Stabilizing Borinium Cations $[X–B–X]^+$ Through Conjugation and Hyperconjugation Effects

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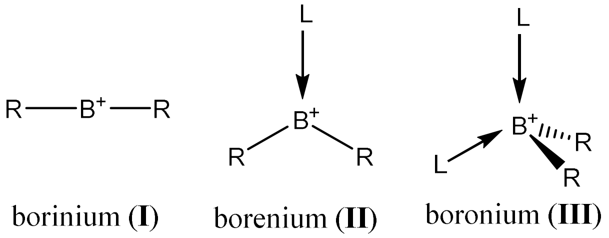
Abstract

Borinium, a two-coordinated boron cation, is a strong Lewis acid that was thought difficult to prepare due to a lower number of coordinating ligands and susceptibility towards nucleophilic reactions. Recently a dimesityl borinium cation (Mes_2B^+) with high thermal stability has been synthesized and characterized by Shoji and co-workers. These findings suggest that, despite being extremely electron-demanding, borinium cations might be stabilized with certain substituted function groups. In the present study, we have studied a series of the borinium cations $[X–B–X]^+$ with different substituted groups using the NBO and the BLW methods. Our computations revealed that both π-conjugation and hyperconjugation effects can effectively stabilize substituted borinium cations $[X–B–X]^+$. Substituents like X = $C=CH_2$ stabilize the borinium center through highly delocalized π-bonding, involving the formally "empty" boron p_x and p_y orbitals. We suggest the borinium cations $[X–B–X]^+$ with X = cyc-$N(CH)_2$ and especially X = $C=CH_2$ as possible synthetic targets of novel borinium cations.

Introduction

Boron compounds with electron deficient B centers[1] have prospects as useful Lewis acids for a variety of organic transformations, and attempts to prepare highly acidic versions of such compounds, i.e., boron cations, continue to attract attention. Depending on the number of coordinated ligands attached to the B center, cationic boron-containing compounds can be classified into three types: the two-coordinated borinium (**I**), the three-coordinated borenium (**II**), and the four-coordinated boronium (**III**) (Figure 1). Among them, borenium (**II**) and boronium (**III**) cations are relatively easy to synthesize,[2,3] as the coordinating ligands largely neutralize the Lewis acidity of the boron center. Borinium cations (**I**), however, are difficult to prepare due to a lower number of coordinating ligands and susceptibility towards nucleophilic reactions.



Scheme 1. Types of cationic boron-containing compounds.

The first attempt to synthesize a borinium cation in solution, i.e., the Ph_2B^+ cation, was recorded as early as 1958.[4] However, later NMR studies revealed that the purported Ph_2B^+ structure actually corresponded to a mixture of three- and four-coordinate borenium and boronium cations coordinated to the surrounding solvent molecules.[5] Following studies combining experimental evidence and semi-empirical calculations suggested a most favorable linear structure for BF_2^+.[6] In 1982, the first crystallographic structures of borinium salts were reported,[7] showing structures with a boron center stabilized by dimethylamine and tetramethylpiperidine ligands. In the same year later, a condensed-phase borinium cation salt,

$[R_2N–B–NR_2]^+AlCl_4^–$, was synthesized.[8] Gas phase reactivities of Me_2B^+, $(CH_3O)_2B^+$, $(CH_3)_2B^+$, and H_2B^+ ions also have been investigated.[9,10,11] In 2002, the synthesis of a unique extended two-coordinate borinium salt $[(tBu_3PN)_2B]^+[B(C_6F_5)_4]^–$ containing a linear arrangement of P=N–B–N=P was reported.[12] In the same paper, theoretical studies were performed on a model $[(H_3PN)_2B]^+$ system at the B3LYP/6-311G** level, confirming preference for the linear arrangement of N–B–N atoms. Extensive efforts to stabilize the vacant boron p-orbitals of cations have been reviewed in several papers.[13,14] In 2014 and 2015, Shoji and co-workers reported the successful isolation of a dimesityl borinium cation (Mes_2B^+) with high thermal stability.[15,16,17] In 2017, Shoji and co-workers found that the dimesityl borinium cation (Mes_2B^+) undergoes a two fold 1,2-carbonboration reaction with diphenylacetylene to yield another isolable two fold coordination borinium cation.[18] These findings suggest importantly that, despite being extremely electron-demanding, borinium cations might be stabilized without additional ligand coordination.

In this paper, we apply computational quantum chemical tools, including the NBO (natural bond orbital)[19,20,21] and the BLW (block-localized wavefunction) methods,[22,23] to quantify the stabilizing effects of π-conjugation and hyperconjugation in borinium cations containing electron-donating substituents. More than 30 electron-donating substituents were examined in our preliminary test set, and those showing the strongest (hyper)conjugative effects are discussed here. The ultimate goal of this research is to design yet more stable borinium cations. The results and discussions are separated into three sections, including a comparison of the bonding properties of $[H_2N–B–NH_2]^+$ vs. $[F_2N–B–NF_2]^+$ (Section 1), followed by analyses for substituted $[X–B–X]^+$ species, containing B–N bonds (Section 2) and B–C bonds (Section 3).

Computational Details

All borinium cation $[X–B–X]^+$ structures were optimized at the B3LYP[24,25]/6-31G(d)[26] level, and characterized by vibrational frequency analysis at the same level of theory. For $[X–B–X]^+$ structures containing B–N bonds, the following substituents were considered: $N[C(Me)_3]_2$, NH_2, $N[Si(Me)_3]_2$, $N(CH_3)_2$, $N{=}CH_2$, NF_2, cyc-$N(CH)_2$. For $[X–B–X]^+$ structures containing B–C bonds, the following substituents were considered: CH_3, cyc-C_3H_5, cyc-C_6H_5, CN, CCH, $C{=}CH_2$, COH). Natural bond orbital (NBO) analyses[19,20,21] were carried out based on computed B3LYP electron densities. Natural atomic charges[27] of the boron atoms quantified the degree of electronic transfer from the substituents to the boron center. Second-order perturbation interaction energies ($E^{(2)}$) were examined to measure the effects of conjugation, hyperconjugation, and through-space electron delocalization. All geometry optimizations and NBO analyses were performed employing the Gaussian 09 program.[28]

