Heteroatom Chemistry
Volume 3, Number 3, 1992

The Correlation of ^{11}B NMR *ASIS* Effects with MO-derived Charge Densities for *Closo*-$C_2B_5H_7$ and Some Chloro Derivatives

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Received 22 November 1991.

ABSTRACT

Aromatic-solvent-induced ^{11}B NMR shifts (^{11}B ASIS *effects), observed for closo-2,4-$C_2B_5H_7$ and its 5-chloro and 5,6-dichloro derivatives, are correlated to* ab initio *STO-3G derived atom charge densities. A near linear relationship is found upon incorporating nearest-neighbor charge density contributions.*

INTRODUCTION

Protons that are located at positive ends of dipolar solute molecules have been observed to shift upfield in the PMR spectrum upon using benzene as the solvent [1–3]. Consistent with this observation, downfield shifts are observed for protons located at, or near, the negative portion of these dipolar solutes. These aromatic solvent induced shifts (*ASIS*) have been attributed to small perturbations from random orientations of a solvent-solute mixture in which a collision complex favors a benzene π-cloud facing the positive end of the solute dipole, while the peripheral edge of the benzene molecule tends to orient alongside the more negatively charged end of the dipole. A combination of ring-current and local atomic anisotropic effects [4] probably accounts for most, or all, of the observed *ASIS* shifts. *ASIS* effects have been observed for protons in cluster boron compounds [5, 61] and quantitatively correlated to MO-derived hydrogen charges [7]. Also, solvent effects on ^{11}B NMR shifts of some metallaboranes and metallacarboranes [8] as well as on decaborane(14) [91] have been previously noted. As cited below, we report ^{11}B *ASIS* effects for *closo*-2,4-$C_2B_5H_7$ and its 5-chloro and 5,6-dichloro derivatives, Figure 1. We have recently carried out *ab initio* STO-3G calculations on these three molecules, and it was of interest to see if the benzene induced ^{11}B NMR shifts could be correlated to MO-derived atom charges.

EXPERIMENTAL AND DATA

Materials:

The parent *closo*-2,4-$C_2B_5H_7$ was obtained from R.E. Williams and used without further purification. Its 5-chloro and 5, 6–dichloro derivatives were prepared according to literature procedures [10-15].

Nuclear Magnetic Resonance:

Boron-11 spectra were recorded on both a Bruker AM-400 instrument at CSULA and a Bruker WM-500 instrument at California Institute of Technology. The boron-11 chemical shift assignments to individual nuclei have been well established for all of the carboranes in this study [10–16].

ASIS *Data:*

A 10-mole% solution of carborane in perdeuterated benzene or carbon tetrachloride was sealed in a 3-mm glass tube. Both proton decoupled, and undecoupled, ^{11}B NMR spectra were obtained at 25°C.

Dedicated to Professor Herbert C. Brown on the occasion of his eightieth birthday.

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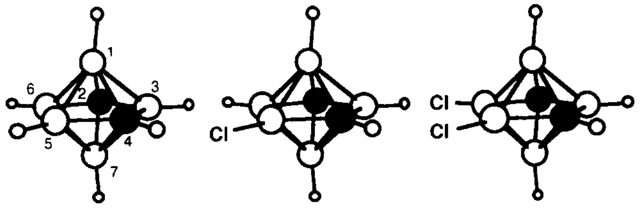

FIGURE 1 Structures of 2,4-$C_2B_5H_7$, 5-Cl-2,4-$C_2B_5H_6$ and 5,6-Cl_2-2,4-$C_2B_5H_5$.

The chemical shift measurements were repeated no less than three times for each sample; and, by averaging the results, an error no greater than 0.01 ppm is indicated for the difference in chemical shifts between any two nuclei in the same molecule in any cited solvent environment, Table 1.

Charge Density Assignments:

Atom charge densities for the compounds in this study were derived from *ab initio* (Gaussian [17]) STO-3G optimization calculations, the results of which are given in Table 2. Each compound optimized to a vibrationally stable entity having the pentagonal bipyramidal cage geometry, and the appropriate symmetry, expected for each compound. It should be mentioned that *ab initio* calculations have been previously carried out [18, 19] on two of the compounds mentioned in this study, but the atom charge densities were not reported.

RESULTS AND DISCUSSION

The ^{11}B *ASIS* effects observed for *closo*-2,4-$C_2B_5H_7$ and its 5-chloro and 5,6-dichloro derivatives (Table 1) are small but measurable, and, for greater accuracy, they are internally referenced. Consequently, the differences in $\delta_{\text{boron-11}}$ shifts, $\Delta\delta$, within the same molecule (in the same solvent) are reported rather than the individual $\delta_{\text{boron-11}}$ shifts themselves. Furthermore, the change in $\Delta\delta$ as the solvent is changed is expressed as $\Delta\Delta\delta$. For example, the chemical-shift-difference, $\Delta\delta$, between the B(3) and B(6) boron resonances in 5-Cl-2,4-$C_2B_5H_6$ changes from a value of 3.78 ppm in benzene to a value of 4.13 ppm in carbon tetrachloride; this results in a $\Delta\Delta\delta$ of −0.35 ppm for $[\delta_{B(3)}\text{-}\delta_{B(6)}]C_6D_6\text{-}[\delta_{B(3)}\text{-}\delta_{B(6)}]CCl_4$. See Table 3 for a compilation of $\Delta\Delta\delta$ values for the three compounds.

