Aromatic Solvent Induced Nuclear Magnetic Resonance Shift (ASIS) Behavior and Charge Distribution in Cage Boron Compounds

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Abstract: The first quantitative relationship between MO-derived hydrogen charges and aromatic solvent induced ^1H NMR chemical shifts (ASIS effect) is derived. In a study of various cage polyboron hydride and carborane hydrogens an upfield ^1H NMR shift follows the general order $HC > H_\mu B > H_t B$ when benzene is used as the solvent; the same order is followed for the downfield shift of these same hydrogens when hexafluorobenzene is used as the solvent. An ASIS-derived charge has been developed which takes into consideration nearest neighbor cage-hydrogen effects on the observed chemical shift change.

Introduction

Protons located at the positive ends of dipolar solute molecules have often been observed to shift upfield in the NMR when benzene is used as the solvent.[1-6] Downfield shifts have also been noted in the same solvent for protons located at, or near, the negative portion of these dipolar solutes. Shifts directed to opposite fields of those observed in benzene are found for the same solute protons when C_6F_6 is used as the solvent. These aromatic solvent induced shift (ASIS) phenomena have been rationalized by considering small perturbations from random orientations of a solvent–solute mixture in favor of collision complexes in which the electron π-cloud of C_6H_6 faces 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. Either ring-current effects or local atomic anisotropies, more likely a combination of both,[7] associated with the solvent are thought responsible for most, or all, of the ASIS shifts observed in the solute molecule. The strong polarity of the CF bonds in C_6F_6 results in a considerably diminished π-cloud electron density for the C_6 ring which could account for the reversal of solute ^1H NMR shifts in this solvent.

At least three factors are involved in promoting a preferred orientation of aromatic solvents about a given solute: (a) extent of solute structural rigidity, (b) a comparable size of solute and solvent molecules, and (c) the geometrically fixed group contributions to the solute dipole.[3,4] The parent small carboranes 1,6-$C_2B_4H_6$, 2,3-$C_2B_4H_8$, and 2,4-$C_2B_5H_7$ and the common polyboranes, B_5H_9 and $B_{10}H_{14}$ (Figure 1) all have rigid frameworks[8] containing 5–10 cage atoms and thus appear to satisfy points (a) and (b). Except for 1,6-$C_2B_4H_6$, the remaining molecules either exhibit[9-11] or are expected to show,[12] net molecular dipoles conforming to point (c); 1,6-$C_2B_4H_6$, of course, contains only bond dipoles.[13] Also, it should be mentioned that only with these five cage boron compounds are both of the following two requisite points satisfied: (a) all ^1H shifts are unambiguously known and (b) the charges are all derived from the same recent molecular orbital approach (see below). With these thoughts in mind the following study was undertaken to examine possible quantitative correlations between aromatic solvent induced shifts and charge concentrations in these boron containing cage compounds. It should be pointed out, though, that in the case of B_5H_9[14] and $B_{10}H_{14}$[15] ASIS effects have been previously observed but not quantitatively correlated with charge.

Experimental Section and Data Sources

Materials. The carboranes were prepared and purified as described earlier[16,17] and both pentaborane and decaborane were obtained from Callery Chemical Co. and K & K Laboratories, respectively.

ASIS Data. NMR samples were prepared using standard high-vacuum techniques; into a 4-mm tube was introduced 0.2 mmol of boron compound, 2.0 mmol of solvent (benzene, hexafluorobenzene, or cyclohexane) and 0.05 mmol of tetramethylsilane; the sample was sealed to protect the boron compound from moisture and oxygen. Undecoupled proton magnetic resonance spectra were obtained both on Varian A-60 and HA-100 spectrometers. ^{11}B decoupled proton spectra were also taken for every compound in all three solvents (in some instances deuterated benzene and cyclohexane were used) in a manner described earlier.[18] The sharpness of the decoupled peaks, when not overlapped with other resonances, allows for an error within ±0.02 ppm (±2 Hz on the 100 MHz instrument). All peaks were measured relative to internal TMS (τ = 10.00); and the aromatic solvent induced shifts, $\Delta\tau_{BC}$ and $\Delta\tau_{HC}$ (B = benzene, H = hexafluorobenzene, C = cyclohexane; $\Delta\tau_{BC} = \tau_B - \tau_C$ and $\Delta\tau_{HC} = \tau_H - \tau_C$), for each solute hydrogen are cited relative to the same hydrogen resonances when cyclohexane is used as the solvent (Table I, columns 2–3).