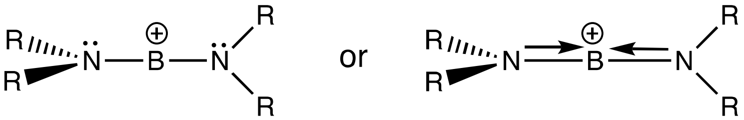
Block-localized wave function (BLW)[22,23] computations were applied to quantify π-electron delocalization effects across the B–X single bonds and to provide complementary insights to the $E^{(2)}$ analyses. BLW measures the amount of π-electron delocalization (DE_π) by comparing the energy of the fully delocalized wavefunction (Ψ_{deloc}) to that of a hypothetical localized wavefunction (Ψ_{loc}), in which electron delocalization into the two orthogonal sets of boron p orbitals were precluded, $DE_\pi = \Psi_{\mathrm{deloc}} - \Psi_{\mathrm{loc}}$. Ψ_{loc} was computed by restricting the expansion of molecular orbitals over basis functions within the selected molecular subspace. Since its introduction in 1998, the BLW method has been applied extensively to study chemical bonding, π-conjugation effects, and aromaticity.[29,30] All BLW computations were performed at the B3LYP/6-31G(d) level employing the GAMESS-R5 program.[31]

Results and Discussion

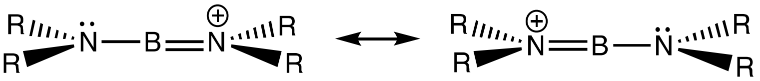
1. π-Conjugation Effects in $[H_2N–B–NH_2]^+$ vs. $[F_2N–B–NF_2]^+$.

Two conformers of $[H_2N–B–NH_2]^+$ and $[F_2N–B–NF_2]^+$, a staggered (D_{2d}) and a co-planar (D_{2h}) structure, were considered (see Figure 1). The D_{2d} structures were predicted to be minima on the potential energy surface. The D_{2h} structures were transition states lying 14.2 kcal/mol (for X = NH_2) and 31.0 kcal/mol (for X = NF_2) above the D_{2d} minima, with imaginary vibrational frequencies corresponding to internal rotation around the N–B–N axis. As shown in Figure 1, the computed B–N distances for the D_{2d} conformers of $[H_2N–B–NH_2]^+$ (1.335 Å) and $[F_2N–B–NF_2]^+$ (1.336 Å) are shorter than their D_{2h} analogs, $[H_2N–B–NH_2]^+$ (1.344 Å) and $[F_2N–B–NF_2]^+$ (1.360 Å), suggesting stronger BN bonding in the D_{2d} conformers.

NBO analyses suggest that the D_{2d} forms of both $[H_2N–B–NH_2]^+$ and $[F_2N–B–NF_2]^+$ exhibit two sets of perpendicular N→B dative π-bonding (see two possible representations below and Figure 2, left). The representation on the right will be used in this work



The D_{2h} forms display three-center-two-electron delocalized B=N π-bonding. As shown by the two equivalent resonance form below, only one set of N lone pair forms a formal B=N π-bond with one set of the empty p orbital of B atom (see also Figure 2, right).



As shown in Table 1, the computed Wiberg Bond Index (WBI) values for the D_{2d} forms of $[H_2N–B–NH_2]^+$ (WBI = 1.36) and $[F_2N–B–NF_2]^+$ (WBI = 1.34) are higher compared to their D_{2h} analogs, $[H_2N–B–NH_2]^+$ (WBI = 1.13) and $[F_2N–B–NF_2]^+$ (WBI = 1.12). Note also the less positive NPA charge on boron for the D_{2d} forms of $[H_2N–B–NH_2]^+$ (1.24) and $[F_2N–B–NF_2]^+$

(1.01) compared to the D_{2h} forms of $[H_2N–B–NH_2]^+$ (1.39) and $[F_2N–B–NF_2]^+$ (1.28) (Table 1), indicating more electron transfer from N to B in the D_{2d} conformer.

Computed second-order perturbation theory (E2PERT) analyses elucidate relevant (hyper)conjugative effects stabilizing the B centers of the D_{2d} and D_{2h} forms of $[H_2N–B–NH_2]^+$ and $[F_2N–B–NF_2]^+$. In D_{2d} $[H_2N–B–NH_2]^+$, the B center is stabilized by hyperconjugative σ(NH) → π*(BN) (four sets, $E^{(2)}$ = 5.12 kcal/mol each) and π(BN) → σ*(NH) (four sets, $E^{(2)}$ = 1.36 kcal/mol each) interactions, back and forth between the N–H σ-bonds and BN π-bonds (Figure 3a). In D_{2d} $[F_2N–B–NF_2]^+$, the related σ(N–F) → π*(B–N) (four sets, $E^{(2)}$ = 1.36 kcal/mol each) interactions are weakened due to the high electronegativity of the F atoms, but the π(BN) → σ*(NF) (four sets, $E^{(2)}$ = 3.67 kcal/mol each) interactions become stronger (Figure 3b). Additionally, in D_{2d} $[F_2N–B–NF_2]^+$, the B center is stabilized by π-conjugative LP(F) → π*(BN) interactions (four sets, $E^{(2)}$ = 8.84 kcal/mol each) and anomeric effects coming from the F lone pairs, LP(F) → σ*(BN) (four sets, $E^{(2)}$ = 3.72 kcal/mol each) (Figure 3c). These conjugative and hyperconjugative interactions stabilize the D_{2d} forms of $[H_2N–B–NH_2]^+$ and $[F_2N–B–NF_2]^+$ in addition to dative BN π-bonding.

