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# GIAO-MP2/SCF/DFT Calculated NMR Chemical Shift Relationships in Isostructural Onium Ions Containing Hypercoordinate Boron, Carbon, Aluminum, and Silicon Atoms

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Good linear correlations between GIAO-MP2 calculated $^{11}$B NMR chemical shifts of boronium−onium cations **1a−h** and $^{13}$C NMR chemical shift of the corresponding isoelectronic carbonium−onium dications **2a−h** as well as between $^{27}$Al NMR chemical shifts of the alonium−onium cations **3a−h** and the $^{29}$Si NMR chemical shifts of the corresponding isoelectronic siliconium−onium dications **4a−h** were found. The close relationship demonstrates that the same factors that determine the chemical shifts of the boron and aluminum nuclei also govern the chemical shifts of the carbon and silicon nuclei, respectively, within the hypercoordinate onium compounds. On the other hand, no correlation exists between $^{13}$C NMR chemical shifts of carbonium−onium dications **2a−h** and the $^{29}$Si NMR chemical shifts of the corresponding siliconium−onium dications **4a−h**. Furthermore, no correlation was found between $^{11}$B NMR chemical shifts of boronium−onium cations **1a−h** and $^{27}$Al NMR chemical shifts of the corresponding alonium−onium cations **3a−h**.

## Introduction

As boron and carbon are consecutive first-row elements, onium−boronium cations **1** are isoelectronic with the corresponding onium−carbonium dications **2** (Scheme 1). Recently we have been able to show[1] a good boronium−carbonium NMR chemical shift relationship for the carbonium dications $H_4CX^{2+}$ **2** and boronium cations $H_4BX^+$ **1** (X = $NH_3$, $PH_3$, $H_2O$, $H_2S$, CO, $N_2$, HF, HCl, $CO_2$, and $CS_2$), based on ab initio/GIAO-MP2 calculations. The general correlation equation is shown below (equation 1). In this equation $\delta^{13}$C is the chemical shift of the cationic carbon of **2** with respect to $(CH_4)_4Si$ (tetramethylsilane), and $\delta^{11}$B is the chemical shift of the corresponding boron of **1** with respect to the $BF_3{:}O(C_2H_5)_2$.

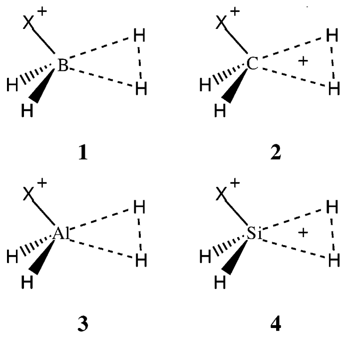
$$\delta^{11}\mathrm{B}_{(\mathrm{BF_3:O(C_2H_5)_2})} = 0.45\,\delta\,^{13}\mathrm{C}_{((\mathrm{CH_4})_4\mathrm{Si})} - 25 \tag{1}$$

Previously, Spielvogel et al.[2] and Nöth and Wrackmeyer[3] have been able to show a close relationship between the experimental $^{13}$C NMR chemical shifts of the carbons in trigonal carbenium ions and the corresponding experimental $^{11}$B NMR chemical shifts of the boron atoms in trigonal isoelectronic boron compounds. The general correlation equation for trigonal species is shown below (equation 2).

$$\delta^{11}\mathrm{B}_{(\mathrm{BF_3:O(C_2H_5)_2})} = 0.40\,\delta\,^{13}\mathrm{C}_{((\mathrm{CH_4})_4\mathrm{Si})} - 25 \tag{2}$$

Prakash et al. reported an extension of the relationship to cage compounds containing trivalent carbon and boron atoms.[4] Williams et al. also derived a similar empirical equation for the hypercoordinate carbocations (carbonium ions) and their corresponding hypercoordinate boron compounds.[5,6] Rasul et al. later derived a similar empirical equation for the hypercoordinate hydrido carbocations and their isoelectronic boron compounds.[7]