^1H NMR Assignments. Because the MO charge assignments (Table I, column 5) are for specific hydrogen sites within each cage molecule it is essential to establish beyond a doubt that the corresponding ^1H NMR assignments are correct. For 1,6-$C_2B_4H_6$[18] and B_5H_9[14] no problem is presented in the proton shift assignments because of the nature of nuclear coupling and observed peak areas. For the remaining three compounds, 2,3-$C_2B_4H_8$, 2,4-$C_2B_5H_7$, and $B_{10}H_{14}$, area equivalencies make it more difficult to sort out all the individual B–H terminal hydrogens on this simple basis. Fortunately, selective decoupling experiments allow definitive assignments to be made for 2,3-$C_2B_4H_8$,[16,19] and for 2,4-$C_2B_5H_7$, selective deuteration of 1,7- and 5,6- boron pairs along with microwave structural studies has allowed unambiguous proton assignments to be made for this *closo*-carborane.[18,20] Also, selective deuterium placement in $B_{10}H_{14}$ permitted a final assignment to an otherwise complicated spectrum.[15,21] The proton chemical shifts observed for all of the five cage compounds (without an aromatic solvent) as reported in the above cited references do not differ significantly from those measured in our work (τ_C, Table I, column 1) in which we used cyclohexane (and perdeuteriocyclohexane in some cases) as the nonaromatic reference solvent.

Charge Assignments. Charge distributions, Q, within the cage boron compounds used in this study were obtained from ab initio minimum basis set molecular orbital calculations. The values for the hydrogen atoms are listed (column 5) along with the references in Table I. Unfortunately, the number of significant figures for available values of Q varies from one to three, and so it is presumed that correlations made within the present work certainly do not warrant confidence beyond two figure significance.

Results and Discussion

Significant ASIS effects in the ^1H NMR spectra are observed for each of the cage boron compounds studied (Table I, columns 2 and 3). With each polyhedral compound the highest observed upfield shift value ($\Delta\tau_{BC}$) when using benzene as the solvent is accompanied by the greatest downfield (or