For comparison, the D_{2h} conformers of $[H_2N–B–NH_2]^+$ and $[F_2N–B–NF_2]^+$ exhibit large conjugative LP(N) → π*(BN) interactions, $E^{(2)}$ = 64.57 and 55.88 kcal/mol (Figure 4a), respectively, indicating delocalized π-bonding between the N–B–N centers. Upon H to F substitution, D_{2h} $[H_2F–B–NF_2]^+$ is stabilized by additional π-conjugative LP(F) → π*(BN) interactions (two sets, $E^{(2)}$ = 8.84 kcal/mol each) and anomeric effects coming from the F lone pairs, LP(F) → σ*(BN) (four sets, $E^{(2)}$ = 3.25 kcal/mol each) (see Figure 4b).

Accordingly, BLW analyses for the D_{2d} vs. D_{2h} forms of $[NH_2–B–NH_2]^+$ and $[NF_2–B–NF_2]^+$ show greater π-electron delocalization (DE_π) effects in the D_{2d} conformers. In $[NH_2–B–$

$NH_2]^+$, the computed π-electron delocalization energy (DE_π) for the D_{2d} structure (106.6 kcal/mol) is ΔDE_π = 10.3 kcal/mol higher than that of the D_{2h} structure (96.3 kcal/mol), and comparable to the computed relative energies (ΔE = 14.2 kcal/mol) of the two conformers (Table 1). In $[NF_2$–B–$NF_2]^+$, the computed DE_π for the D_{2d} structure (146.5 kcal/mol) is ΔDE_π = 27.9 kcal/mol higher than that of the D_{2h} structure (118.6 kcal/mol), and comparable to the computed relative energies (ΔE = 31.0 kcal/mol) of the two conformers (Table 1).

2. Stabilization of $[X\text{–}B\text{–}X]^+$cations containing B–N bonds.

Scherpf and co-workers reported examples of ylide-stabilized borinium salts that displayed high thermal stability and can be stored for months.[32] Following these experimental findings, we chose to investigate the stabilization of borinium using five strong electron-donating substituents, including: $N[C(Me)_3]_2$, $N[Si(Me)_3]_2$, $N(CH_3)_2$, $N{=}CH_2$, and cyc-$N(CH)_2$. Optimized structures of these species are shown in Figure 5. All structures have two sets of orthogonal B=N bonds, similar to the D_{2d} structures of $[X\text{–}B\text{–}X]^+$, X = NH_2 and NF_2. The B–N bonds in these cations are significantly shorter than the experimentally reported B–N single bond (1.673Å),[33] and range from 1.306Å to 1.348Å, indicating a much higher bond order.

Table 2 lists the computed BLW delocalization energies and NPA charges for $[X\text{–}B\text{–}X]^+$ structures containing B–N bonds. The BLW-derived π-delocalization energies, DE_π, increase in the order: X = $N[C(Me)_3]_2$ < $N[Si(Me)_3]_2$ < $N(CH_3)_2$ < $N{=}CH_2$ < cyc-$N(CH)_2$. Notably, substituted $[X\text{–}B\text{–}X]^+$ species with a higher DE_π exhibit lower NPA charges at the B atom, indicating that electron delocalization effectively quenches positive charge at the electron deficient boron center.

NBO second order perturbative energy $E^{(2)}$ analyses reveal especially large conjugative and hyperconjugative effects for the substituted $[X\text{–}B\text{–}X]^+$, X = $N{=}CH_2$ and cyc-$N(CH)_2$, as π-electron delocalization from the C=N and C=C π-bonds to B help quench the positive charge on the boron center (see large $E^{(2)}$ values below). These effects are much less pronounced in X = $N[C(Me)_3]_2$, NH_2, $N[Si(Me)_3]_2$ analogs ($E^{(2)}$ values all below 5 kcal/mol).

In X = $N{=}CH_2$, the π-bonding pattern resembles that of cumulene (pentatetraene), and two sets of π-conjugative interactions back and forth between the π(CN) and π(BN) bonds are present: π(CN) → π*(BN) (two sets, $E^{(2)} = 24.67$ kcal/mol each) and π(BN) → π*(CN) (two sets, $E^{(2)} = 5.93$ kcal/mol each) (Figure 6a). Hyperconjugative interactions between the σ(CH) and π(BN) bonds also stabilize the B center: σ(CH) → π*(BN) (four sets, $E^{(2)} = 3.66$ kcal/mol each) and π(BN) → σ*(CH) (four sets, $E^{(2)} = 7.89$ kcal/mol each) (Figure 6b).

In X = cyc-$N(CH)_2$, two azacyclopropenyl groups are connected to the B center, and both conjugative and hyperconjugative interactions involving the ring CC and CN bonds stabilize the boron center. The ring CC π-bonds donate electrons to the BN π-bond, resulting in two π-conjugative interactions, π(CC) → π*(BN) (two sets, $E^{(2)} = 19.25$ kcal/mol each) (Figure 7a), and the ring CC σ-bonds donate electrons to the BN σ-bond, resulting in two hyperconjugative interactions, σ(CC) → σ*(BN) (two sets, $E^{(2)} = 11.37$ kcal/mol each) (Figure 7b). Additional stabilizing effects come from hyperconjugative interactions back and forth between the σ(CN) and BN π-bonds: σ(CC) → π*(BN) (four sets, $E^{(2)} = 4.93$ kcal/mol each) and π(BN) → σ*(CN) (four sets, $E^{(2)} = 2.28$ kcal/mol each) (Figure 7c).

3. Stabilization of $[X–B–X]^+$ cations containing B–C bonds.

Seven substituted $[X–B–X]^+$ systems containing the B–C bonds were studied, including X = CH_3, cyc-C_3H_5, cyc-C_6H_5, CN, CCH, $C{=}CH_2$, and COH. Optimized geometries of all structures are shown in Figure 8, and their computed BLW-DE's and NBO data listed in Table 3. The computed B–C bonds of these structures (ranging from 1.398Å to 1.496Å) are all shorter than the average B–C single bond in molecules containing three-coordinated boron atom (1.556 Å) or four-coordinated boron atom (1.606 A),[34] suggesting that the conjugation effect for borinium cation is stronger than those for the higher coordinated boron atom. Following geometry optimization for X = COH, the B center became tetracoordinated (two B–O bonds formed with a OCCO dihedral angle of close to 90˚). This molecule is *boronium*, and thus is not discussed further.

