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Chemistry

Calculated ^{11}B–^{13}C NMR chemical shift relationship in hypercoordinate methonium and boronium ions

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ABSTRACT **The boronium-carbonium continuum was extended to include hypercoordinated protonated methanes and their boron analogs. The ^{11}B NMR chemical shifts of the hypercoordinated hydriodo boron compounds and the ^{13}C NMR chemical shifts of the corresponding isoelectronic and isostructural carbocations were calculated by using the GIAO-MP2 method. The data show good linear correlation between ^{11}B and ^{13}C NMR chemical shifts, which indicates that the same factors that determine the chemical shifts of the boron nuclei also govern the chemical shifts of carbon nuclei of these hypercoordinated hydriodo compounds.**

A trivalent carbocation is isoelectronic with the corresponding neutral trivalent boron compounds. Olah *et al.* (1) in 1971 discussed the relationship between $(CH_3)_3C^+$ and $B(CH_3)_3$ based on infrared and Raman spectroscopy. These studies provided unambiguous evidence that the two species possessed analogous structures and bondings. The close relationship between the ^{13}C NMR chemical shifts of the carbons in carbocations and the corresponding ^{11}B NMR chemical shifts of the boron atoms in isoelectronic boron compounds was first shown by Spielvogel and Purser (2, 3) and by Nöth and Wrackmeyer (4). The general correlation equation for trigonal species is shown below.‡

$$\delta^{11}\mathrm{B}(\mathrm{BF_3{:}OEt_2}) = 0.40\ \delta^{13}\mathrm{C}_{(\mathrm{TMS})} - 46. \qquad [1]$$

In Eq. **1**, the δ^{13}C is the chemical shift of the cationic carbon of the carbocation with respect to tetramethylsilane and the δ^{11}B is the chemical shift of the corresponding boron atoms with respect to the BF_3:OEt_2. The empirically derived Eq. **1**, however, is in good agreement with most of the available data that span some 600 ppm on the ^{13}C NMR chemical shift scale. Recently, Prakash *et al.* (5) reported an extension of the relationship to cage compounds.

Williams *et al.* (6) derived a similar empirical Eq. **2** for the hypercoordinate (7) carbocations (carbonium ions) and their corresponding hypercoordinate boron compounds.

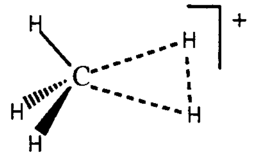
$$\delta^{11}\mathrm{B}(\mathrm{BF_3{:}OEt_2}) = 0.33\ \delta^{13}\mathrm{C}_{(\mathrm{TMS})} - 30. \qquad [2]$$

These relationships show that the same factors that determine the chemical shifts of the boron nuclei also govern the chemical shifts of carbon nuclei. We now extend this boronium-carbonium continuum to hypercoordinated hydriodo boron compounds and their isoelectronic and isostructural carbocations, hitherto not yet observed under long-lived superacidic stable ion conditions, based on GIAO-MP2 calculations.

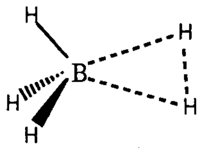
RESULTS AND DISCUSSION

The structures of the hypercoordinate protonated methanes and their boron analogs have been optimized at the MP2/6–31G** level by using the GAUSSIAN-94 (8) package of programs. ^{13}C and ^{11}B NMR chemical shifts were calculated by the correlated GIAO-MP2 method (9, 10) (tzp/dz basis set; refs. 9 and 10) using the ACES II programs (11). ^{13}C NMR chemical shifts are referenced to tetramethylsilane, and ^{11}B NMR chemical shifts are referenced to BF_3:OEt_2.

CH_5^+ and BH_5. CH_5^+ (protonated methane) is considered the parent of nonclassical carbocations containing a five-coordinate carbon atom. The C_s symmetrical structure **1a** with a three-center, two-electron (3c-2e) bond is the preferred ground-state structure for the CH_5^+ (12–16). The isoelectronic boron analog of CH_5^+ is neutral BH_5 and is also C_s symmetrical **1b** based on high-level *ab initio* calculations (17, 18).