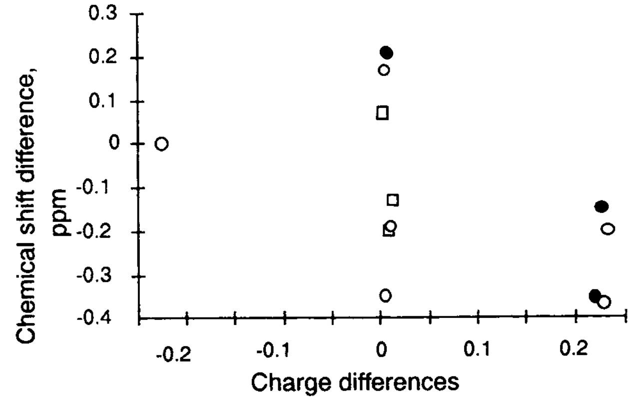

FIGURE 2 Plot of Gaussian STO-3G generated charge density differences, ΔQ, versus ^{11}B chemical shift differences, $\Delta\Delta\delta$, •=5,6-Cl_2-2,4-$C_2B_5H_5$, ○=5-Cl-2,4-$C_2B_5H_6$, □ =2,4-$C_2B_5H_7$.

For those measurements made in benzene as the solvent, it is obvious that the primary attraction, or repulsion, of the benzene π-cloud will be at the surface atoms of the carborane cages; and this in turn could influence the NMR chemical shifts of the carborane. The question then arises: can a simple relationship between ΔQ (Q = atom charge density, Table 2) and $\Delta\Delta\delta$ (aromatic solvent induced shifts, *ASIS*) (see Tables 1 and 3) be found? A plot, Figure 2, of ΔQ against $\Delta\Delta\delta$ for the compounds reported here shows essentially no evidence of a linear, or any other elementary relationship. A more reasonable approach, developed for proton shifts earlier [7], brings into play the effect of neighboring atoms at the surface of the cage molecule. In a simple "nearest-neighbor" approach, an effective charge density ΔQ_e difference, Table 3 can be defined by the relationship $\Delta Q_e = \Delta(Q_p + k\Sigma Q_n)$ where Q_p is the primary charge density on the surface atom attached to the boron under consideration, and Q_n is the charge density on a "nearest-neighbor" surface atom (or on the immediately attached boron atom), and k is

TABLE 1 Solvent Induced Chemical Shift Differences Between Boron-11 Nuclei

Compd	*Solvent*	*Δδ (Chemical Shift Differences; B(x) − B(y))*[a]					
		(1)-(3)	*(1)-(5)*	*(3)-(5)*	*(1)-(6)*	*(3)-(6)*	*(5)-(6)*
5,6-Cl_2-2,4-$C_2B_5H_5$	C_6D_6	−20.23	−29.08	−8.85	−29.08	−8.85	0.00
5,6-Cl_2-2,4-$C_2B_5H_5$	CCl_4	−20.44	−28.93	−8.50	−28.93	−8.50	0.00
5-Cl-2,4-$C_2B_5H_6$	C_6D_6	−24.98	−34.01	−9.03	−21.21	3.78	12.77
5-Cl-2,4-$C_2B_5H_6$	CCl_4	−25.15	−33.81	−8.66	−21.02	4.13	12.77
2,4-$C_2B_5H_7$	C_6D_6	−28.63	−25.67	2.96	−25.67	2.96	0.00
2,4-$C_2B_5H_7$	CCl_4	−28.70	−25.54	3.16	−25.54	3.16	0.00

[a] e.g., δ(B1) − δ(B3)

TABLE 2 Atom Charges Densities, Q, on *Closo*-$C_2B_5H_7$ and 5-Cl- and 5,6-Cl_2- Derivatives, as Generated from Gaussian STO-3G Calculations

Compd	*B(1)*	*C(2)*	*B(3)*	*C(4)*	*B(5)*	*B(6)*	*B(7)*
5,6-Cl_2-2,4-$C_2B_5H_5$	0.150	−0.275	0.167	−0.275	0.169	0.169	0.150
5-Cl-2,4-$C_2B_5H_6$	0.141	−0.274	0.160	−0.276	0.163	0.051	0.141
2,4-$C_2B_5H_7$	0.132	−0.275	0.152	−0.275	0.043	0.043	0.132
	H(1)	H(2)	H(3)	H(4)	H or Cl(5)	H or Cl(6)	H(7)
5,6-Cl_2-2,4-$C_2B_5H_5$	−0.011	0.131	−0.018	0.131	−0.239	−0.239	−0.011
5-Cl-2 4-$C_2B_5H_6$	−0.020	0.119	−0.025	0.124	−0.255	−0.031	−0.020
2,4-$C_2B_5H_7$	−0.029	0.112	−0.033	0.112	−0.042	−0.042	−0.029