### SCHEME 1



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 report our study of the relationship between GIAO-MP2 calculated $^{11}$B NMR chemical shifts of boronium−onium caions **1** and $^{13}$C NMR chemical shift shifts of the corresponding isoelectronic carbonium−onium dications **2** as well as between $^{27}$Al NMR chemical shifts of the alonium−onium cations **3** and the $^{29}$Si NMR chemical shifts of the corresponding isoelectronic siliconium−onium dications **4** (Scheme 1). We also report our study of the relationship between $^{13}$C NMR chemical shifts of carbonium−onium dications **2** and the $^{29}$Si NMR chemical shifts of the corresponding siliconium−onium dications **4** and the correlation between $^{11}$B NMR chemical shifts of boronium−onium cations **1** and $^{27}$Al NMR chemical shifts of the corresponding alonium−onium cations **3**.

## Results and Discussion

The Gaussian 03 program was used for all calculations.[8] The geometry optimizations were performed at the MP2/6-311+G** level. The $^{11}$B, $^{13}$C, $^{27}$Al, and $^{29}$Si NMR chemical shifts were calculated by the GIAO[9]-SCF, GIAO-MP2, and GIAO-DFT methods using the 6-311+G** basis set. The density functional theory (DFT) calculations were carried out at the B3LYP/6-

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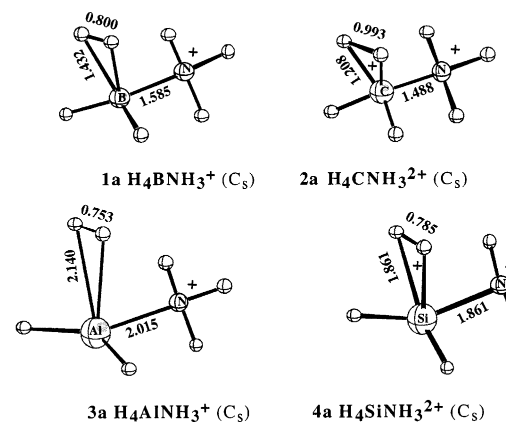

**Figure 1.** MP2/6-311+G** optimized structures of **1**−**4a**.

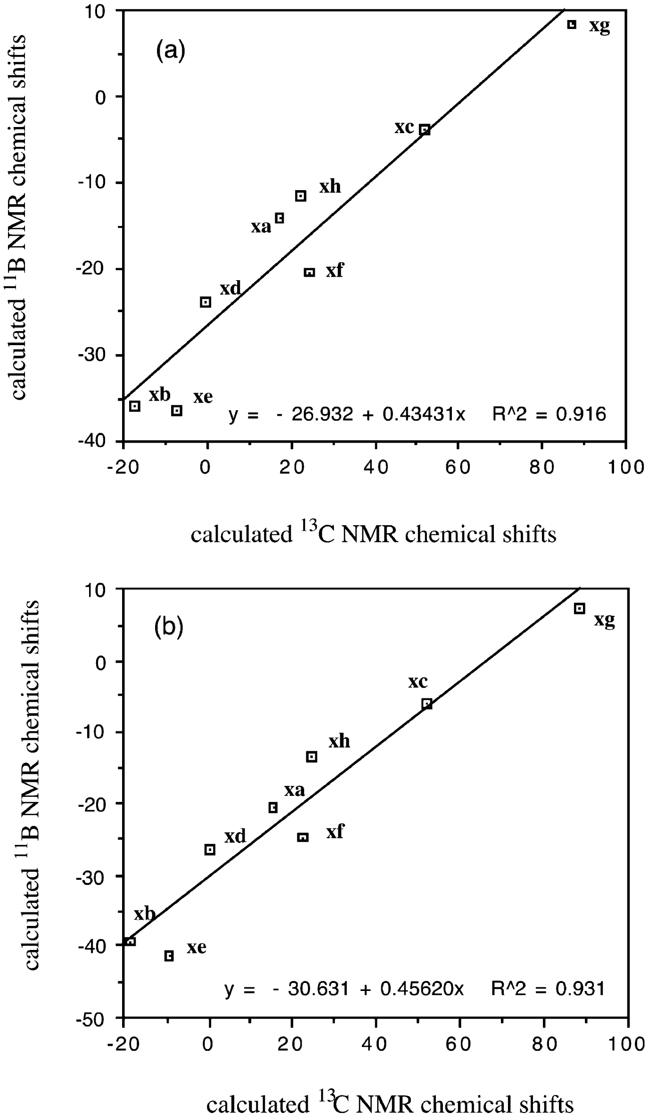

**Figure 2.** GIAO-MP2 (a) and GIAO-DFT (b) calculated $^{13}$C NMR chemical shifts of **2a**−**h** vs calculated $^{11}$B NMR chemical shifts of **1a**−**h**.