CH_5^+, **1a**



BH_5, **1b**

The ^{13}C and ^{11}B NMR chemical shifts of **1a** and **1b** were calculated by using the GIAO-MP2 method (9, 10) (Table 1). Calculation of the ^{13}C and ^{11}B NMR chemical shifts by the correlated GIAO-MP2 method was shown to reproduce well experimental values for carbocations and boron compounds, respectively (19, 20). The calculated δ^{13}C value of **1a** is -11.5, 7.1 ppm more shielded than that of CH_4 ($\delta^{13}C = -4.4$) at the same level of calculations. The experimental δ^{13}C of methane is -2.3. The shielding effect in **1a**, however, is expected for such a hypercoordinate (nonclassical) carbocation (6, 7). Evidence for CH_5^+ in the condensed phase came from hydrogen-deuterium exchange on methane in deuteriated superacids (21, 22) and ESCA studies (G.A.O., unpublished results). Direct NMR spectroscopic observation of the ion was not yet achieved and is difficult because of its expected low concentration and fast exchange in superacids.

The calculated δ^{11}B of **1b** is -28.8. We also estimated the δ^{11}B values in **1b** by applying Eq. **2** and by using the δ^{13}C value of **1a**. This yielded a δ^{11}B value of -33.8 for the neutral boron compound **1b**. The boron chemical shift of -33.8 is reasonably close to the GIAO-MP2 calculated value of -28.8 and thus reconfirms the close relationship between the ^{11}B and ^{13}C chemical shifts of isoelectronic carbon and boron analogs **1a** and **1b**, respectively.

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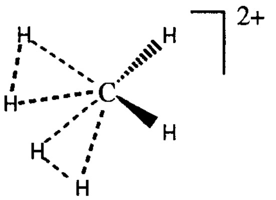
‡This is paper 40 in the series "Chemistry in Superacids." Paper no. 39 is ref. 29.

Table 1. GIAO-MP2/tzp/dz calculated and estimated NMR chemical shifts*

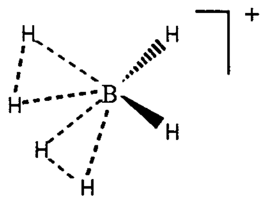
No.	**a**, δ^{13}C (GIAO-MP2)	**b**, δ^{11}B (GIAO-MP2)	**b**, δ^{11}B (estimated)†
1	−11.5	−28.8	−33.8
2	−25.7	−32.4	−38.5
3	−13.0	−35.6	−34.3
4	332.9	62.4	79.8

*Calculated ^{13}C and ^{11}B NMR chemical shifts were referenced to tetramethylsilane and BF_3:OEt_2, respectively.
†Estimated by using Eq. **2**.

CH_6^{2+} and BH_6^+. The calculated parent six-coordinate carbocation, diprotonated methane (CH_6^{2+}), has two two-electron, three-center (2e-3c) bonding interactions in its minimum-energy structure **2a** (C_{2v}) (23, 24). The calculated δ^{13}C value of the dication **2a** is −25.7, 14.2 ppm more shielded than that of five-coordinate monocation CH_5^+ **1a.**



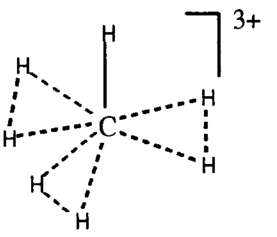
CH_6^{2+}, **2a**



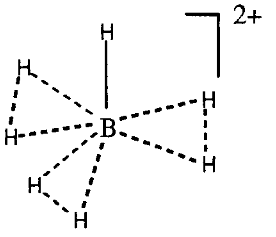
BH_6^+, **2b**

The structure and energetics of the parent hexacoordinate boronium ion BH_6^+ **2b**, isoelectronic with CH_6^{2+} **2a**, recently have been studied (25). The C_{2v} symmetric form **2b** with two three-center, two-electron (3c-2e) bonds was found to be a stable minimum for BH_6^+. Structure **2b** is isostructural with CH_6^{2+} **2a**. Recently, DePuy *et al.* (26) were able to generate the BH_6^+ in the gas phase. We calculated δ^{11}B of **2b** as −32.4, 3.6 ppm more shielded than that of five-coordinate neutral BH_5 **1b**. The estimated δ^{11}B of **2b** obtained from applying Eq. **2** and using a δ^{13}C value of −25.7 for **2a** is −38.5 ppm, close to that of the GIAO-MP2 calculated value of −32.4 ppm.