Table 3 lists the computed BLW delocalization energies and NPA charges for $[X–B–X]^+$ structures containing B–C bonds. The BLW-derived π-delocalization energies, DE_π, increase in the order: X= CH_3 < cyc-C_3H_5 < cyc-C_6H_5 < CN < CCH < C=CH_2, and species with a higher DE_π exhibit lower NPA charges at the B atom. The surprisingly low NPA charge on the B atom of the X = C=CH_2 species (and enormous DE_π value) is eye catching, and suggests a highly stabilized boron center. Notably, the computed NPA_B for X = C=CH_2 (NPA_B = 0.60) is close to that of the tetracoordinated X = COH species (NPA_B = 0.72), but only half compared to that of the X = cyc-C_6H_5 species (NPA_B = 1.21), an analogue of Shoji et al.'s dimesityl borinium cation[18] (Mes_2B^+). According to NBO analysis, the especially favorable $[CH_2=C–B–C=CH_2]^+$ species exhibits π-conjugative interactions from the two C=C π-bonds to the B center: π(CC) → p*(B) (two sets, $E^{(2)}$ = 33.80 kcal/mol), and in the perpendicular direction, a three-center-two-electron (3c-2e) π-bond involving the two inner C's and the B center (see Figure 9).

Among the substituted boriniums considered, π-bonding of the $[CH_2=C–B–C=CH_2]^+$ borinium is especially interesting. The inner carbon atoms have one (π_y) electron each and form 3c-2e bonding involving the empty B p_y orbital (see HOMO, Figure 10). The two C=C π-bonds (π_x) donate electrons to the empty boron p_x orbital, resulting in delocalized five-center four electron, 5c-4e, bonding (see HOMO–1 and HOMO–2, Figure 10). Together these delocalized π-bonding interactions, in both the x and y directions, quench positive charge at the boron center.

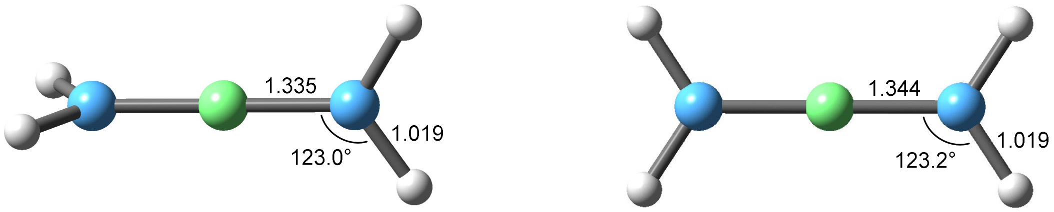
Triplet $[CH_2=C–B–C=CH_2]^+$ has D_{2d} symmetry and is 16.9 kcal/mol higher in energy than the singlet D_{2h} structure at the B3LYP/6-31G(d) level, due to weaker π-bonding. As shown in Figure 11, the singly occupied molecular orbitals (SOMOs) are a pair of degenerate (π_x, π_y) orbitals corresponding to two orthogonal sets of C=B π-bonds, and the HOMO–1 is a doubly degenerate set of 3c-2e CCB π-bonds.

Conclusions

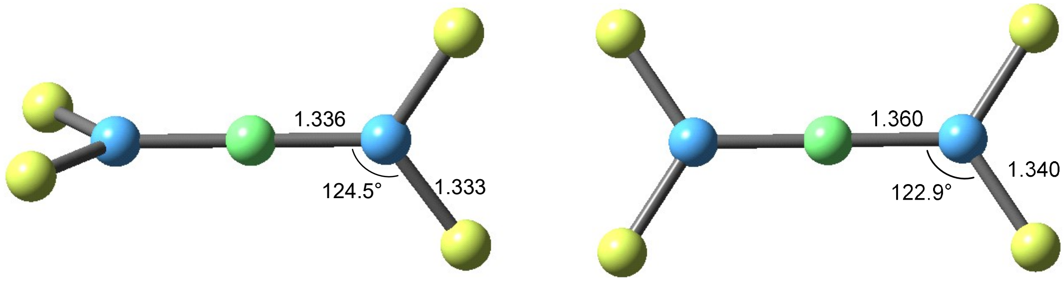
Computations based on natural bond orbital (NBO) and block-localized wavefunction (BLW) analyses reveal that both π-conjugation and σ-hyperconjugation effects can effectively stabilize substituted borinium cations $[X–B–X]^+$. (Hyper)conjugative stabilizations of the B center in substituted $[X–B–X]^+$ structures containing B–N bonds follow the order: NH_2 < $N[C(Me)_3]_2$ < $N[Si(Me)_3]_2$ < $N(CH_3)_2$ < $N=CH_2$ < NF_2 < cyc-$N(CH)_2$ based on their delocalizaton energies, and those of borinium species containing B–C bonds follow the order: CH_3 < cyc-C_3H_5 < cyc-C_6H_5 < CN < CCH < $C=CH_2$. Substituents like X = $C=CH_2$ stabilize the borinium center through highly delocalized π-bonding, involving the formally “empty” boron p_x and p_y orbitals. Importantly, our findings suggest borinium cations $[X–B–X]^+$ with X = cyc-$N(CH)_2$ and especially X = $C=CH_2$ as possible synthetic targets of novel borinium cations.

Acknowledgements

The research was supported by the U.S. National Science Foundation, Grant CHE-1661604 (University of Georgia), and by CHE-1751370 (University of Houston). This work was also supported by 111 project of China (Grant No. B08044) and Discipline Development program of Minzu University of China (Grant No. YLDX01013).



$[H_2N–B–NH_2]^+$ (D_{2d}, 0.0) **$[H_2N–B–NH_2]^+$ (D_{2h}, 14.2)**



$[F_2N–B–NF_2]^+$ (D_{2d}, 0.0) **$[F_2N–B–NF_2]^+$ (D_{2h}, 31.0)**

Figure 1. Optimized structures of $[X–B–X]^+$ ($X = NH_2$, NF_2) at the B3LYP/6-31G(d) level. The relative energies (in parentheses) are in kcal/mol, and the bond distances are in Å.