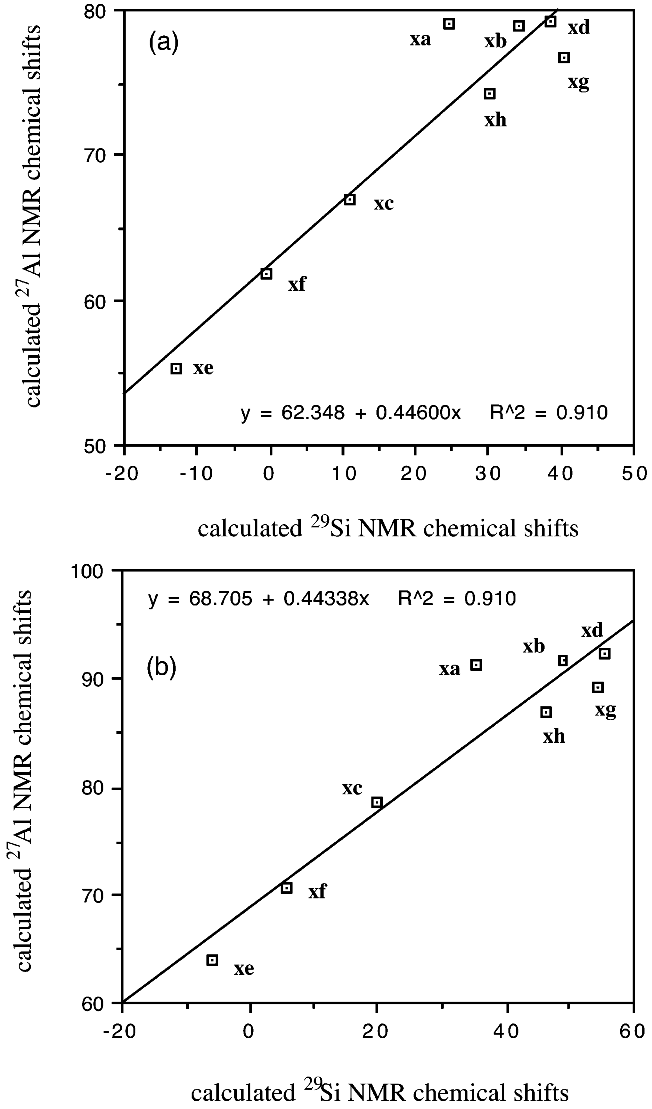

**Figure 3.** GIAO-MP2 (a) and GIAO-DFT (b) calculated $^{29}$Si NMR chemical shifts of **4a**−**h** vs calculated $^{27}$Al NMR chemical shifts of **3a**−**h**.

**TABLE 1: Calculated $^{11}$B NMR Chemical Shifts[a]**

| no. | (GIAO−SCF) | (GIAO-MP2) | (GIAO-DFT) |
|---|---|---|---|
| **1a** | −11.7 | −14.2 | −20.6 |
| **1b** | −28.7 | −36.2 | −39.4 |
| **1c** | 0.2 | −3.9 | −6.1 |
| **1d** | −17.4 | −23.8 | −26.5 |
| **1e** | −29.3 | −36.7 | −41.5 |
| **1f** | −13.9 | −20.4 | −24.7 |
| **1g** | 12.5 | 8.3 | 7.4 |
| **1h** | −5.9 | −11.6 | −13.4 |

[a] Calculated $^{11}$B NMR chemical shifts were referenced to $BF_3$: $O(C_2H_5)_2$.

