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Research Article

Theoretical Study of Mixed Hydrogen and Dihydrogen Bond Interactions in $BH_4(NH_3)_n^-$ Clusters

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Ab initio calculations were used to analyze interactions of BH_4^- with 1–4 molecules of NH_3 at the MP2/6-311++G(d,p) and the B3LYP/6-311++G(d,p) computational levels. In addition to H_3B–H$\cdots$H–NH_2 dihydrogen bond, the H_2N–H$\cdots NH_3$ hydrogen bonds were also predicted in clusters. Negative cooperativity in clusters constructed from mixed H_3B–H$\cdots$H–NH_2 dihydrogen and H_2N–H$\cdots NH_3$ hydrogen bonds are more remarkable. The negative cooperativity increases with size and number of hydrogen bonds in cluster. The B–H stretching frequencies show blue shifts with respect to cluster formation. Greater blue shift in stretching frequencies was predicted for B–H bonds which did not contribute to dihydrogen bonding with NH_3 molecules. The structures were analyzed with the atoms in molecules (AIM) methodology.

1. Introduction

Hydrogen is an ideal energy carrier; therefore, the binary boron-hydrogen compounds or boranes are the core of hydrogen storage and are an extremely rich area of boron-based cluster chemistry. In addition, the borohydride complexes $NaBH_4$ and $LiBH_4$ possess a high capacity for hydrogen retention, and the release of hydrogen from $NaBH_4$ is only possible via hydrolysis [1–4]. Many salts of this anion, such as $LiBH_4$ and $NaBH_4$, are essentially ionic and have been used for nearly 60 years as reducing agents [5].

Despite extensive experimental and theoretical studies on dihydrogen (DHB) and hydrogen bonded (HB) complexes [6–18], few studies were simultaneously oriented toward systems containing both DHB and HB interactions [19].

An important aspect of HB and DHB interactions is their cooperativity or negative cooperativity (anticooperativity) when increasing the number of H$\cdots$X or H$\cdots$H contacts in self-association of molecular systems [20–23].

Quantum-chemical calculations performed on dimers, trimers, and more complicated self-associates of simple molecules, like H_2O and HCN, revealed that the hydrogen-bonding energies in the linear associates are remarkably higher than the values in dimers, which is due to mutual polarization of bonds. This cooperativity effect increases with the chain length of the associates. In contrast to those aforementioned, theoretical investigations of branched complexes in which two or more hydrogen bonds are formed by one proton-acceptor group predicted an inverse effect. In this case, mutual polarization weakens the hydrogen bonds, leading to negative cooperativity [24–26]. Moreover, presence of cooperativity in DHB clusters has been reported recently [7]. The aim of this work is to investigate the binding energy and cooperativity of systems containing mixed DHB and HB interactions. For this purpose, the model clusters $BH_4(NH_3)_n^-$, $n = 1$–4, have been considered. Moderate negative charge of BH_4^- allows the coexistence of both HB and DHB interactions in the cluster. Ab initio and DFT calculations for such complexes were

