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Na…B Bond in $NaBH_3^-$: Solving the Conundrum

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Keywords: Charge-Shift Bonds, Chemical Bonding, Odd bonds, one-electron bond, Valence Bond theory.

Abstract: Bonding in the recently synthesized $NaBH_3^-$ cluster is investigated using the high level Valence Bond BOVB method. Contrary to earlier conclusions, the Na–B bond is found to be neither a genuine dative bond, nor a standard polar-covalent bond at equilibrium. It is rather revealed as a split and polarized weakly coupled electron-pair, which allows this cluster to be more effectively stabilized by a combination of (major) dipole-dipole electrostatic interaction and (secondary) resonant one-electron bonding mechanism. Our analysis of this unprecedented bonding situation extends to similar clusters, and the VB model unifies and articulates the previously published variegated views on this exotic "bond".

The chemical bond is undoubtedly a cornerstone concept in chemistry. Although the foundation of modern understanding of the chemical bonding was put forward by Gilbert Newton Lewis more than 100 years ago,[1–3] the theory of the chemical bond is still an active and evolving field. The interpretation of the nature of the Na-B bond in the recently synthesized $NaBH_3^-$ cluster[4] is one such example, as it challenges the chemical bonding community and recently became a topic of intense discussions. The debates started with a controversy around the dative $Na:^- \rightarrow BH_3$ vs. classical polar-covalent nature of this bond.[4–6] Subsequently, more exotic characterizations of this bond followed: a unique combination of strong coulombic attraction and high degree of electron sharing coined

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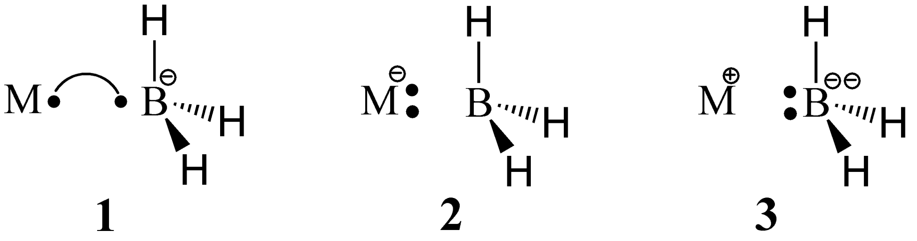
"ionic-enforced covalency",[7] while its large diradicaloid character lead others[8] to propose a new "Spin-Polarized Bond" category for it. At this stage, although this bond clearly shows unusual characteristics, the final picture still appears fuzzy, with different contributions which are seemingly disconnected and sometimes conflicting in nature. We will see in the following that Valence Bond (VB) theory[2] enables to clarify the matter and reconcile the different viewpoints on this unique bond.

The "classical" VB wave function of a bond[2] utilizes localized orbitals, and as such it is a superposition of specific Lewis structures (see Supporting Information). The different VB/Lewis structures for the Na – B electron pair bond in $NaBH_3^-$ system, and more generally in MBH_3^- clusters (with M=Li, Na, K), are displayed in Scheme 1.



Scheme 1. The three Lewis VB structures describing the M–B bond in the MBH_3^- anions: the covalent (**1**), "no bond" (**2**), and minor ionic (**3**) structures.

Here, structure **1** corresponds to the original Heitler-London wavefunction, also called usually the covalent structure. In **1**, the alkali atom transfers a single electron to the borane, so the two electrons can undergo spin-pairing giving rise to the "electron sharing" character of the Na–B bond. In structure **2**, the two fragments interact predominantly via electrostatic interactions: it corresponds to ionic bonding when the two fragments bear opposite formal charges, while it has been coined as a "no bond" structure in e.g. the prototype $H_3N{:}\rightarrow BH_3$ dative bonded system, where the fragments are neutral and therefore expected to interact rather weakly.[9] Finally, structure **3** is shown for completeness, since its contribution is expected to be negligible, as is confirmed by our calculations.