some fraction that is obviously somewhere between the values of zero and one. A value of zero for *k* would indicate that neighboring effects are absent, an assumption that does not seem reasonable. A value of 1.0 (or more) for *k* implies that the neighboring atom charge density effect is equal, or greater, than the primary atom charge density effect, again an unreasonable assumption. Earlier, when *ASIS* effects were correlated to atom charges for polyborane *proton* shifts, a value of 0.3 for *k* gave the best linear fit to the data [7]. When this same value for *k* was used in the present boron-11 shift study, a significantly better linear relationship of charge-density/solvent shifts was observed than when a value of zero was used; however, a better fit was obtained when a *k* value of 0.5 was employed throughout for all the compounds, Figure 3.

The implication that the contribution of neighboring charges is slightly more important for boron *ASIS* shifts than for proton *ASIS* shifts is not unreasonable from geometry considerations of these cage systems. Each boron atom is farther from the surface of the cage than is each hydrogen; thus, the distance between a boron nucleus and a solvent molecule which is located next to a *contiguous* (surface) X-B (X = H or Cl) atom is not dramatically different than the distance between the same boron and a solvent molecule located next to a *neighboring* surface atom (i.e., nearest neighbor proton or chlorine to the B-X group under scrutiny). By way of contrast, the distance between a cage-surface proton and an immediately adjacent solvent molecule would be considerably smaller than the distance between that same cage-surface proton and a solvent molecule interacting strongly with a *neighboring* cage-surface proton. Put in another way, the solvent-to-solvent viewing angle of the (interior) boron atoms is expected to be considerably less than the corresponding solvent-to-solvent viewing angle of the (surface) protons [20].

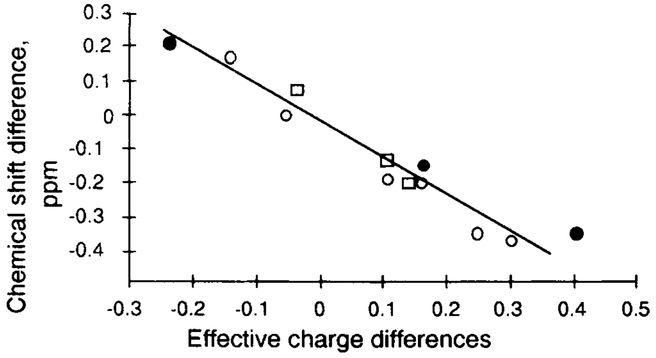

FIGURE 3 Plot of "effective" charge density differences, ΔQ_e, versus ^{11}B chemical shift differences, $\Delta\Delta\delta$, ●=5,6-Cl_2-2,4-$C_2B_5H_5$, ○=5-Cl-2,4-$C_2B_5H_6$, ☐ =2,4-$C_2B_5H_7$. ΔQ_e is based on $k = 0.5$ for nearest neighbor effects, see text.

ACKNOWLEDGMENTS

The authors wish to thank the NSF, CHE-8922339, for partial support of this project. S.G. thanks the NIH-MBRS for partial support. Boron-11 spectra were recorded on both a Bruker WM-500 instrument at California Institute of Technology and a Bruker AM-400 instrument at CSULA funded by

TABLE 3 Effective Charge Density Differences, ΔQ_e versus Chemical Shift Differences, $\Delta\Delta\delta$, for *Closo*-$C_2B_5H_7$ and Its 5-Cl- and 5,6-Cl_2- Derivatives

Compd	*Surface Atom Positions*	ΔQ_e[a]	$\Delta\Delta\delta$[b] *ppm*
5,6-Cl_2-$C_2B_5H_5$	(1)-(3)	−0.238	0.21
	(1)-(5)	0.166	−0.15
	(3)-(5)	0.405	−0.35
5-Cl-2,4-$C_2B_5H_6$	(1)-(3)	−0.140	0.17
	(1)-(5)	0.163	−0.20
	(3)-(5)	0.303	−0.37
	(1)-(6)	0.110	−0.19
	(3)-(6)	0.250	−0.35
	(5)-(6)	−0.053	0.00
$C_2B_5H_7$	(1)-(3)	−0.035	0.07
	(1)-(5)	0.105	−0.13
	(3)-(5)	0.140	−0.20

[a] $\Delta Q_e = \Delta(Q_p + k\Sigma Q_n)$; $k = 0.5$ (see text).
[b] e.g., the chemical shift difference for the first row: $[\delta_{B(1)} - \delta_{B(3)}]C_6D_6 - [\delta_{B(1)} - \delta_{B(3)}]CCl_4$; etc.

NIH grant RR-08101-13S1, by NSF grant DMB-8503839, and by the Keck and Dreyfus Foundations. We also thank California State University, Sacramento, CA, for access to the Multiflow Trace (NSF Grant CHE-8822716) minisupercomputer facilities and San Diego State University for access to the San Diego Supercomputer Regional Facility.

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