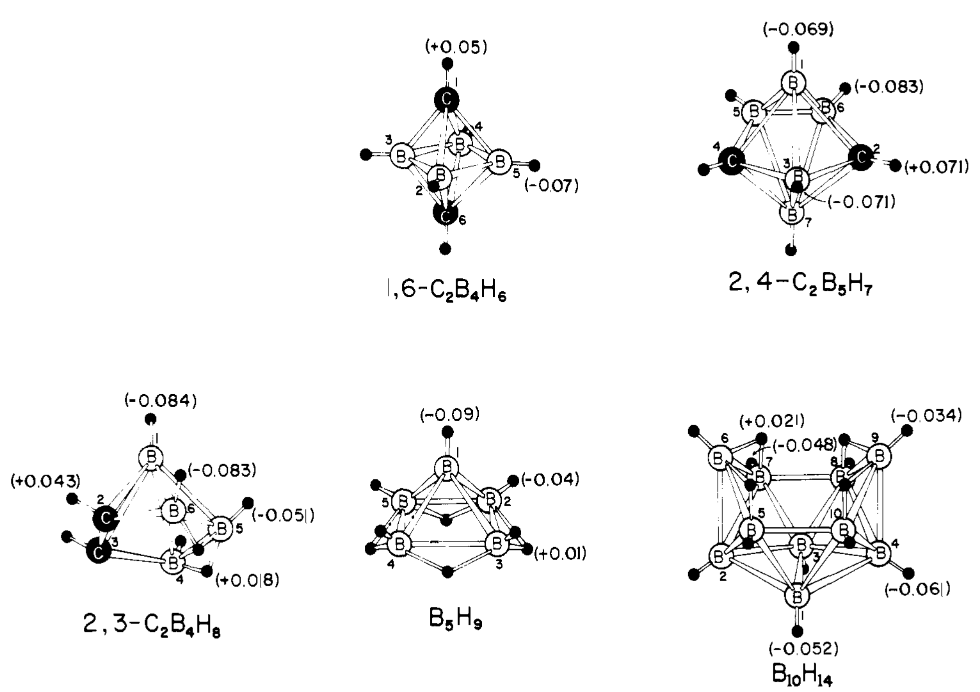

Figure 1. Ball and stick structures for the polyhedral boranes in this study; hydrogen charges, obtained from MO calculations (see text and table), are given in parentheses.

lowest upfield) shift ($\Delta\tau_{HC}$) for the same proton when C_6F_6 is used as the solvent. This extends to a general trend (Figure 2) in which an inverse linear relationship,

$$\Delta\tau_{BC} = -1.12(\Delta\tau_{HC}) + 18.5 \qquad (r = 0.91) \qquad (1)$$

can be derived when comparing data in the two separate solvents.

More specifically, upfield proton shifts for each boron compound in benzene follow the order H-C > H_μ-B > H_t-B with the reverse order being observed when C_6F_6 is the solvent. This is in qualitative agreement with preferred solvent orientations reckoned from calculated charge distributions (see Introduction) within the cage compounds. In those compounds with more than one kind of H_t-B proton the solvent-induced shifts also tend to conform to the trends in MO charge distributions (column 5) found for the various terminal hydrogens. Overall then, it can be seen that with minor exceptions reasonably good qualitative agreement exists between hydrogen charge distributions and ASIS effects in these cage compounds. Not unexpectedly, there is generally better agreement within a given polyborane than when comparisons are made between compounds.

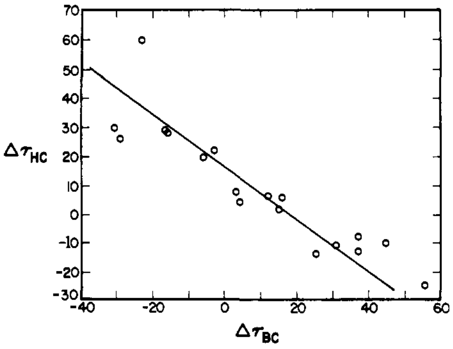

Figure 2. Plot of $\Delta\tau_{HC}$ vs. $\Delta\tau_{BC}$; see eq 1

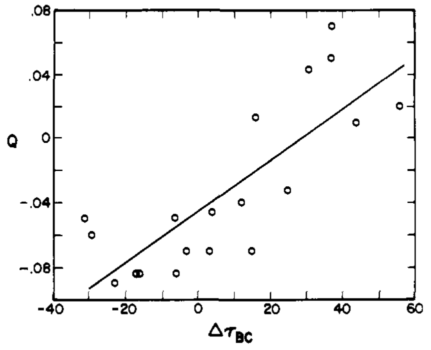

Figure 3. Plot of Q vs. $\Delta\tau_{BC}$; see eq 2.