$[R_2N–B–NR_2]^+$ (D_{2d}) **$[R_2N–B–NR_2]^+$ (D_{2h})**

Figure 2. Illustrations showing B=N π-bonding for the D_{2d} and D_{2h} conformers of $[R_2N–B–NR_2]^+$ (R = H or F).

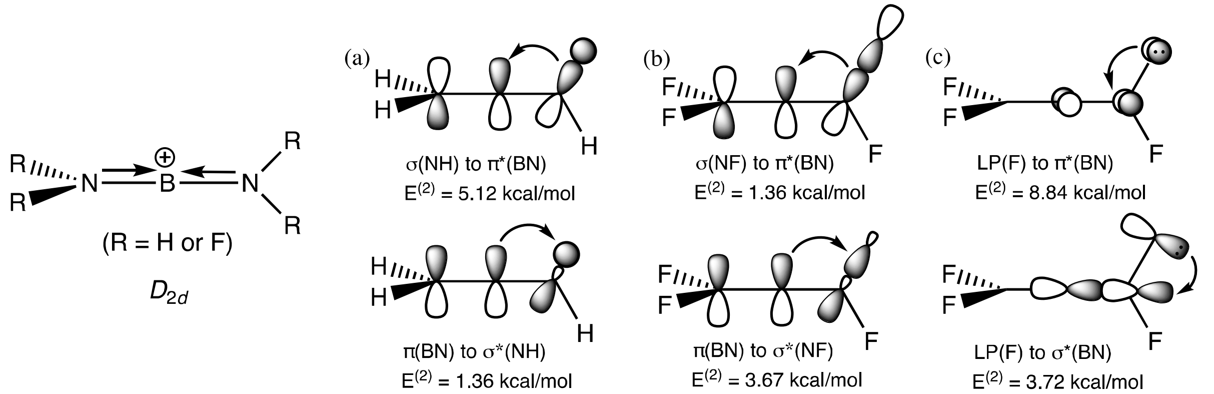


Figure 3. Schematic illustrations of conjugative and hyperconjugative interactions stabilizing the B centers of D_{2d} (a) $[NH_2–B–NH_2]^+$ and (b) $[NF_2\ B–NF_2]^+$ based on E2PERT analyses. Formal charges on the atoms are shown for clarity purposes.

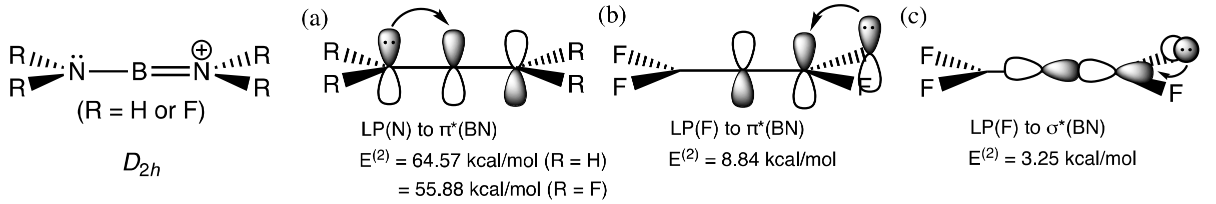
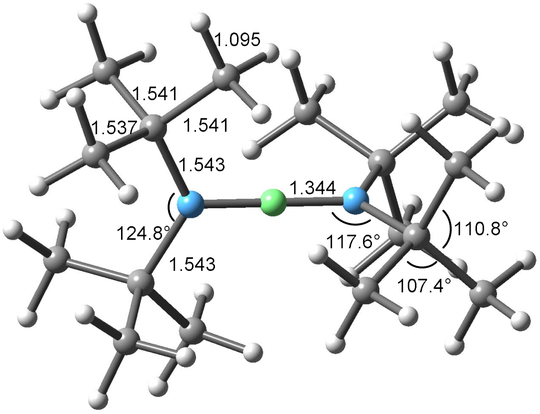
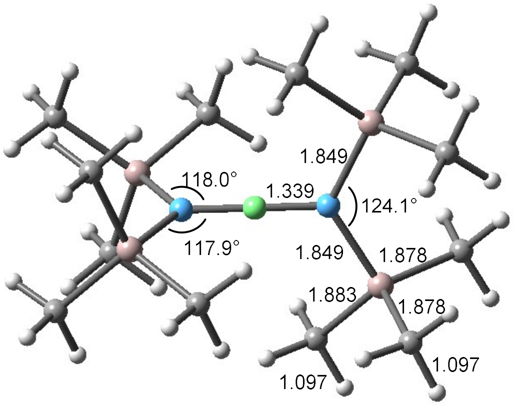


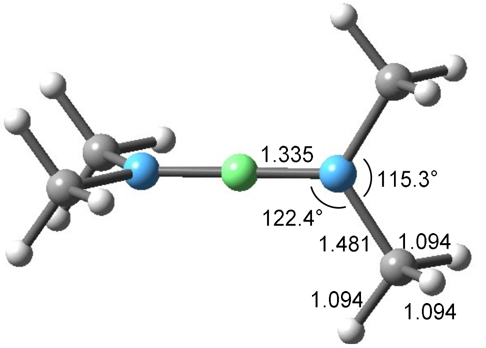
Figure 4. Schematic illustration of (a) delocalized π-bonding in D_{2h} $[R_2N–B–NR_2]^+$, as well as (b) π-conjugative and (c) anomeric effects stabilizing the B center of D_{2h} $[NF_2–B–NF_2]^+$ based on E2PERT analyses.