Within the Classical VB approach,[a] a wavefunction for (polar-)covalent bond would correspond to a predominant structure **1**, wherein the electron-sharing mechanism accounts by itself for the main part of the bonding energy. Quite differently, a genuine dative bond would be associated to a major "no bond" structure **2** in the wave function, together with a large resonance stabilization due to the **1**↔**2** mixing, also called "Charge Shift Resonance Energy" (RE_{CS}). A dative bond thus appears as a particular type of "Charge Shift Bond" (CSB).[9] Therefore, one may directly ask: does $Na–BH_3^-$ clearly show the characteristics of a dative, or rather of a polar-covalent bond? Figure 1 answers this question quite clearly.

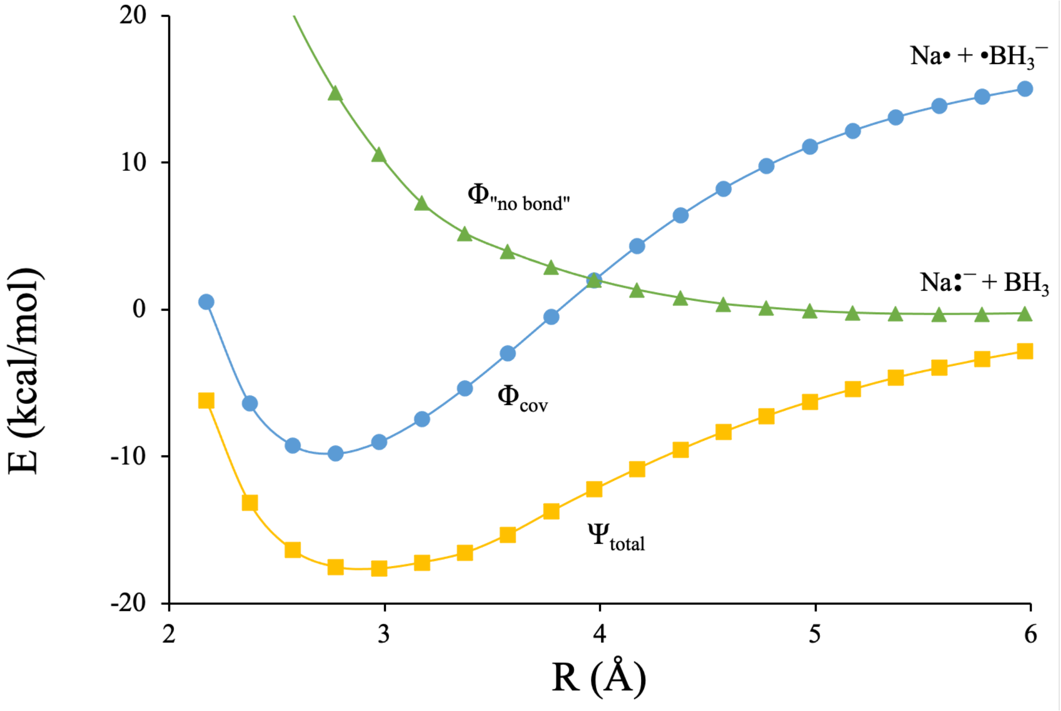


Figure 1. Relative energies E (in kcal.mol^{-1}) vs. the distance R (in Å) between the Na and B in $NaBH_3^-$, for the Covalent Structure **1** (blue curve with circles), the "no bond" structure **2** (green curve with triangles), and full BOVB wave function (yellow curve with squares).

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[a] A brief introduction to the three different classes of chemical bonds (covalent, ionic, "Charge-Shift") from classical VB theory, and to the BOVB method used here, can be found in Supporting Information.