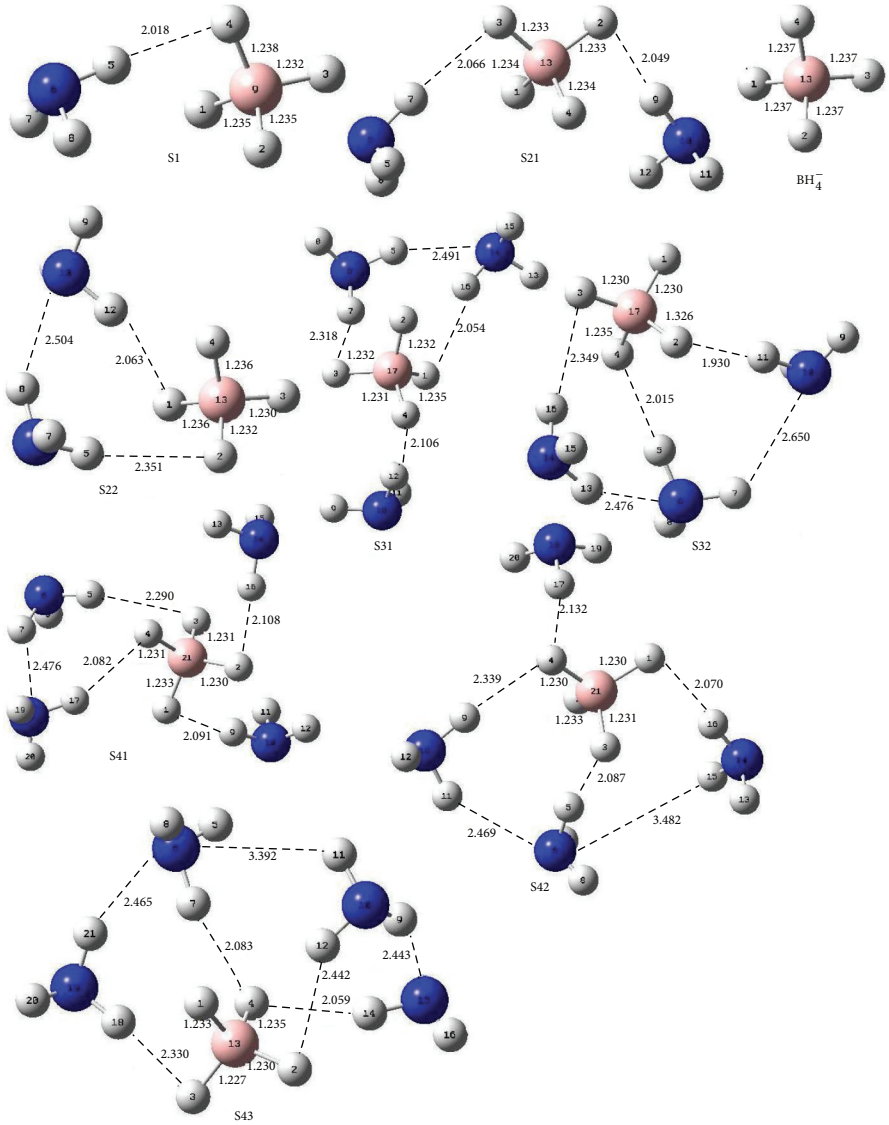

Figure 1: Geometries of clusters of BH_4^- with NH_3 optimized at MP2/6-311++g(d,p) level.

performed, and the Bader theory was applied to analyze H···H interactions.

2. Computational Methods

Calculations were performed using the Gaussian 03 package of codes [27]. The geometries of the isolated BH_4^- and NH_3 moieties and their complexes were fully optimized at the MP2/6-311++G(d,p) and the B3LYP/6-311++G(d,p) computational levels. Both MP2 and B3LYP computations have their own supporting instances from the point of agreement between theoretical prediction and experimental measurement [28, 29]. Harmonic vibration frequency calculations at MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels confirmed the structures as minima and enabled the evaluation of zero-point vibration energies (ZPVE). The counterpoise procedure [30] was used to correct the interaction energy for basis set superposition error (BSSE). The AIM2000 package [31] was used to obtain bond properties and to plot molecular graphs.

3. Results and Discussion

Figure 1 illustrates optimized geometries for clusters which could be obtained from the interaction of BH_4^- with up to 4 molecules of NH_3.

Association of BH_4^- with one molecule of the NH_3 gives a 1 : 1 cluster which is denoted S1.

For a 1 : 2 ratio the S21 and S22 clusters were predicted, and the S21 has two discrete (H_2N–H···H–B) dihydrogen bonds. The S22 could be considered as a cluster which is obtained from interaction of an H_2N–H···NH_3 dimer with a BH_4^- ion, and it consists of two DHBs and an HB interaction. The stability of S22 because of the presence of an additional

Table 1: BSSE, stabilization energy corrected with ZPE, uncorrected stabilization energy, and cooperative effect (CE) calculated at MP2/6-311++G(d,p).