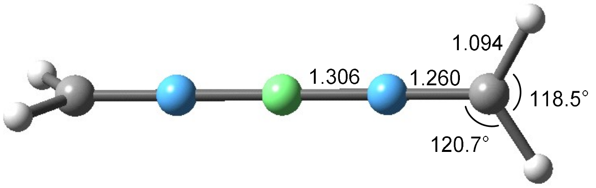
$[(C(Me)_3)_2N\text{-}B\text{-}N(C(Me)_3)_2]^+$ (S_4)



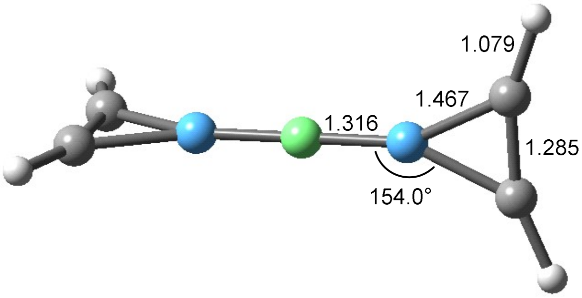
$[(Si(Me)_3)_2N\text{-}B\text{-}N(Si(Me)_3)_2]^+$ (S_4)



$[(CH_3)_2N\text{-}B\text{-}N(CH_3)_2]^+$ (D_{2d})



$[H_2CN\text{-}B\text{-}NCH_2]^+$ (D_{2d})



$[(CH)_2N\text{-}B\text{-}N(CH)_2]^+$ (D_{2d})

Figure 5. Optimized structures of $[X–B–X]^+$ (X=N[C(Me)$_3$]$_2$, N[Si(Me)$_3$]$_2$, N(CH$_3$)$_2$, N=CH$_2$, and cyc-N(CH)$_2$) at the B3LYP/6-31G(d) level.

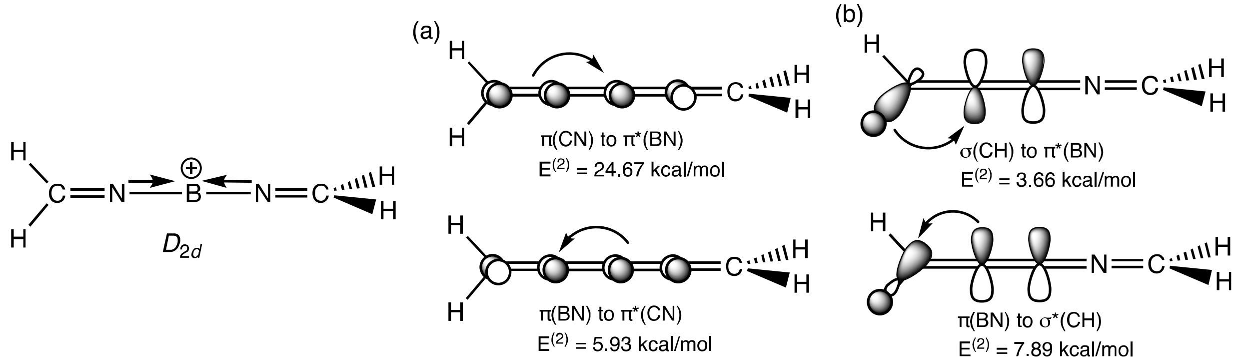


Figure 6. Schematic illustration of (a) conjugative and (b) hyperconjugative interactions stabilizing the B center of D_{2d} [X–B–X]$^+$, X = N=CH$_2$, based on E2PERT analyses.

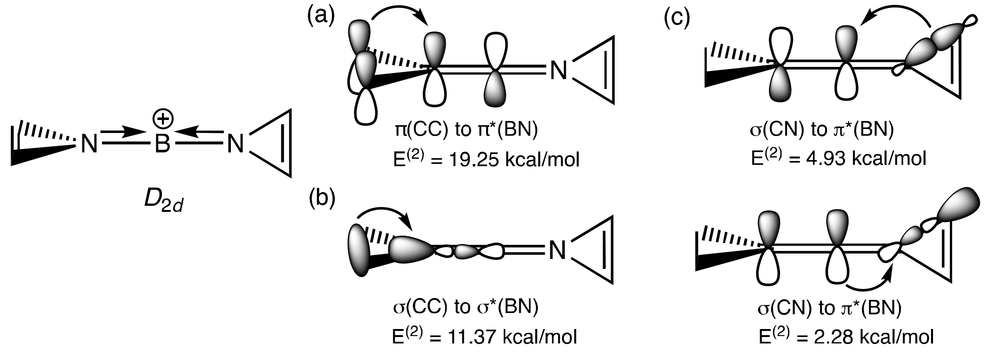
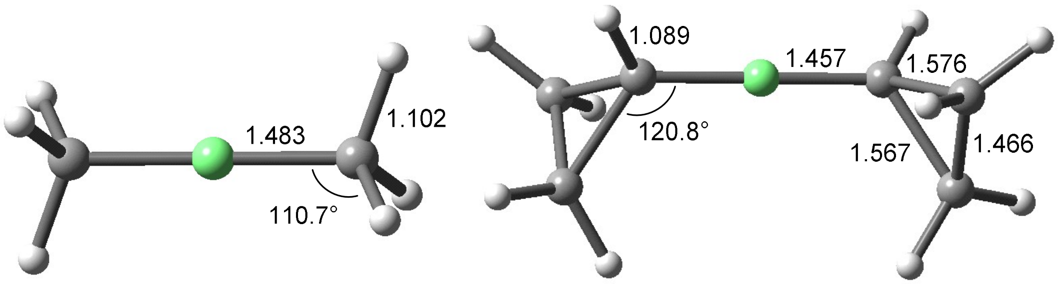
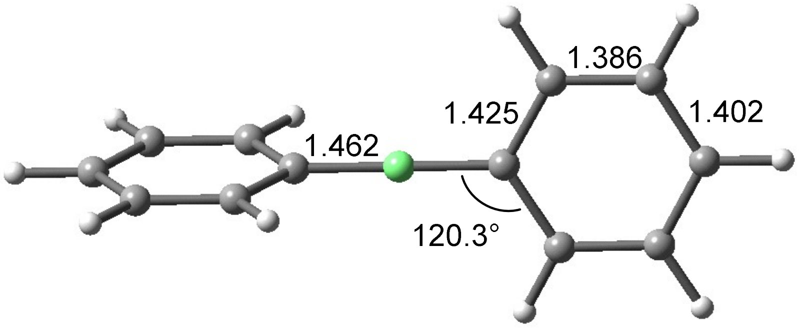


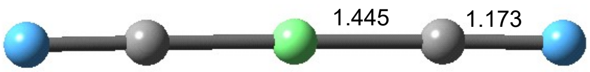
Figure 7. Schematic illustration of (a) conjugative and (b), (c), hyperconjugative interactions stabilizing the B center of D_{2d} [X–B–X]$^+$, X = cyc-N(CH)$_2$, based on E2PERT analyses.