The Figure displays the energy evolution along the Na…B distance of the covalent and "no bond" structures, computed separately (also called diabatic states), together with the full ground state wave function, using the high level BOVB method which includes both static and dynamical correlation. The "no bond" structure **2** is logically found to be of the lowest energy, at large inter-fragment distances, because the $\mathrm{Na}{:}^{-}$ + BH_3 heterolytic dissociation limit is thermodynamically preferred.[4] Nevertheless, the covalent diabatic state which lies much higher than the "no bond" structure at infinite separation, becomes the lowest in energy due to curve crossing at ≈4Å. As such, this crossover establishes unambiguously that the Na–B bond *is not* a dative bond at equilibrium distance, and supports the conclusion of Pan and Frenking;[6] though the latter was deduced from a less lucid DFT-EDA analysis as argued by Liu *et al.* [5]

Table 1. Revealing quantities extracted from the ground state BOVB wave functions of a few molecules. Columns 1-4: structure weights (ω), overlaps (S) between bonding orbitals, covalent/ionic Resonance Energy RE_{CS} (kcal.mol^{-1}). Subsequent columns are: electron density at the bond critical point (ρ), Laplacian of the density at the bond critical point ($\nabla^2\rho_{tot}$) and its decomposition into covalent ($\nabla^2\rho_{cov}$), ionic ($\nabla^2\rho_{ion}$) and resonance ($\nabla^2\rho_{res}$) components.[c] The final column characterizes the nature of the bonds.

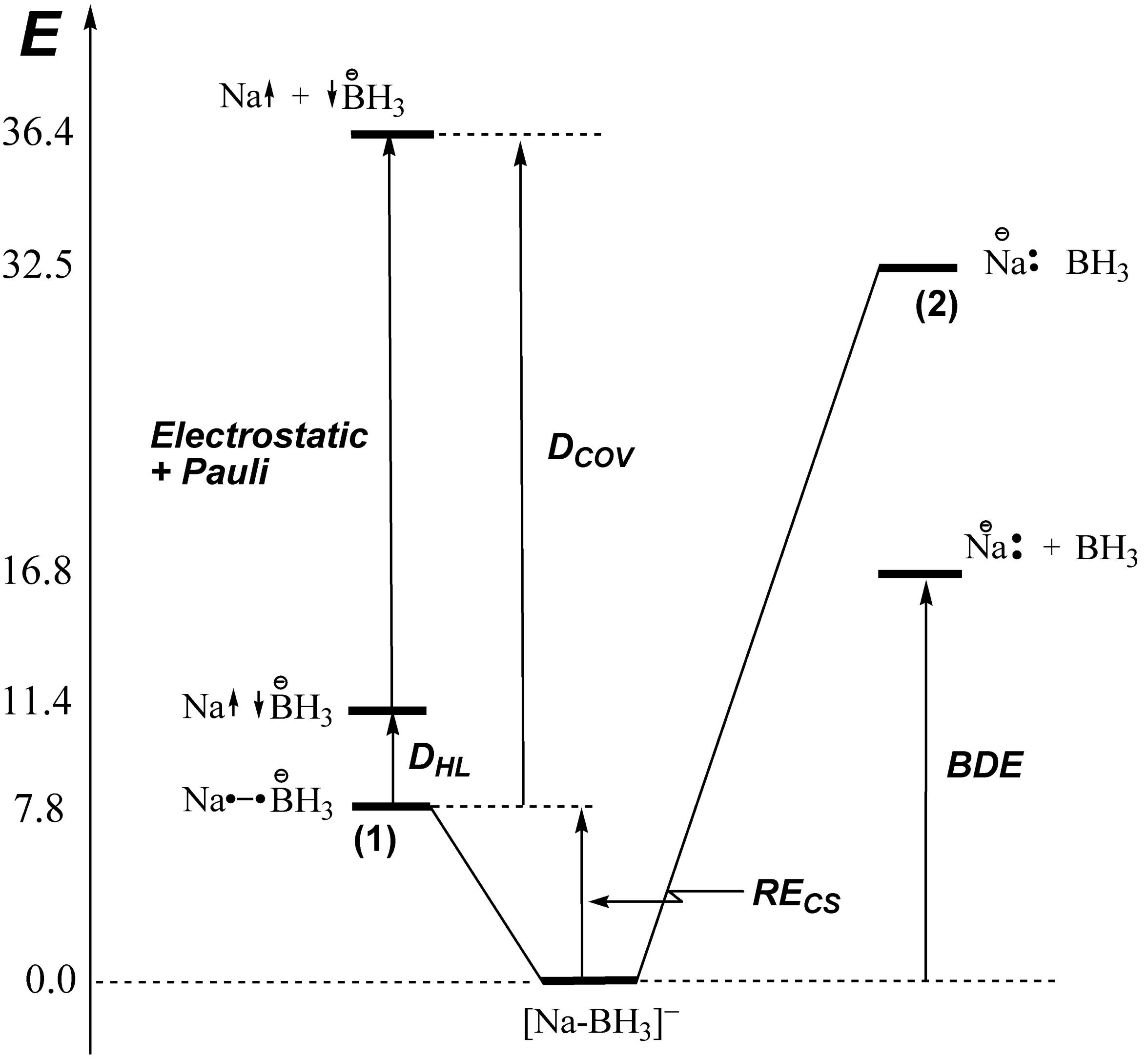
	ω_{cov}	$\omega_{ion/nb}$	S	RE_{CS}	ρ_{bcp}	$\nabla^2\rho_{tot}$	$\nabla^2\rho_{cov}$	$\nabla^2\rho_{ion}$	$\nabla^2\rho_{res}$	Nature
H_2[a]	.74	.13	.69	7.6	0.27	-1.21	-0.59	-0.39	-0.23	Covalent
NaF[a]	.28	.72	–	9.0	0.05	0.37	0.08	0.27	0.02	Ionic
F_2[a]	.69	.16	.21	62.2	0.25	0.58	1.00	0.41	-0.83	CSB
$H_3N:BH_3$[b]	.32	.68	–	41.8	0.09	0.39	0.03	0.56	-0.20	CSB-Dative
$LiBH_3^-$	.73	.23	.16	6.4	0.01	0.04	0.04	0.00	0.00	
$NaBH_3^-$	.71	.28	.19	8.6	0.01	0.03	0.02	0.01	0.00	
KBH_3^-	.66	.34	.15	7.9	0.01	0.02	0.01	0.01	0.00	