CH_7^{3+} and BH_7^{2+}. The structures of parent heptacoordinate carbocation (27), CH_7^{3+}, and its isoelectronic boron analog (26), BH_7^{2+}, recently have been reported. The C_{3v} symmetric forms **3a** and **3b** were found to be the stable minima for CH_7^{3+} and BH_7^{2+}, respectively. The ^{13}C and ^{11}B NMR chemical shifts of **3a** and **3b** were calculated. The calculated δ^{13}C of **3a** is −13.0, and the δ^{11}B value of **3b** is −35.6. δ^{11}B for **3b**, estimated by the application of Eq. **2** and by using the δ^{13}C value in **3a** was assessed to be −34.3 ppm, which shielded by only 1.3 ppm more than the GIAO-MP2 calculated value of −35.6 ppm.



CH_7^{3+}, **3a**



BH_7^{2+}, **3b**

CH_4^{2+} and BH_4^+. The planar C_{2v} symmetrical structures containing a three-center, two-electron (3c-2e) bond are preferred for both CH_4^{2+} **4a** (28) and BH_4^+ **4b** (25). The calculated δ^{13}C value of **4a** is 332.9. The estimated δ^{11}B value in **4b** obtained by applying Eq. **2** is 79.8, differing by 17.4 ppm from the GIAO-MP2 values of 62.4.

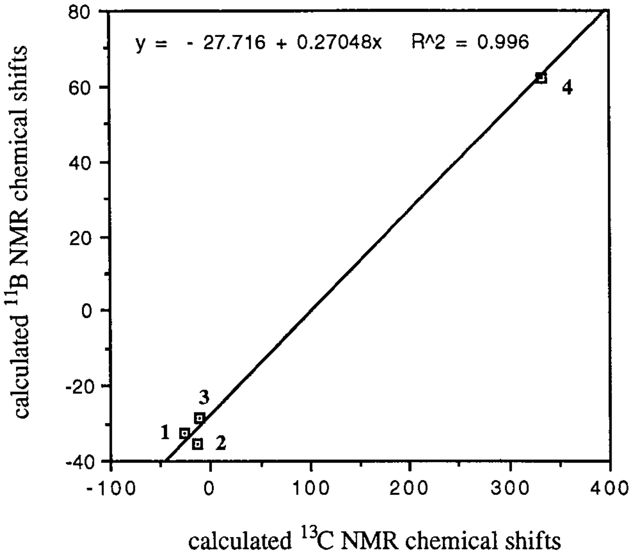
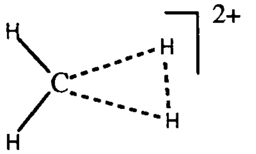
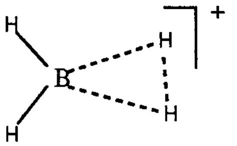


FIG. 1. Calculated ^{13}C NMR chemical shifts vs. calculated ^{11}B NMR chemical shifts of structures **1–4**.



CH_4^{2+}, **4a**



BH_4^+, **4b**

Correlation of ^{13}C and ^{11}B NMR Chemical Shifts. The calculated ^{13}C NMR chemical shifts of studied methonium ions, in general, correlate well with the calculated ^{11}B NMR chemical shifts of the corresponding isoelectronic boron analogs (Fig. 1). This correlation indicates that these small hypercoordinate methonium ions and their boron analogs also follow Eq. **2**, which was derived for their nonclassical systems (6). The correlation line derived from Fig. 1 corresponds closely to the correlation line of Eq. **2**.

In conclusion, we have extended the ^{11}B–^{13}C NMR chemical shift relationship of boronium-carbonium ions to include the parent hypercoordinated methonium ions and their boron analogs. By using the correlated GIAO-MP2 method the ^{11}B NMR chemical shifts of the hydriodo boron compounds and the ^{13}C NMR chemical shifts of their corresponding isoelectronic and isostructural carbonium ions were calculated. The data showed good linear correlation between ^{11}B and ^{13}C NMR chemical shifts. This finding indicates that these small parent carbonium and boronium ions also follow Eq. **2**, derived for the nonclassical systems (6). It seems that the same factors that determine the chemical shifts of the boron nuclei also govern the chemical shifts of the carbon nuclei within the hypercoordinated hydriodo compounds.

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