Cluster	BSSE kcal mol^{-1}	SE (uncorr.) kcal mol^{-1}	SE (corr.) kcal mol^{-1}	CE kcal mol^{-1}
S1	0.83	−7.87	−6.54	—
S21	1.66	−15.24	−12.59	0.49
S22	2.37	−16.20	−12.78	2.48
S31	3.18	−23.33	−18.71	3.09
S32	3.56	−23.57	−18.63	3.16
S41	3.94	−29.83	−24.31	4.02
S42	4.12	−29.83	−24.12	4.20
S43	4.77	−30.10	−24.69	5.82

Table 2: BSSE, stabilization energy corrected with ZPE, uncorrected stabilization energy, and cooperative effect (CE) calculated at B3LYP/6-311++G(d,p).

Cluster	BSSE kcal mol^{-1}	SE (uncorr.) kcal mol^{-1}	SE (corr.) kcal mol^{-1}	CE kcal mol^{-1}
S1	0.10	−6.93	−5.50	—
S21	0.22	−13.33	−10.58	0.42
S22	0.23	−13.34	−10.60	2.16
S31	0.28	−19.29	−14.96	3.30
S32	0.54	−19.51	−15.40	4.62
S41	0.67	−24.80	−19.43	4.33
S42	0.67	−25.03	−19.45	4.32
S43	0.84	−25.69	−19.60	5.91

(H_2N–H$\cdots NH_3$) hydrogen bond is slightly greater than the stability of S21 (Tables 1 and 2).

For a 1 : 3 ratio S31 and S32 clusters at MP2 and B3LYP levels were optimized. The S31 has three DHBs and a hydrogen bond interaction and is aggregated from interactions of a H_2N–H$\cdots NH_3$ and an NH_3 molecule with a BH_4^- ion. The S32 is optimized from the interaction of a chain of $(NH_3)_3$ trimer with a BH_4^-, and its stability is in the order of S31 cluster.

In a 1 : 4 mole ratio, the starting geometries go to S41, S42, and S43 at two levels of computations. The S41 was assembled from interactions of an H_2N–H$\cdots NH_3$ dimer and two separated NH_3 molecules with BH_4^- and consists of four DHBs and an HB interaction. The S42 that consist of four DHBs and an HB interaction might be considered as complexation between an S32 with an NH_3 molecule. Of course, The AIM analysis shows a weak $NH_3\cdots NH_3$ interaction with a bond length of 3.482 in S42 that it might not be considered as an HB interaction, usually HB interactions have bond lengths around 1.7–2.4 Å. The S43 might be considered as interactions of two $NH_3\cdots NH_3$ dimers with BH_4^- and consist of four DHB and two HB interactions. Also AIM analysis revealed a weak $NH_3\cdots NH_3$ interaction with a bond length of 3.392 in S43; therefore, it was not considered as an HB interaction. The stability of 1 : 4 complexes are close together, see Tables 1 and 2, and it shows that $NH_3\cdots NH_3$ interactions are too weak; therefore, they did not have considerable effects on the stabilities of corresponding clusters. According to data given in Tables 1 and 2, stabilities of clusters increased with increasing the cluster size.

Results of intra and intermolecular bond lengths are given in Figure 1 and Table 3. At MP2 level, the H$\cdots$H distance in S1 is 2.018 which for similar bonds increased to 2.066 and 2.049 in S21, 2.106 in S31, 2.091 and 2.108 in S41 and 2.070 and 2.132 in S42 complexes. Similarly, at B3LYP level the H$\cdots$H distance in S1 is 1.991 which rose to 2.008 and 2.011 in S21, 2.015 in S31, 2.028 and 2.155 in S41 and 2.110 in S42 complexes. Elongation of H$\cdots$H bonds show that it weakens with increasing the cluster size. Also, comparing H$\cdots$H distances in S22, S31, S41, S42, and S43 complexes showed that NH_3 molecules in $NH_3\cdots NH_3$ dimers have different

Table 3: Bond lengths (Å) of hydrogen bonded clusters at B3LYP/6-311++G(d,p) level.