[a]Taken from ref.[10] [b]Taken from SI of ref.[9] [c]See ref.[10] for details about this methodology.

Let us now check whether the Na–B bond is a classical (polar-)covalent type, as concluded by Pan and Frenking.[6] Following previous work,[7] the same analysis is extended to the complete series of M–BH_3^- systems. Table 1 assembles different quantities extracted from the BOVB wave function, for four reference molecules representative of the different families of bonding, and for three $M–BH_3^-$ clusters (M=Li, Na, K). Based on QTAIM we use the Laplacian ($\nabla^2\rho$) at the bond critical point, and decompose it to its VB component, following a methodology already used before.[10] Typical covalent bonds (H_2) and ionic bonds (NaF) display one dominant VB structure that accounts for the major part of the bond energy, while the respective covalent/ionic resonance energy RE_{CS} is an additional but marginal component. In the QTAIM analysis, strong covalent bonds usually have a large ρ_{bcp}, along with a large negative $\nabla^2\rho_{cov}$. Ionic bonds display a small ρ_{bcp} with a large positive $\nabla^2\rho_{ion}$. Finally, in Charge Shift Bonds (CSBs), RE_{CS} is the major contributor to the bond strength, and the bonds display a significant ρ_{bcp} (~0.1 or above), whereas the Laplacian decomposition yields a large positive $\nabla^2\rho_{cov}$ and/or $\nabla^2\rho_{ion}$ which are partially counterbalanced by the large negative $\nabla^2\rho_{res}$.

Quite strikingly, the $M–BH_3^-$ ions do not appear to match any of these three particular trends, corresponding to the three main families of chemical bond with the Classical VB perspective. Both a dominant covalent structure and small RE_{CS} are compatible with polar-covalent bonding, but the ρ_{bcp} and the different components of $\nabla^2\rho$ all appear to be very small, similarly to what can be found in a stretched bond close to dissociation. The very small overlaps (<0.2) between bonding orbitals in the covalent structure, and the very small ρ_{bcp} and $\nabla^2\rho$, are compatible with a weakly coupled electron pair having a large diradical character, as proposed by Andrada et al.[8] Similar overlap values can be found in H_2 only when the bond is stretched to three times its equilibrium interatomic distance, a point where the residual bond energy is only a few kcal/mol, and the electron pair bond basically splits into a diradical.

