

IR Spectra of Boron-Stabilized Anions in the Gas Phase

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Action spectroscopy of gaseous Me₃BF⁻ and Me₂BCH₂⁻, determined using IR multiple photon dissociation (IRMPD), exhibits experimental peak positions in good agreement with those predicted by anharmonic DFT calculations at the B3LYP/aug-cc-pVTZ level. Comparing spring constants among boron-carbon bonds and consideration of isoelectronic systems reveals that the anions have B-CH₃ bonds a factor of 1.3-1.4 weaker than those in neutral trimethylboron, suggesting a greater role for hyperconjugation in B(CH₃)₃ than inferred from previous vibrational spectroscopic studies.

Isoelectronic relationships have had a powerful influence on chemical thinking. Trivalent boron stabilizes adjacent negative charges, behaving much like a carbonyl carbon¹ or a carbocation. This report looks at a 4-coordinate borate and a boron-stabilized carbanion to address a longstanding question about hyperconjugation to boron having three ligands.

Trimethylboron, 1, contains unusually strong B-C bonds. Vibrational spectroscopy indicates that adding ammonia to 1 to make the Lewis acid-base complex diminishes the experimental force constant for stretching a B-CH₃ bond only slightly, from 3.69 N/m to 3.53 N/m.² A more detailed analysis compares the force constants for the symmetric BC stretching mode of gaseous 1 with that of the BMe_4^- anion in a crystal (4.10 N/m vs 3.38 N/m).³ The relatively small changes in going from sp^2 to sp^3 boron suggest that the electronegativity difference between carbon and boron may act as the principal determinant of B-CH₃ bond strength, with hyperconjugation playing only a minor role.

Subsequent crystallographic studies by Boese et al.⁴ compared the experimental bond angles in triethylborane with those in the tetraethylborate anion (Et₄B⁻). The 119° C-C-B bond angle in Et₃B diminishes to 116° in the Et₄B⁻

anion. Hence, these authors apportioned the contributions of electronegativity and hyperconjugation more equally. Recent theoretical work estimates the hyperconjugation energy of MeBH₂ to be on the order of 27 kJ mol⁻¹ (nearly half the value for a classical ethyl cation).⁵ Later experiments have measured scalar NMR spin-spin coupling in trimethylboron and its higher homologues,⁶ confirming the significance of hyperconjugation in trialkylboranes.

$$(CH_3)_3 B \xrightarrow{F^-} (CH_3)_3 B F^- \xrightarrow{-HF} (CH_3)_2 B = CH_2^-$$
(1)
1 2 3

The aforementioned comparisons of vibrational force constants are complicated by the necessity of looking at sp^3 boron in condensed phases. Filling the vacant *p*-orbital of boron, either by attaching a nucleophile to it or placing a negative charge on an adjacent center, ought to attenuate boron/ C-H hyperconjugation greatly. The IR spectra of the anions in eq 1 offer insight, displaying a larger difference between sp^2 and sp^3 boron than previously recognized.

Anionic conjugate bases of trialkylboranes have been generated in solution by a variety of approaches, including abstraction of a proton from a neutral precursor by a strong base.^{6,7} The use of sterically hindered substituents allows the production of solid salts of anions stable enough for crystallography.⁷ Available structural and NMR evidence support the inference of the B=C double bond character.

One of the simplest examples, the conjugate base of trimethylboron, $Me_2BCH_2^-$, is unknown in condensed phases but has been previously prepared in the gas phase by electron ionization of trimethylboron, 1, or by its ion-molecule reaction with strongly basic anions.^{8,9} Adherence to the octet rule implies that Me₂BCH₂⁻ and isobutene are isoelectronic. This report presents, for the first time, the IR spectra of the Me₂BCH₂⁻ anion and its precursor ion, fluorotrimethylborate (Me_3BF^- , 2) in the gas phase.

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Figure 1. Experimental IRMPD spectrum of the gaseous fluoro-trimethylborate anion (upper panel) compared with the theoretical spectrum predicted for structure **2** by an unscaled B3LYP/aug-cc-pVTZ anharmonic calculation (lower panel) using harmonic intensities.⁷.