A direct linear regression comparison (Figure 3) of MO-derived charges, Q (Table I, column 5), with the benzene induced shifts, $\Delta\tau_{BC}$, (column 2), eq 2,

$$Q = 1.61 \times 10^{-3}(\Delta\tau_{BC}) - 4.53 \times 10^{-2} \qquad (2)$$

gives a correlation coefficient of $r = 0.80$, which might be as good as can be expected when considering the problems inherent in estimating MO charges as well as the experimental error in measuring the ASIS shifts (approximately 0.01-0.02 ppm, 1-2 Hz, when peaks are clearly observed and perhaps slightly higher when overlap between two peaks is observed, e.g., H-B(4) and H-B(5) of $C_2B_4H_8$). But it is unlikely that this comparison would improve much even when better values for both MO-derived charges and ASIS effects are available. This can be attributed, in part, to a lack of peripheral effects which should be taken into account for a more complete physical picture of a charge-ASIS relationship. Clearly, when a benzene solvent molecule approaches a polyboron cage molecule, any preferred geometrical alignment of the π-cloud adjacent to a positively charged hydrogen of the polyborane will be partially offset by negatively charged neighboring atoms, and will be somewhat reinforced in this alignment by neighboring positively charged atoms. Obviously, the atoms having the largest effect will be nearest-neighbor solute hydrogens, for all solute hydrogens are exo to the polyboron cage and capable of close "contact" with the approaching solvent. In an approach which takes into account the effect of these "nearest-neighbor" atoms on the ASIS phenomena the skeletal

Table I. Aromatic Solvent Induced NMR Shifts and Charges on Hydrogens

Compound	Hydrogen position	(1) τ_C	(2) $\Delta\tau_{BC}$[a]	(3) $\Delta\tau_{HC}$[b]	(4) $\Delta\tau_{BH}$[c]	(5) Q[d]	(6) ΣQ_{nn}[d]	(7) $Q(ASIS)_{BC}$[d]	(8) $Q_d(ASIS)_{BC}$[d]	(9) $Q(ASIS)_{HC}$[d]	(10) $Q_d(ASIS)_{HC}$[d]	(11) $Q(ASIS)_{BH}$[d]	(12) $Q_d(ASIS)_{BH}$[d]
1,6-$C_2B_4H_6$	H–B(2)	8.01	−3	+22	−25	−0.07[e]	−0.04	−0.097	−0.097	−0.103	−0.091	−0.101	−0.096
	H–C(1)	7.03	+37	−8	+45	+0.05	−0.28	−0.024	+0.096	−0.042	+0.071	−0.030	+0.089
2,3-$C_2B_4H_8$	H–B(1)	10.96	−16	+28	−44	−0.084[f]	−0.131	−0.121	−0.078	−0.115	−0.076	−0.120	−0.080
	H–B(4)	6.44	−6	+20	−26	−0.083	−0.074	−0.103	−0.066	−0.099	−0.061	−0.102	−0.065
	H–B(5)	6.44	−6	+20	−26	−0.051	−0.214	−0.103	−0.021	−0.099	−0.014	−0.102	−0.018
	$H\mu$–B(4,5)	12.17	+16	+7	+9	+0.018	−0.116	−0.062	−0.027	−0.072	−0.037	−0.067	−0.031
	H–C(2)	3.66	+31	−11	+42	+0.043	−0.124	−0.035	+0.007	−0.035	+0.005	−0.033	+0.009
2,4-$C_2B_5H_7$	H–B(5)	5.82	−17	+29	−46	−0.083[g]	−0.150	−0.123	−0.085	−0.117	−0.089	−0.122	−0.089
	H–B(3)	5.03	+15	+2	+13	−0.071	+0.004	−0.064	−0.069	−0.062	−0.070	−0.062	−0.070
	H–B(1)	9.90	+3	+8	−5	−0.069	−0.095	−0.086	−0.043	−0.074	−0.014	−0.081	−0.030
	H–C(2)	4.49	+37	−13	+50	+0.071	−0.292	−0.024	+0.051	−0.031	−0.026	−0.025	+0.043
B_5H_9	H–B(1)	9.28	−23	+60	−83	−0.09[h]	−0.160	−0.134	−0.104	−0.180	−0.178	−0.159	−0.143
	H–B(2)	7.52	+12	+7	+5	−0.04	−0.150	−0.070	−0.024	−0.072	−0.002	−0.071	−0.013
	H_μ–B(2,3)	12.32	+44	−10	+54	+0.01	−0.060	−0.011	+0.002	−0.037	−0.022	−0.021	−0.008
$B_{10}H_{14}$	H–B(2)	9.28	−29	+26	−55	−0.0607[i]	−0.2326	−0.145	−0.086	−0.111	−0.070	−0.131	−0.080
	H–B(1)	6.27	−31	+30	−61	−0.0518	−0.2686	−0.148	−0.057	−0.119	−0.047	−0.137	−0.054
	H–B(5)	6.88	+4	+3	+1	−0.0477	−0.1725	−0.084	−0.032	−0.064	−0.022	−0.075	−0.028
	H–B(6)	6.27	+25	−14	+39	−0.0336	−0.1135	−0.046	−0.011	−0.029	+0.007	−0.036	−0.001
	H_μ–B(5,6)	12.22	+56	−25	+81	+0.0213	−0.0600	+0.011	+0.018	−0.007	−0.002	+0.006	+0.012