Interestingly, the corresponding M–B bond energies are in apparent contradiction with this conclusion (Table S1), the homolytic BDE (Bond Dissociation Energy) values into M• and $\bullet BH_3^-$ being over 30 kcal.mol^{-1}.


E
36.4
32.5
16.8
11.4
7.8
0.0
Na↑ + ↓B̊H3
Na: BH3
(2)
Electrostatic + Pauli
DCOV
Na: + BH3
Na↑ ↓BH3
DHL
BDE
Na•—•BH3
(1)
REcs
[Na-BH3]⁻

Scheme 2. A VB interaction diagram for $NaBH_3^-$ (kcal.mol^{-1}).

How could a mere weakly coupled diradical pair lead to such a large stabilization energy between the interacting fragments? This contradiction can be resolved from inspection of the full VB interaction diagram of $NaBH_3^-$ (Scheme 2). The D_{HL} quantity is the energy arising from the mixing of the two spin-exchange determinants in the Heitler-London wave function (covalent structure) measured at the equilibrium distance. It is thus an *in situ* measure of the stabilization due to the spin-sharing mechanism, which is very large in genuine covalent bonds. D_{HL} here is on the contrary extremely small (3.6 kcal.mol^{-1}) for the Na–B bond, typical of a diradical pair. There is however a large stabilizing interaction embedded in structure **1**. This is the electrostatic interaction between the two Na• and •BH_3^- fragments. As seen from Scheme 2 above, this electrostatic interaction builds up from infinite separation to the equilibrium distance, where it amounts to net 25 kcal.mol^{-1} with Pauli repulsions included (of the bonding σ-electrons with the fully symmetric BH_3 orbital). We therefore conclude, in agreement with Foroutan-Nejad,[7] that the bond energy possesses a dominant electrostatic component in the Na–B bond. However, this large interaction is quite uniquely incorporated into a formally covalent structure, *and not in a standard ionic structure*.

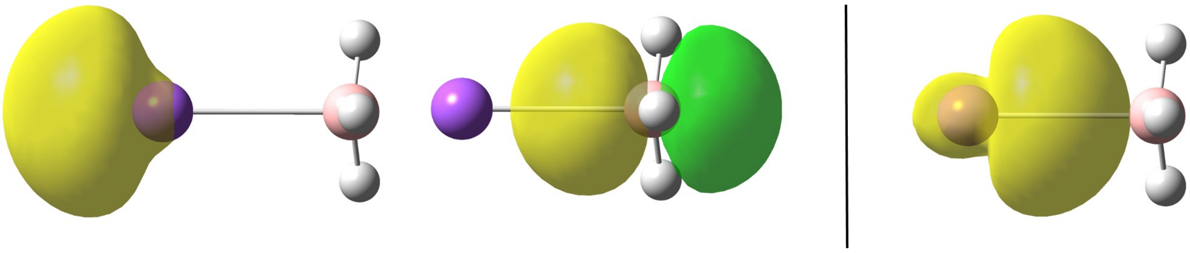
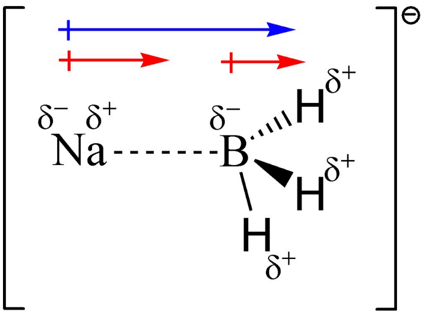


Figure 2. Active orbitals on Na (left) and BH_3 (center) involved in structure **1**. Right: the second hybrid active orbitals on Na involved in structure **2**.