311+G** level.[10,11] The $^{11}$B NMR chemical shifts were first computed using $B_2H_6$ (calculated absolute shift, i.e., $\sigma$(B) = 102.2 (GIAO−SCF), 96.1 (GIAO-MP2), and 84.1 (GIAO-DFT)). The $^{11}$B NMR chemical shifts were finally referenced to $BF_3$: $O(C_2H_5)_2$ ($\delta$ ($B_2H_6$) 16.6 vs $BF_3$: $O(C_2H_5)_2$). The $^{27}$Al NMR chemical shifts were referenced to $AlH_4^-$ (calculated absolute shifts, i.e., $\sigma$(Al) = 518.3 (GIAO−SCF), 513.4 (GIAO-MP2), and 492.5 (GIAO-DFT)). The $^{29}$Si and $^{13}$C NMR chemical shifts were referenced to $(CH_4)_4Si$ (calculated absolute shifts i.e., $\sigma$(Si) = 396.7 (GIAO−SCF), 379.3 (GIAO-MP2), and 340.8 (GIAO-DFT); $\sigma$(C) = 194.6 (GIAO−SCF), 198.4 (GIAO-MP2), and 184.2 (GIAO-DFT)).

We have previously calculated[12] the structures of $H_4BX^+$ (X = $NH_3$, $PH_3$, $H_2O$, $H_2S$, and CO) at the ab initio MP2/6-31G** level. We have now calculated the structures of $H_4BX^+$ **1a**−**h** at the MP2/6-311+G** level (Scheme 1). Each of the structures

**TABLE 2: Calculated $^{13}$C NMR Chemical Shifts$^a$**

| no. | (GIAO−SCF) | (GIAO-MP2) | (GIAO-DFT) |
|---|---|---|---|
| **2a** | 14.8 | 17.1 | 15.6 |
| **2b** | −18.0 | −17.6 | −18.5 |
| **2c** | 47.8 | 51.7 | 51.7 |
| **2d** | −0.8 | −0.3 | 0.5 |
| **2e** | −8.1 | −7.3 | −9.2 |
| **2f** | 23.5 | 24.2 | 22.7 |
| **2g** | 84.6 | 87.1 | 88.6 |
| **2h** | 22.1 | 22.3 | 24.5 |

[a] Calculated $^{13}$C NMR chemical shifts were referenced to $(CH_4)_4Si$.

**TABLE 3: Calculated $^{27}$Al NMR Chemical Shifts$^a$**

| no. | (GIAO-SCF) | (GIAO-MP2) | (GIAO-DFT) |
|---|---|---|---|
| **3a** | 68.9 | 79.1 | 91.3 |
| **3b** | 70.9 | 79.0 | 91.7 |
| **3c** | 58.4 | 67.0 | 78.5 |
| **3d** | 69.8 | 79.3 | 92.3 |
| **3e** | 50.7 | 55.4 | 64.0 |
| **3f** | 56.4 | 61.9 | 70.8 |
| **3g** | 68.4 | 76.7 | 89.2 |
| **3h** | 65.4 | 74.2 | 86.9 |

[a] Calculated $^{27}$Al NMR chemical shifts were referenced to $AlH_4^-$.

**TABLE 4: Calculated $^{29}$Si NMR Chemical Shifts$^a$**

| no. | (GIAO-SCF) | (GIAO-MP2) | (GIAO-DFT) |
|---|---|---|---|
| **4a** | 23.4 | 24.7 | 35.4 |
| **4b** | 35.8 | 34.1 | 48.7 |
| **4c** | 10.8 | 11.1 | 19.9 |
| **4d** | 36.3 | 38.5 | 55.2 |
| **4e** | −7.7 | −13.0 | −5.7 |
| **4f** | 2.2 | −0.4 | 5.8 |
| **4g** | 38.1 | 40.2 | 54.2 |
| **4h** | 28.1 | 30.3 | 46.0 |

[a] Calculated $^{29}$Si NMR chemical shifts were referenced to $(CH_4)_4Si$.