Anion 2, the fluoride adduct of 1 (m/z 75 for the isotope ¹¹B), was formed in the external source of an FT-ICR mass spectrometer by electron ionization of a mixture of 1 and SF₆⁸ then injected into the ICR cell, and isolated by a set of SWIFT ejection pulses to remove other ions.¹⁰ Infrared resonant multiple photon dissociation (IRMPD) of 2 using the free-electron laser FELIX¹¹ leads to expulsion of HF, yielding an m/z 55 anion. Monitoring disappearance of 2 simultaneously with the appearance of m/z 55 as a function of wavelength gives the gas-phase IRMPD spectrum reproduced in the upper panel of Figure 1, which matches the DFT-calculated spectrum¹² in the lower panel.

Theoretical band positions (B3LYP with anharmonic corrections) match those of the experimental IRMPD. The largest discrepancy occurs for the symmetric methyl rock (calculated at 709 and seen at 725 cm⁻¹). The symmetric breathing mode (calculated at 606 and seen at 597 cm⁻¹) has a predicted harmonic intensity 2 orders of magnitude less than is observed. The biggest experimental band corresponds to three closely spaced vibrations with substantial BC stretching character. It is seen near 1000 cm⁻¹, not far from the fundamental of a CO₂ laser.

The question then arises as to the structure of the m/z 55 ion produced by HF loss. Two alternative isomers seem possible: either the product of simple vicinal elimination, Me₂BCH₂⁻ (**3**), or a rearranged structure, MeBCH₂CH₃^{-,13} To probe the structure of gaseous BC₃H₈⁻, ion **2** was stored for several seconds in the ICR and irradiated by the output of a quasi-cw CO₂ laser. Infrared photolysis converts **2** nearly quantitatively via HF loss to the m/z 55 anion, whose IR spectrum was then determined by resonant IR multiple photon electron detachment using the free electron laser.



Figure 2. Experimental IRMPD spectrum of the conjugate base anion of trimethylboron (top panel) compared with spectra calculated for structure **3** (middle panel) and for MeBCH₂CH₃⁻⁻ (bottom panel) using unscaled B3LYP/aug-cc-pVTZ anharmonic calculations with harmonic intensities.⁷.

Frequency-dependent electron detachment from $BC_3H_8^$ was monitored by production of SF_6^- and F^- from electron attachment to traces of SF_6 in the ICR cell, ¹⁴ as well as by disappearance of m/z 55. Figure 2 reproduces the IRMPD spectrum, along with the theoretically predicted spectra of $Me_2BCH_2^-$ ($C_{2\nu}$ symmetry) and of MeBCH₂CH₃⁻ (C_1 symmetry). The absence of strong absorptions between 700 and 1000 cm⁻¹ shows that m/z 55 does not have the MeBCH₂-CH₃⁻ structure. The pronounced band seen near 1440 cm⁻¹ is consistent with predictions for the sp^2-sp^2 B=C bond of the Me₂BCH₂⁻ anion, **3**: a pair of overlapping A_1 bands at 1439 and 1454 cm⁻¹, corresponding to the B=C stretch coupled with three HCH scissor vibrations.

Table 1 lists experimental frequencies for ions 2 and 3 along with assignments based on animation of calculated peaks. Theory gives an excellent fit to the experimental peak positions, the biggest discrepancy being the bands of 3 corresponding to the CBC symmetric stretch coupled with the B=C stretch and methyl umbrella motions. The two A_1 CBC stretches are predicted to be closer together (1260 and 1243 cm⁻¹) than seen experimentally (1292 and 1235 cm⁻¹), even though the antisymmetric combination of methyl umbrella motions (the B_1 mode seen at 1262 cm⁻¹) occurs not far from where it is calculated (1255 cm⁻¹).

