in [6] for B₁₂H₁₂²⁻. Atoms of boron in B₁₀H₁₀²⁻ can have C.N. (coordination number) of 5 (B1, B10 atoms in Fig. 1) and of 6 (B2 atom in Fig. 1). As it is known from the experimental data [8], a substitution of hydrogen atoms upon boiling in the acidic solution takes place at vertices of the B₁₀H₁₀²⁻ polyhedron with C.N. = 6. Terminal

hydrogen atoms near boron atoms with less saturated coordination (C.N. = 5) remain in place under those conditions. The authors of [9] explained the mechanism of such substitution in terms of higher activation barrier (ca. 35.3 kcal/mol) for the H₂ removal from B1 as compared to that (ca. 22.8 kcal/mol) of its removal from B2. Thus, a much higher value (for thermodynamically unstable B₁₀H₁₁⁻) of the activation barrier for the H₂ removal from B1 as compared to the moderate value for the H₂ removal from B2 may explain the selectivity in the substitution. However, in the present work, we deduce the same substitution mechanism from different considerations. Rather than comparing relative energies, we include solvent molecules in our considerations of the substitution mechanism; moreover, we show that the local configuration of CH₃CN molecules around B₁₀H₁₁⁻ defines the isomerism of B₁₀H₁₁⁻.

2. Methods

The geometries of molecular systems of interest involving large number of atoms such as B₁₀H₁₀²⁻·H⁺·20CH₃CN were fully optimized using the Density Functional Theory calculations at the B3LYP/6-31G* level [12,13]. To provide a better description of hydrogen bonding in the solvate, the use of a basis set that includes diffuse functions, for example, 6-31+G*, would normally be recommended.

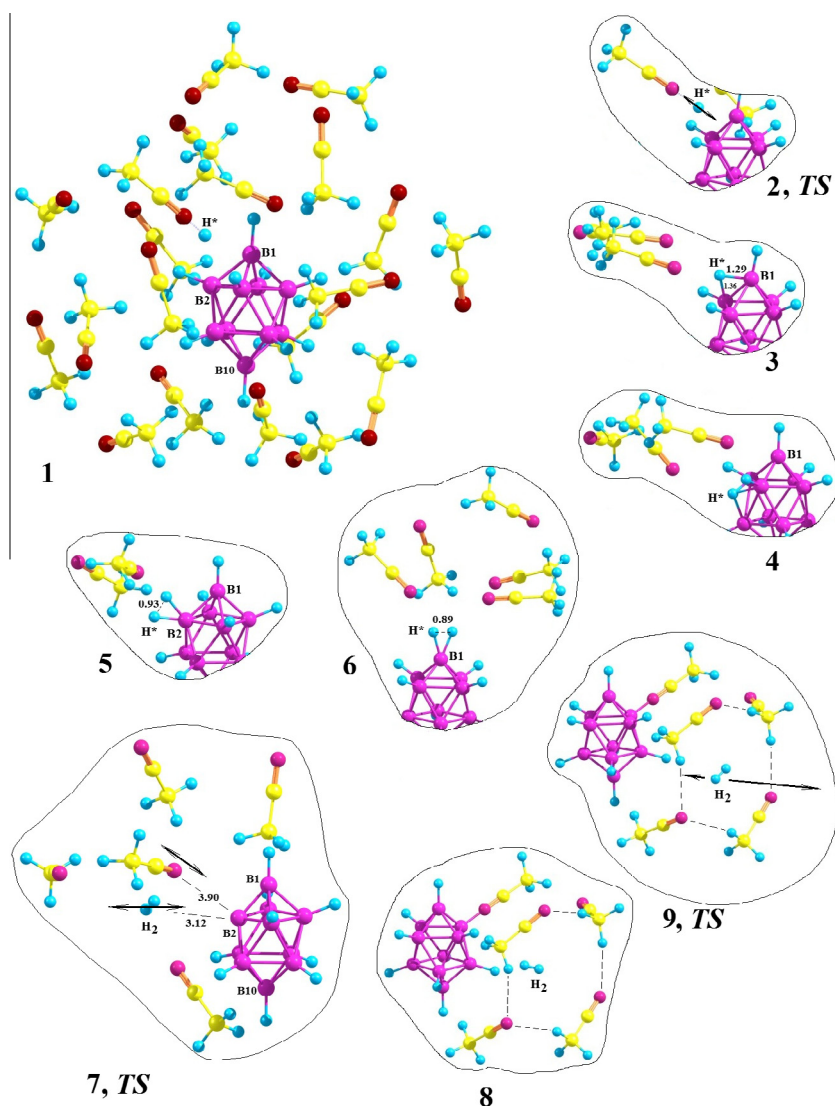


Fig. 1. Stationary points of interest on PES for B₁₀H₁₀²⁻·H⁺·20CH₃CN stoichiometry.

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