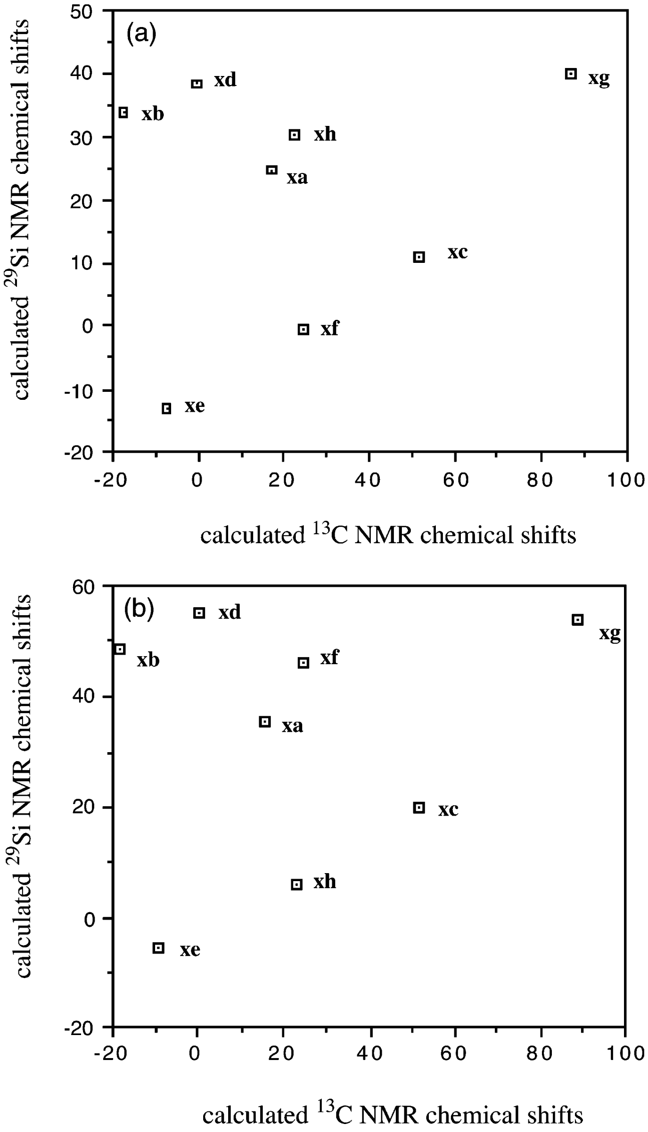

**Figure 4.** GIAO-MP2 (a) and GIAO-DFT (b) calculated $^{13}$C NMR chemical shifts of **2a**−**h** vs calculated $^{29}$Si NMR chemical shifts of **4a**−**h**.

contains a hypercoordinate boron with a 2e−3c bond and a onium ion group X and therefore can be considered as a boronium−onium cation. Corresponding isoelectronic carbon analogues $H_4CX^{2+}$ **2a**−**h** were also calculated at the same MP2/6-311+G** level. Each of the structures contains a hypercoordinate carbon with a 2e−3c bond and an onium ion group X and can be considered as a carbonium−onium dication. Similarly, the structures of $H_4AlX^+$ **3a**−**h** and isoelectronic silicon analogues $H_4SiX^{2+}$ **4a**−**h** were also calculated at the MP2/6-311+G** level and can be considered as alonium−onium cations and siliconium−onium dications, respectively. Computed selected structures are displayed in Figure 1.

We have calculated the $^{11}$B, $^{13}$C, $^{27}$Al, and $^{29}$Si NMR chemical shifts of **1**−**4** using the correlated GIAO-MP2 method with the 6-311+G** basis set and using MP2/6-311+G** geometries (Tables 1−4). For comparison we have also computed the chemical shifts using noncorrelated GIAO-SCF and density functional theory GIAO-DFT methods, and these are listed in Tables 1−4. The GIAO-MP2 method has been shown to give very good results for $^{11}$B NMR chemical shift calculations in $H_3BX$ (X = $NH_3$, $PH_3$, $H_2O$, $H_2S$, and CO) complexes.[12] The GIAO-MP2 method has also given reliable results for $^{13}$C, $^{27}$Al, and $^{29}$Si NMR chemical shift calculations.[13−15]