Correspondence between experiment and theory warrants the use of DFT (B3LYP/aug-cc-pVTZ, the computational level used to predict the spectra in Figures 1 and 2) to look at the isoelectronic series in Scheme 1. Vibrational spectra of the gaseous cations^{15,16} and neutrals¹⁷ are published. In this series 1 and the carbocations are isoelectronic; anion 2 and

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Table 1. Prominent IR Absorption Bands in the $600-1800 \text{ cm}^{-1}$ Domain Observed in the Experimental Spectra of Fluorotrimethylborate Anion (2) and the Conjugate Base of Trimethylboron (3) in the Gas Phase

(CH ₃) ₃ BF ⁻ (2 , <i>C</i> ₃ symm)		$(CH_3)_2BCH_2^-$ (3 , C_{2v} symm)		
obsd	assignment	obsd	assignment	
1235	CH ₃ umbrella (<i>A</i>)	1437	B=C stretch/HCH scissor (A_1)	
1222	CH_3 umbrella (<i>E</i>)	1292	CBC/B=C stretch/ CH ₃ umbrella (A_1)	
1012	CBC asym stretch (E) and BMe ₃ umbrella (A)	1262	CBC asym stretch/ CH ₃ umbrella (B_2)	
		1235	CBC/B=C stretch/ CH ₃ umbrella (A_1)	
725	Sym CH_3 rock (A)	1045	CBC asym stretch/ CH ₂ in-plane bend (B_2)	
597	Sym breathing (A)	649	CH_3 out-of-plane wag (B_1)	

Scheme 1. Isoelectronic Sequences for Which IR Spectra Are Known

(CH ₃) ₂ X-Y − F ⁻	(CH ₃) ₂ X [₩] F -HF	CH ₃ XY=CH ₂
1, X=B, Y=CH ₃ ^{3,17a}	2, X=B ⁻ , Y=CH ₃	3, X=B ⁻ , Y=CH ₃
4, X=C ⁺ , Y=CH ₃ ¹⁵	5, X=C, Y=CH ₃ ^{17b}	6, X=C, Y=CH ₃
7, X=C ⁺ , Y=F ¹⁶	8, X=C, Y=F ^{17e,f}	9, X=C, Y=F ^{17d}

the neutral, saturated molecules are isoelectronic; and anion **3** and the neutral alkenes are isoelectronic.

Kraka and Cremer¹⁸ have described a method for extracting adiabatic frequencies from vibrational spectra, which isolate the motions of individual bonds. A nearly equivalent approach involves computing Hooke's Law spring constants for a bond by stretching and compressing it by a small amount (0.025 Å) relative to the equilibrium geometry.^{16,19} The Hooke's Law approach does not give force constants identical to those calculated for adiabatic frequencies, because the displacements do not, in general, correspond to a superposition of normal modes (since the center of mass is not constrained to remain stationary in such calculations). Nevertheless, these two approaches do not differ greatly,¹⁹ and Hooke's Law spring constants can more easily be compared among different types of atoms.

Table 2 summarizes DFT results for the isoelectronic series in Scheme 1, compared with experimental stretching force constants, where available, in parentheses. The first two rows summarize the double and single bonds in the unsaturated systems: **3**, isobutene (**6**), and 2-fluoropropene (**9**), respectively. The third row lists results for the trigonal species: **1**, *tert*-butyl cation (**4**), and 2-fluoropropyl cation (**7**). The fourth row lists results for the tetrahedral species.

The spring constant ratios listed in Table 3 provide the focus for the following discussion. The first row of Table 3 compares sp^2-sp^2 double-bond with sp^2-sp^3 single-bond stretches within the same molecule (3 and its isoelectronic alkenes), including theory and experiment for the neutral examples. The calculated ratios all have values close to 2, consistent with the notion that a double bond has twice the strength of a single bond (in accord with X-ray studies that show short B=C distances in boron-stabilized carbanions).⁷

The remaining entries use the corresponding sp^3-sp^3 spring constants for **2**, for 2-fluoro-2-methylpropane (**5**), and for 2,2-difluoropropane (**8**), respectively, as the denominators of the ratios. The second row of Table 3 compares sp^2-sp^3 single

Table 2. Spring Constants Calculated at B3LYP/aug-cc-pVTZ in N/m for Bond Stretches in Species $1-9^a$