The origin of this electrostatic stabilization deserves further analysis. Figure 2 displays on the left the valence active orbital on the sodium atom in the Heitler-London structure (**1**). This hybrid originates in 3s-3p hybridization,[11] which forms two opposing hybrids one pointing inwards and one outwards (Figure 2). Quite surprisingly, at first sight, the bonding orbital on sodium in structure **1** is polarized oppositely to the BH_3 fragment, to which the Na atom is bonded, and minimizes the bond overlap, unlike the situation in standard polar-covalent bonds. This explains why, despite a rather short Na–B distance, the overlap between the bonding orbitals in the structure **1** is so small (0.19 at the BOVB level) and within a similar range as in quasi-dissociated covalent bonds.

Clearly, therefore, structure **1** does not describe a classical polar-covalent bond. Rather, the valence orbital on Na leads to a polarization of the electronic density on the atom, which induces *a local dipole moment* oriented as represented in red in Scheme 3. This local dipole moment is quite large: 6.911 D from our calculations,[b] and leads to a stabilizing dipole – dipole interaction with the local dipole moment on the BH_3. All in all, our analysis reveals that despite the formal covalent appearance of the dominant structure **1** in the BOVB wave function, this structure actually corresponds to a weak spin-coupled diradical pair, which is sustained by the large stabilization due to dipole – dipole electrostatic interaction between the two fragments. As such, this large electrostatic stabilization in **1** is both the main source of stabilization in $Na–BH_3^-$, and also the root cause of the diabatic curve crossing shown in Figure 1, corresponding to the change of nature in the $Na–BH_3^-$ electronic ground state from infinity to equilibrium.



Scheme 3. Schematic representation of total dipole moment for structure **1** (blue arrow) and its components on each fragments (red arrows).

What is then the role of structure **2**? Its weight is not negligible at equilibrium, and this "no bond" structure leads to a resonance stabilization RE_{CS} that, although secondary compared to the electrostatic stabilization in structure **1**, also contributes to the final BDE as much as 7.8 kcal.mol^{-1}. Note from Scheme 1 that in structure **2**, the bond electron pair of Na–B is fully localized on the sodium atom. As explained above, the latter possesses two s/p types spin-coupled hybrids,[11] which are poised at an angle of 180°.

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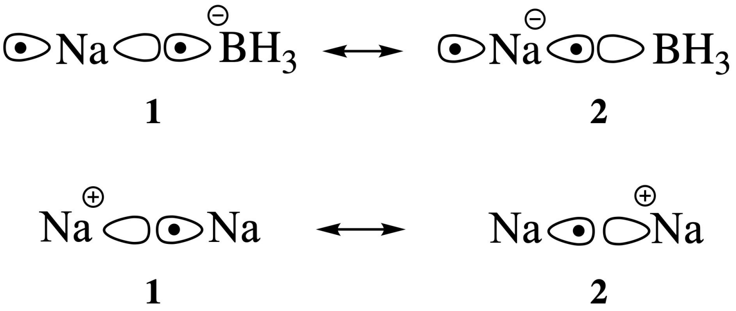
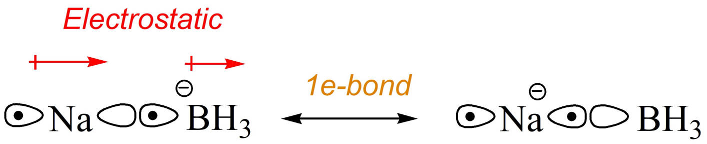
[b] Value obtained by calculating the separate Na atom using the orbitals of structure **1** in the BOVB wave function. (see Supporting Information)



Scheme 4. One-electron bond mechanisms in $NaBH_3^-$ and Na_2^+.