	H$\cdots$H	B–H1	B–H2	B–H3	B–H4
BH_4^-	—	1.238	1.238	1.238	1.238
S1	1.991	1.236	1.236	1.233	1.240
S21	2.008, 2.011	1.234	1.235	1.235	1.234
S22	2.012, 2.012	1.238	1.235	1.231	1.234
S31	1.984, 2.015, 2.187	1.229	1.237	1.230	1.236
S32	2.051, 2.029, 2.031	1.233	1.233	1.233	1.233
S41	2.027, 2.155, 2.173, 2.283	1.232	2.231	2.232	2.232
S42	2.016, 2.110, 2.116, 2.327	1.232	1.232	1.231	1.232
S43	2.654, 2.246, 2.176, 2.172	1.234	1.231	1.228	1.235

abilities for DHB interactions with BH_4^-. Results indicated that the NH_3 molecules which are located in the head of these dimers have a greater tendency for DHB. In contrast, the NH_3 at the end of these dimers has a smaller tendency for DHB interaction with BH_4^- in the related clusters. For example, at the MP2 level the H$\cdots$H bond lengths for the first (head) and second (tail) NH_3 in the S22 are 2.063 and 2.351, respectively. They show that the interaction of BH_4^- with the first NH_3 molecule is stronger than the second one. Similarly, in S31, S32, S41, S42, and S43 clusters the DHB lengths for the first NH_3 of $NH_3\cdots NH_3$ dimers are 2.054, 2.015, 2.082, 2.087, and 2.059 and 2.083 while for the tail NH_3 bond lengths increased to 2.318, 2.349, 2.290, 2.339, and 2.330 and 2.442, respectively. Thus, stronger interactions for the first NH_3 in $NH_3\cdots NH_3$ dimers could be deduced for these clusters. Such the conclusion might also be received from results of B3LYP level. It seems the presence of cooperativity in HB part of $NH_3\cdots NH_3$ chains is responsible for this behavior.

The B–H bonds lengths in BH_4^- are 1.237 and 1.238 at MP2 and B3LYP levels, respectively. Comparison of these bond lengths with predicted values in optimized clusters requires dealing with the shortening of B–H bonds upon cluster formation. Often contraction of B–H bonds with stronger H$\cdots$H interactions is less sizeable. For example,

Table 4: Unscaled vibration frequencies (cm^{-1}) with corresponding intensities (values given in parenthesis, $km\,mol^{-1}$) of HB clusters calculated at MP2/6-311++G(d,p) level.

cluster	νH$\cdots$H	ν_{B-H}			
		B–H1	B–H2	B–H3	B–H4
BH_4^-	—	2311 (637)	2311 (637)	2311 (637)	2311 (637)
S1	201 (8)	2321 (197)	2325 (544)	2347 (533)	2303 (409)
S21	144 (60), 170 (60)	2327 (20)	2336 (444)	2340 (615)	2341 (435)
S22	170 (37), 182 (35)	2320 (187)	2344 (384)	2364 (520)	2326 (440)
S31	149 (18), 150 (21), 184 (64)	2330 (141)	2357 (474)	2357 (474)	2359 (499)
S32	192 (12), 202 (11)	2372 (494)	2325 (191)	2358 (362)	2332 (379)
S41	158 (34), 176 (50), 197 (18)	2338 (53)	2355 (312)	2363 (456)	2368 (472)
S42	164 (42), 170 (42), 210 (13)	2349 (309)	2368 (384)	2386 (469)	2332 (153)
S43	162 (30), 170 (41), 177 (20)	2348 (309)	2367 (384)	2386 (469)	2332 (153)

Table 5: Unscaled vibration frequencies (cm^{-1}) with corresponding intensities (values given in parenthesis, $km\,mol^{-1}$) of HB clusters calculated at B3LYP/6-311++G(d,p) level.

Cluster	νH$\cdots$H	ν_{B-H}			
		B–H1	B–H2	B–H3	B–H4
BH_4^-	—	2224 (567)	2224 (567)	2224 (567)	2224 (567)
S1	201 (18)	2246 (575)	2258 (490)	2275 (133)	2224 (568)
S21	120 (17), 133 (65)	2263 (501)	2255 (704)	2255 (704)	2263 (501)
S22	103 (20), 175 (42)	2242 (518)	2259 (500)	2289 (169)	2270 (407)
S31	157 (26), 173 (33), 198 (15)	2304 (234)	2248 (423)	2293 (456)	2259 (413)
S32	176 (30), 180 (62), 194 (32)	2272 (391)	2274 (521)	2273 (537)	2273 (391)
S41	151 (34), 171 (41), 176 (47), 195 (43)	2285 (550)	2287 (399)	2285 (550)	2287 (399)
S42	138 (24), 171 (13)	2280 (431)	2283 (547)	2287 (401)	2297 (21)
S43	163 (30), 165 (42), 170 (41), 177 (20)	2348 (309)	2367 (384)	2386 (469)	2332 (153)