	$\begin{array}{l} X = B, \\ Y = CH_3 \end{array}$	$\begin{array}{l} X = C, \\ Y = CH_3 \end{array}$	$\begin{array}{l} X = C, \\ Y = F \end{array}$
$sp^2 - sp^2$ $sp^2 - sp^3$	$k_{\rm B=C} = 5.59$ $k_{\rm BC} = 2.72$	$k_{\rm C=C} = 9.24 \ (8.23^{17c})$ $k_{\rm CC} = 4.26 \ (4.16^{17c})$	$k_{\rm C=C} = 9.55 (8.95^{17\rm d})$ $k_{\rm CC} = 4.58 (5.10^{17\rm d})$
sp^3-sp^3	$k_{\rm BMe} = 3.48$ $k_{\rm MeB} = 2.51$	$k_{\rm CMe} = 4.65$ $k_{\rm MeC} = 3.98$	$k_{\rm CMe} = 4.83$ $k_{\rm MeC} = 4.18 \ (4.19^{17b})$

^{*a*} Values in parentheses summarize reported force constants derived from experimental vibrational spectra. See text for explanation of symbols.

Table 3. Ratios of Spring Constants Calculated at B3LYP/aug-cc-pVTZ^{*a,b*}

	$X = B, Y = CH_3$	$X = C, Y = CH_3$	$\mathbf{X} = \mathbf{C}, \mathbf{Y} = \mathbf{F}$
$\frac{k_{X=C}/k_{XC}}{k_{XC}/k_{MeX}}$ $\frac{k_{X=C}}{k_{MeX}}$ $\frac{k_{XMe}}{k_{XMe}}$	2.06 (3)	2.17 (6 , 1.98 ^c)	2.09 (9, 1.75 ^d)
	1.08 (3 vs 2)	1.07 (6 vs 5)	1.10 (9 vs 8)
	2.23 (3 vs 2)	2.32 (6 vs 5)	2.28 (9 vs 8)
	1.39 (1 vs 2)	1.17 (4 vs 5)	1.16 (7 vs 8)

^{*a*} This work. ^{*b*} Values in parentheses represent ratios of experimental force constants. ^{*c*} From experimentally derived force constants in ref 17c. ^{*d*} From experimentally derived force constants in ref 17d

bonds of the unsaturated systems with the sp^3-sp^3 single bonds of the tetrahedral systems. The sp^2-sp^3 single bonds are tighter than the sp^3-sp^3 bonds, consistent with expectation based on hybridization effects: the greater fraction of *s*-character in the former makes them stiffer. Comparing the unsaturated anion **3** vs the tetrahedral anion **2** gives nearly the same ratio as do comparisons of isobutene (**6**) vs neutral **5** or 2-fluoropropene (**9**) vs neutral **8**.

The third row of Table 3 lists the entries in the first row multiplied by the entries in the second row. The ratio for the double bond in 9 (CH₃CF=CH₂) versus the single bond in 8 ((CH₃)₂CF₂) lies halfway between the ratios for 2 vs 3 and 6 vs 5, with differences on the order of 2%.

An outlying point, $k_{BMe}/k_{MeB} = 1.39$, emerges when the trigonal systems are contrasted. The last row of Table 3 looks at the single bonds in 1 and the isoelectronic carbocations vs the sp^3-sp^3 single bonds in the respective tetrahedral species. The ratio for *tert*-butyl cation (4) vs *tert*-butyl fluoride (5) has a value nearly the same as for cation 7 vs neutral 2,2-difluoropropane (8), but the spring constant for 1 exhibits a much greater value (relative to the corresponding sp^3-sp^3 single bond in the tetrahedral anion) than do the cations or do examples previously discussed.^{2,3}

Gas phase spectroscopy validates the computational level used here. The calculated spring constant ratios exclude effects of solvation, packing forces, or counterions. They indicate that electronegativity and hyperconjugation act together for 1 vs 2 to give a larger ratio than is found in comparing carbocations with saturated neutral molecules.

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Note Added after ASAP Publication. This paper was published on the Web on June 28, 2010, with a misplaced radical in eq 1. The corrected version was reposted on June 30, 2010.

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Supporting Information Available: Anharmonic frequencies computed for 1–3, labeled spectra, and full ref 12. This material is available free of charge via the Internet at http:// pubs.acs.org.