We have found a good linear correlation when we plotted (Figure 2a) GIAO-MP2 calculated $^{11}$B NMR chemical shifts of boronium−onium cations **1a**−**h** and the GIAO-MP2 calculated $^{13}$C NMR chemical shifts of the corresponding isoelectronic carbonium−onium dications **2a**−**h**. Similar linear correlation was also obtained from GIAO-DFT calculated values (Figure 2b). We have also found a good linear relationship (Figure 3a) between GIAO-MP2 calculated $^{27}$Al NMR chemical shifts of the alonium−onium cations **3a**−**h** and the GIAO-MP2 calculated $^{29}$Si NMR chemical shifts of the corresponding isoelectronic siliconium−onium dications **4a**−**h**. Good linear correlation was also obtained from GIAO-DFT calculated values (Figure 3b). The close relationship demonstrates that the same factors that determine the chemical shifts of the boron and aluminum nuclei also govern the chemical shifts of the carbon and silicon nuclei, respectively, within the hypercoordinate onium compounds. The correlation line (3) derived from Figure 2a closely corresponds to the correlation line (1).

$$\delta^{11}B_{(BF_3:O(C_2H_5)_2)} = 0.43\,\delta\,^{13}C_{((CH_4)_4Si)} - 27 \qquad (3)$$

The correlation line (4) derived from Figure 3a is given below.

$$\delta^{11}A1_{(A1H_4^-)} = 0.45\,\delta\,^{13}Si_{((CH_4)_4Si)} + 62 \qquad (4)$$

We have plotted (Figure 4a) GIAO-MP2 calculated $^{11}$B NMR chemical shifts of boronium−onium cations **1a**−**h** and the GIAO-MP2 calculated $^{27}$Al NMR chemical shifts of the

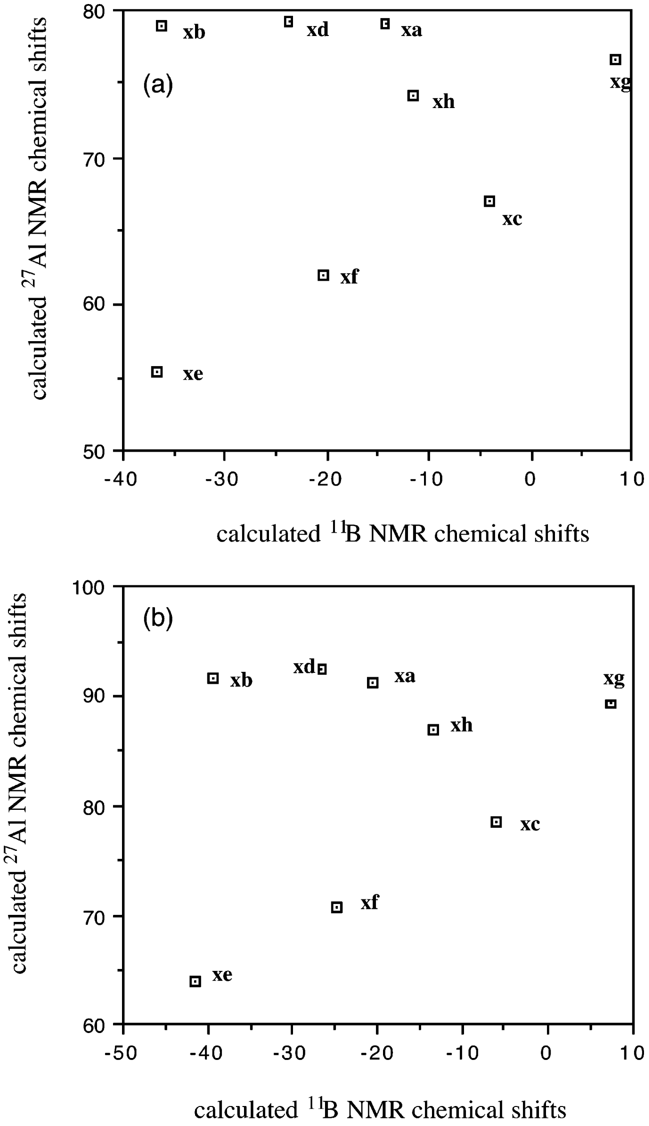

**Figure 5.** GIAO-MP2 (a) and GIAO-DFT (b) calculated $^{11}$B NMR chemical shifts of **1a**−**h** vs calculated $^{27}$Al NMR chemical shifts of **3a**−**h**.