Quite interestingly, the active orbital of BH_3 in **1** overlaps significantly with the active orbital of Na in **2** pointing towards the BH_3 fragment (S=0.40 in our BOVB wave function). This feature allows a large overlap between the structures, and thus a significant **1**↔**2** resonance mixing (7.8 kcal.mol^{-1}). As shown in Scheme 4, this mixing thus introduces some two-center one-electron (2c,1e) bonding. This type of bonding is found in the H_2^+ prototype[12] for instance, and it is a particular type of "Charge-Shift" Bond physically akin to two-center three-electron (2c,3e) bonds.[9] Note that alkali atoms form (2c,1e) bonded cation dimers (M_2^+ with M=Li, Na, K) that are more stable than the corresponding neutral (2c,2e) M_2 dimers, while the boron atom has been shown to lead to stable (2c,1e) bonded adducts that can potentially act as a radical scavenger.[13] However, (2c,1e) bonding is here only a secondary component of bonding in $NaBH_3^-$, amounting to 7.8 kcal.mol^{-1}, because optimal **1**↔**2** resonance mixing would require the two structures involved to have the same energy, which is obviously the case in Na_2^+ but not in $NaBH_3^-$.



1 **2**

71% *28%*

Scheme 5. VB-based model proposed for $NaBH_3^-$ and similar clusters.

All in all, using VB theory, we were able to dissect and accurately quantify the different bonding components involved in making of $NaBH_3^-$. The Na–B bond is revealed to be neither a genuine Dative Bond at equilibrium, nor a standard polar-covalent bond, and neither a typical CSB. Rather, the final picture corresponds to Scheme 5, with two main stabilizing contributions found, of different magnitudes. This dimer is found to be mainly stabilized by electrostatic dipole-dipole interaction, that amounts to 25.0 kcal.mol^{-1} (BOVB level) together with the repulsive Pauli repulsion. This electrostatic term is quite uniquely contained into the formally covalent structure **1**, which is the major structure at equilibrium distance, while the "spin-exchange" covalent bonding mechanism *per se* amounts to a very minor extra stabilization of 3.6 kcal.mol^{-1} only (See Scheme 2 above). Further stabilization of $NaBH_3^-$is the secondary effects of 7.8 kcal.mol^{-1}, arising from the **1**⟷**2** resonance mixing within the (2c,1e) bonding.

Both the large dipole-dipole interaction, and (2c,1e) resonance interaction are enabled by the polarization of the electron pair, that manifests as a split diradical, one in a hybrid orbital pointing oppositely to the Boron atom, the second pointing towards B.

In summary, this final picture of the Na–B bond in $NaBH_3^-$ contains and explains all the seemingly disconnected perspectives previously published, showing: i) a change of electronic nature from the lowest heterolytic dissociation limit (**2** is dominant) to equilibrium (**1** is dominant),[6] ii) an unusual high level of static and dynamical correlation,[4–6] iii) a unique combination of coulombic stabilization with Charge-Shift

Bonding character,[7] iv) a large diradical character.[8] What a multifaceted little bond it is!

Acknowledgment

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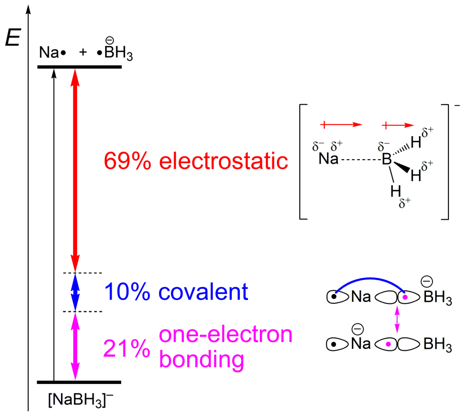
Table of Contents graphical abstract


E
Na• + •BH3 ⊖
69% electrostatic
10% covalent
21% one-electron bonding
[NaBH3]⁻
δ⁻ δ⁺ Na
δ⁻ B
H δ⁺
H δ⁺
H δ⁺
Na ⊖ BH3
⊖ Na BH3

A multifaceted bond. High level Valence Bond calculations show that the $NaBH_3^-$ cluster is stabilized neither by a dative bond nor by a standard polar-covalent bond, but rather by a unique combination of three distinct components that are accurately quantified.