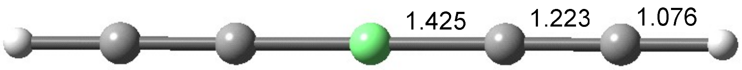
$[H_3C\text{-}B\text{-}CH_3]^+$ (D_{3d}) **$[H_5C_3\text{-}B\text{-}C_3H_5]^+$ (C_2)**



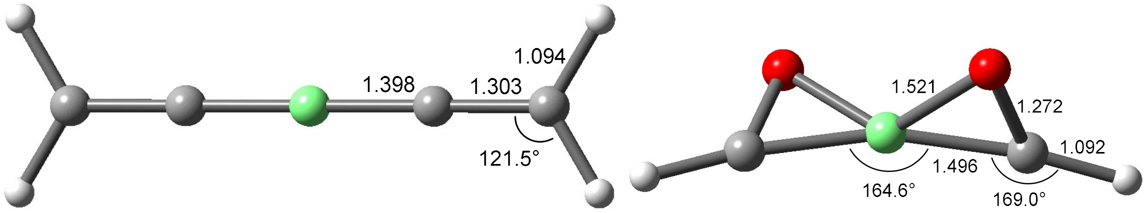
$[H_5C_6\text{-}B\text{-}C_6H_5]^+$ (D_{2d})



$[NC\text{-}B\text{-}CN]^+$ ($D_{\infty h}$)



$[HCC\text{-}B\text{-}CCH]^+$ ($D_{\infty h}$)



$[H_2CC\text{-}B\text{-}CCH_2]^+$ (D_{2h}) **$[HOC\text{-}B\text{-}COH]^+$ (C_2)**

Figure 8. Optimized structures of $[X\text{–}B\text{–}X]^+$ (X = CH_3, cyc-C_3H_5, cyc-C_6H_5, CN, CCH, C=CH_2, COH) at the B3LYP/6-31G* level.

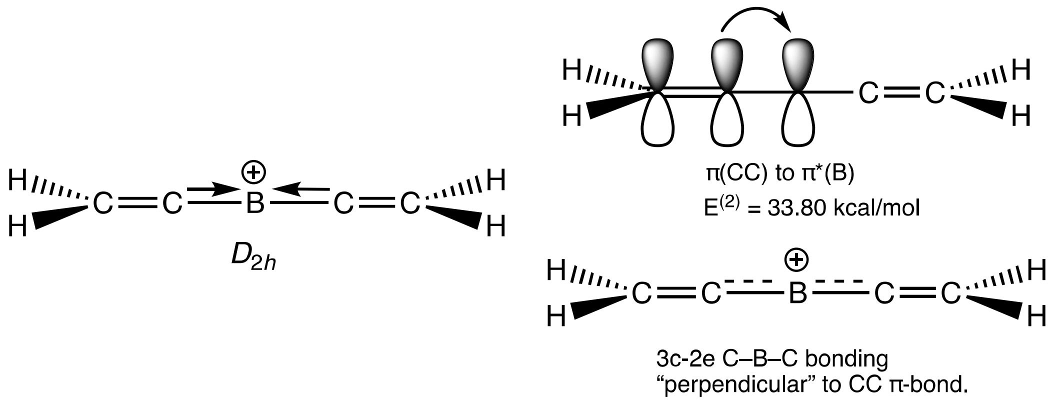


Figure 9. Lewis structure for D_{2h} $[X–B–X]^+$, X = C=CH$_2$, and schematic illustration of conjugative stabilizations and three-center-two-electron (3c-2e) bonding involving the B center.

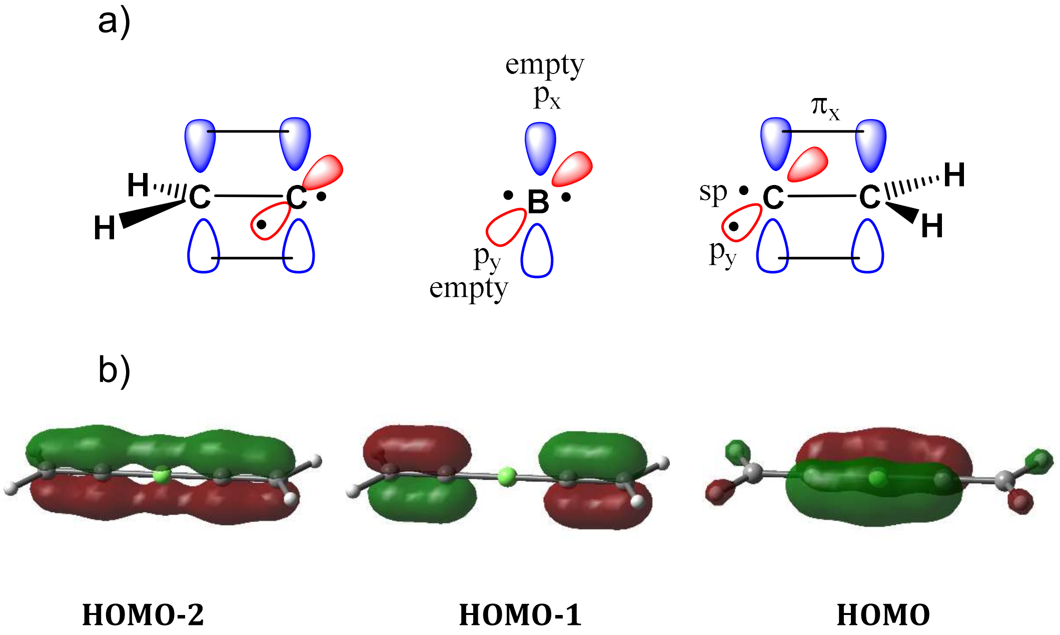
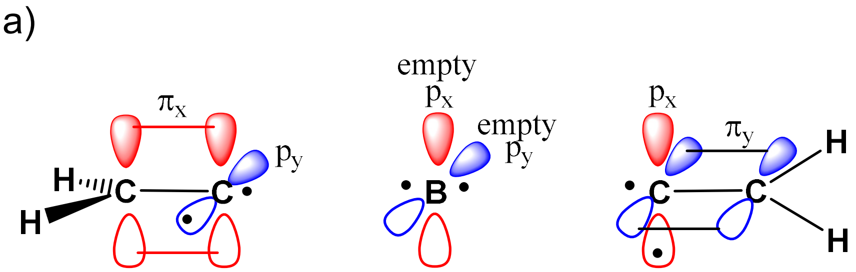
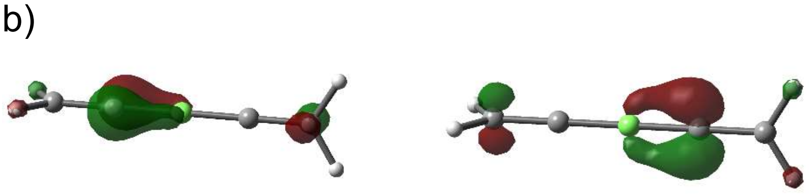