corresponding alonium−onium cations **3a**−**h**. There is no apparent correlation between $^{11}$B and $^{27}$Al NMR chemical shifts. We have also plotted (Figure 5a) GIAO-MP2 calculated $^{13}$C NMR chemical shifts of carbonium−onium dications **2a**−**h** and the GIAO-MP2 calculated $^{29}$Si NMR chemical shifts of the corresponding siliconium−onium dications **4a**−**h**. Again, there is no correlation between $^{13}$C and $^{29}$Si NMR chemical shifts.

It appears that only the NMR chemical shifts of isoelectronic analogues correlate well within the isostructural hypercoordinate onium compounds. Therefore, $^{11}$B NMR chemical shifts of **1a**−**h** correlate well with the $^{13}$C NMR chemical shifts of the corresponding isoelectronic and isostructural **2a**−**h** as the boron and carbon are the consecutive first row elements. However, $^{13}$C NMR chemical shifts of the **2a**−**h** do not correlate with the $^{29}$Si NMR chemical shifts of the isostructural **4a**−**h**, although the carbon and silicon are consecutive group IV elements.

## Conclusion

In summary, we have found good linear correlation between GIAO-MP2 calculated $^{11}$B NMR chemical shifts of boronium−onium cations **1a**−**h** and $^{13}$C NMR chemical shift shifts of the corresponding isoelectronic carbonium−onium dications **2a**−**h** as well as between $^{27}$Al NMR chemical shifts of the alonium−onium cations **3a**−**h** and the $^{29}$Si NMR chemical shifts of the corresponding isoelectronic siliconium−onium dications **4a**−**h**. The close relationship demonstrates that the same factors that determine the chemical shifts of the boron and aluminum nuclei also govern the chemical shifts of the carbon and silicon nuclei, respectively, within the isostructural hypercoordinate onium compounds. There is, however, no correlation found when $^{13}$C NMR chemical shifts of carbonium−onium dications **2a**−**h** were plotted against the $^{29}$Si NMR chemical shifts of the corresponding siliconium−onium dications **4a**−**h**. There is also no correlation observed between $^{11}$B NMR chemical shifts of boronium−onium cations **1a**−**h** and $^{27}$Al NMR chemical shifts of the corresponding alonium−onium cations **3a**−**h**.

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## References and Notes

(1) Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 9635.

(2) Spielvogel, B. F.; Nutt, W. R.; Izydore, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 7, 1609.

(3) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3089.

(4) Prakash, G. K. S.; Rasul, G.; Yudin, A. K.; Williams, R. E. In *Borane, Carborane, Carbocation Continuum*; Casanova, J., Ed.; Wiley-Interscience: New York, 1998; Ch. 8, p 147.

(5) Williams, R. E.; Prakash, G. K. S.; Field, L. D.; Olah, G. A. In *Advances in Boron and Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; pp 191−224.

(6) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. In *Hypercarbon Chemistry*; John Wiley & Sons: New York, 1987; pp 191−213.

(7) Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 7257.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Hona, Y.; Kitao, K.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03 (revision B.04), Gaussian, Inc.: Pittsburgh, PA, 2003.

(9) London, F. J. *Phys. Radium* **1937**, *8*, 3974. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. Wolinski, K.; Himton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(12) Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Inorg. Chem.* **1999**, *38*, 44.

(13) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629. Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987.

(14) Gauss, J.; Schneider, U.; Ahlrichs, R.; Dohmeier, C.; Schnöckel, H. *J. Am. Chem. Soc.* **1993**, *115*, 2402.

(15) Ottosson, C.-H.; Cremer, D. *Organometallics* **1996**, *15*, 5495.