B–H1 (S22, S31), B–H2 (S32), and B–H4 (S1 and S32) have less contraction at MP2 level. The predicted changes of bond distances are in the same direction in both MP2 and B3LYP levels, see Figure 1 and Table 3.

The selected vibration stretching frequencies (cm^{-1}) with corresponding intensities ($km\,mol^{-1}$) for clusters at two levels are given in Tables 4 and 5. In B–H bonds, except for S1(B–H4) that shows a red shift with respect to free BH_4^- at the MP2 level, in the other cases blue shifts for B–H stretching frequencies were predicted. Also in agreement with bond contractions greater blue shifts are corresponding to B–H bonds that did not contribute to H$\cdots$H interactions [32, 33].

The shortening of B–H bonds and blue shifts of their stretching frequencies might be ascribed to the diminishing of their $\sigma \rightarrow \sigma^*$ transition which is due to the interaction of BH_4^- with NH_3 molecules.

Results indicate that the stabilities of predicted clusters are not consistent with cooperative effects (CEs), and cooperative effect is defined as $\Delta E_{CE} = \Delta E_{cluster} - \Sigma\Delta E_{dimer}$, where the sum is over the 1:1 clusters that make up the original complex [34], which means if the cluster S21 is considered to consist of two 1:1 clusters, then $\Delta E_{CES21} = \Delta E_{S21} - 2\Delta E_{S1} = -12.59 - 2 \times (-6.54) = 0.49$ which is partially consistent with negative cooperativity. Since presence of cooperativity results in negative values of CE, the positive values of CEs gathered in Tables 1 and 2 return to negative cooperativity for corresponding clusters. This negative cooperativity enhanced by increasing the cluster size. The CE of S21 is 0.49 which increased to 3.16 in 3:1 clusters and 5.82 in 4:1 clusters. Competition of several NH_3 molecules for taking electron density from BH_4^- does not hold a chance for DHB interactions and leads to negative cooperativity in these clusters.

Data given in Tables 1 and 2 show that CE inversely changes with the number of hydrogen bonds in the clusters. For instance, S21 does not have an HB but S22 has an HB, and their CEs are 0.49 and 2.48, respectively. This shows that structures with further HBs have more negative cooperativity with respect to structures with less HBs.

Also, the nature of CE for greater clusters might be deduced from their smaller ones. If we propose the S31 as a combination of S1 and S22, then $\Delta E_{CE(S31)} = \Delta E_{(S31)} - (\Delta E_{(S22)} + \Delta E_{(S1)}) = -18.63 - ((-6.53) + (-12.78)) = 0.68$, which shows that S31 is not cooperative with respect to S1 and S22. Similarly, $\Delta E_{CE(S42)} = \Delta E_{(S42)} - (\Delta E_{(S32)} + \Delta E_{(S1)}) = -24.12 - ((-18.63) + (-6.54)) = 1.05$, or $\Delta E_{CE(S43)} = \Delta E_{(S43)} - 2\Delta E_{(S22)} = -24.69 - 2 \times (-12.78) = 0.87$.

The atoms in molecule (AIM) theory applied to analyze the characteristics of the DHB bond critical points (BCPs) appeared in the aforementioned clusters. The parameters ($\nabla^2\rho_{BCP}$ is the Laplacian of electron density at BCP, and H_C is the energy density at BCP and is the sum of the kinetic

Table 6: Topological parameters for optimized clusters at MP2/6-311++G(d,p).