Figure 10. a) Bonding analysis for the C=CH$_2$ ligands, and b) molecular orbitals corresponding to π-bonding in the singlet $[CH_2=C–B–C=CH_2]^+$ (D_{2h}).





The doubly-degenerate set of SOMO

The doubly-degenerate set of HOMO–1

Figure 11. a) Bonding analysis for the $C{=}CH_2$ ligands, b) doubly degenerate SOMOs, and the degenerate HOMO–1 orbitals for triplet $[CH_2{=}C{-}B{-}C{=}CH_2]^+$ (D_{2d}).

Table 1. Computed relative energies, B–N distances, Wiberg bond index (WBI) values, natural population analysis (NPA) charges on B, and BLW-derived π-delocalization energies (DE_{π}) for the D_{2d} vs. D_{2h} forms of $[X–B–X]^+$ (X = NH_2 and NF_2) at B3LYP/6-31G(d).

		Relative energy (kcal/mol)	**B–N length (Å)**	**B–N WBI**	**NPA charge on B atom**	**NPA charge on N atom**	**BLW-*DEπ* (kcal/mol)**
$[H_2N–B–NH_2]^+$	D_{2d}	0.00	1.335	1.36	1.24	-1.09	106.6
$[H_2N–B–NH_2]^+$	D_{2h}	14.2	1.344	1.13	1.39	-1.18	96.3
$[F_2N–B–NF_2]^+$	D_{2d}	0.00	1.336	1.34	1.01	0.18	146.5
$[F_2N–B–NF_2]^+$	D_{2h}	31.0	1.360	1.12	1.28	0.05	118.6

Table 2. Computed B–N distances, Wiberg bond index (WBI) values, natural population analysis (NPA) charges on B, and BLW-derived π-delocalization energies (DE_{π}) for $[X–B–X]^+$ (X = $N[C(Me)_3]_2$, NH_2, $N[Si(Me)_3]_2$, $N(CH_3)_2$, $N{=}CH_2$, cyc-$N(CH)_2$).

X		**B–N length (Å)**	**B-N WBI**	**NPA charge on B atom**	**BLW-*DEπ* (kcal/mol)**
$N[C(Me)_3]_2$	C_2	1.348	1.249	1.24	109.8
$N[Si(Me)_3]_2$	C_1	1.339	1.314	1.20	112.9
$N(CH_3)_2$	C_2	1.335	1.290	1.22	121.0
$N{=}CH_2$	D_{2d}	1.306	1.358	1.11	139.2
cyc-$N(CH)_2$	D_{2d}	1.316	1.334	1.03	149.2

Table 3. Computed B–N distances, Wiberg bond index (WBI) values, natural population analysis (NPA) charges on B, and BLW-derived π-delocalization energies (DE_{π}) for $[X–B–X]^+$ (X=CH_3, cyc-C_3H_5, cyc-C_6H_5, CN, CCH, $C{=}CH_2$, COH).

X		**B–C length (Å)**	**B–C WBI**	**NPA charge on B atom**	**BLW-*DEπ* (kcal/mol)**
CH_3	D_{3d}	1.483	1.074	1.38	42.2
cyc-C_3H_5	C_2	1.457	1.108	1.25	60.8
cyc-C_6H_5	D_{2d}	1.462	1.113	1.21	63.7
CN	$D_{\infty h}$	1.445	1.129	1.16	64.5
CCH	$D_{\infty h}$	1.425	1.189	1.11	80.6
$C{=}CH_2$	D_{2h}	1.398	1.471	0.60	135.2
COH	C_2	1.496	0.938	0.72	N/A[b]

[a] Boron center in X = COH is a tetracoordinated boronium.

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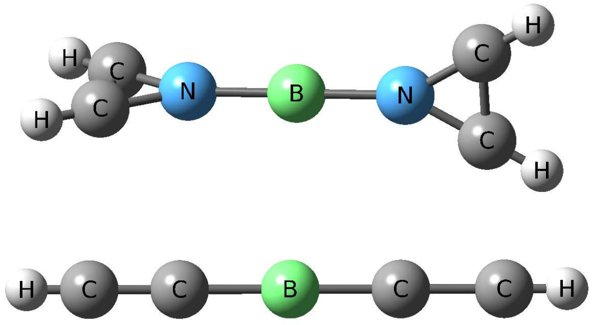

Both π-conjugation and hyperconjugation effects stabilize the substituted borinium cations $[X\text{–}B\text{–}X]^+$. Those with X = cyc-$N(CH)_2$ and X = C=CH_2 should be important synthetic targets.