Cluster	Bond	ρ	∇^2	$-G_C$	V_C	$-G_C/V_C$	H_C
S1	H4···H5	0.0128	0.0368	0.0078	0.0065	1.2107	−0.0014
S21	H2···H9	0.0121	0.0351	0.0074	0.0061	1.2212	−0.0014
	H3···H7	0.0119	0.0355	0.0074	0.0060	1.2240	−0.0014
S22	H1···H12	0.0128	0.0384	0.0081	0.0065	1.2359	−0.0015
	H2···H5	0.0081	0.0256	0.0053	0.0042	1.2572	−0.0011
S31	H1···H16	0.0127	0.0378	0.0079	0.0064	1.2333	−0.0015
	H3···H7	0.0082	0.0255	0.0053	0.0042	1.2585	−0.0011
	H4···H12	0.0111	0.0327	0.0069	0.0059	1.2326	−0.0013
S32	H2···H11	0.0073	0.0329	0.0045	0.0036	1.2609	−0.0009
	H4···H5	0.0126	0.0355	0.0076	0.0063	1.2051	−0.0013
	H3···H16	0.0147	0.0410	0.0089	0.0075	1.1837	−0.0014
S41	H1···H9	0.0109	0.0324	0.0068	0.0055	1.2337	−0.0013
	H2···H16	0.0111	0.0328	0.0069	0.0056	1.2317	−0.0013
	H3···H5	0.0121	0.0366	0.0076	0.0061	1.2481	−0.0015
	H4···H17	0.0083	0.0251	0.0052	0.0042	1.2514	−0.0011
S42	H1···H16	0.0115	0.0335	0.0071	0.0058	1.2249	−0.0013
	H3···H5	0.0120	0.0360	0.0075	0.0060	1.2494	−0.0015
	H4···H9	0.0081	0.0257	0.0053	0.0042	1.2649	−0.0011
	H4···H17	0.0106	0.0314	0.0066	0.0053	1.2341	−0.0013
S43	H2···H12	0.0071	0.0222	0.0046	0.0037	1.2549	−0.0009
	H3···H18	0.0077	0.0235	0.0049	0.0038	1.2634	−0.0010
	H4···H7	0.0121	0.0368	0.0077	0.0062	1.2422	−0.0015
	H4···H14	0.0126	0.0377	0.0079	0.0064	1.2347	−0.0015

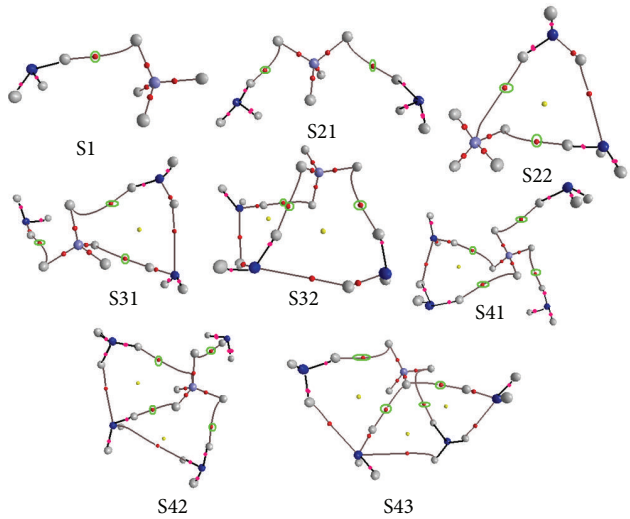

Figure 2: Molecular graphs of clusters between BH_4^- and NH_3 at MP2/6-311++G(d,p) level.

electron energy density (G_C) and the potential electron density (V_C)) are derived from the Bader theory and indicate the nature of interactions.

The molecular graphs and values of topological parameters for each intermolecular BCPs of clusters are given in Table 6 and Figure 2. All predicted DHBs of clusters under investigations have $\nabla^2\rho_{BCP} > 0$, $-G_C/V_C > 1$, and $H_C < 0$; therefore they could be considered as interactions with noncovalent characters in their nature.

4. Conclusion

Results indicate the presence of negative cooperativity in DHB clusters of BH_4^- with NH_3. It seems that the

competition of NH_3 molecules for taking electron density from a BH_4^- leads to such negative cooperativity. Also, CE inversely changes with the number of hydrogen bonds in the studied clusters. This part of negative cooperativity mainly arises from the weakening of $NH_3 \cdots NH_3$ hydrogen bonds by DHB interactions.

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