[a] $(\tau_{benzene} - \tau_{cyclohexane}) \times 10^2$ where $\tau_{benzene}$ is the chemical shift of the carborane hydrogen using benzene as the solvent and $\tau_{cyclohexane}$ is the chemical shift using cyclohexane as the solvent. Using a 100-MHz instrument the cited shifts are in Hz. [b] $(\tau_{hexafluorobenzene} - \tau_{cyclohexane}) \times 10^2$. [c] $(\tau_{benzene} - \tau_{hexafluorobenzene}) \times 10^2$. [d] Charge; see text. [e] I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 92, 7019 (1970). [f] D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, 94, 8699 (1972). The value for H–C(2) is a misprint in the original article and has been corrected to +0.043. [g] D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, 94, 8692 (1972). [h] E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 92, 3837 (1970). [i] E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 94, 4467 (1972). The value for H_μ–B(5,6) in the original article is a misprint and has been corrected +0.0213.

boron and carbon atoms are ignored for the reasons that they do not come in direct contact with the solvent, and in any case, they are usually a reflection of the charges of directly attached hydrogens (or perhaps it would be best said that the trend in hydrogen charges are a mirror of the attached cage boron or carbon atoms) and so are difficult to include as separate or partial charge entities.

In the "nearest-neighbor" approach that is developed here, each of the hydrogens, H_{nn}, immediately adjacent to the hydrogen, H_c, under consideration is treated as having a small but significant charge contribution toward an effective charge, Q_e, of H_c. This is simply expressed

$$Q_e = Q + k\Sigma Q_{nn} \quad (3)$$

where ΣQ_{nn} (Table I, column 6) is the sum of all nearest-neighbor Q values, and where k is a factor that controls the magnitude of the nearest neighbor effects. Realistically, the value of k should be less than 1.00; also k should appear after, rather than preceding, the summation sign because it is obvious that slightly different factors apply to each kind of nearest neighbor hydrogen. Since the H··H distance is certainly an important factor governing the magnitude of k, it is to be noted, for example, that in 2,4-$C_2B_5H_7$ the distances to H(5) are: H(1)··H(5) 3.49 Å, H(4)··H(5) 2.86 Å, H(6)··H(5) 3.12 Å.[11,22] So it is not unreasonable to expect that H(4) should have a greater effect on Q_e of H(5) than would either H(1) or H(6). In some of the other cage compounds this is further complicated by bridge vs. terminal neighboring hydrogens and just how "exposed" each might be to the approaching solvent. But just what the variation in k will be as a function of nearest-neighbor H···H distance is not known and cannot be easily calculated. Therefore, for the sake of simplicity, as well as out of necessity, all nearest-neighbor (adjacent- and geminal-terminal and geminal-bridge) hydrogens are treated as having the same contributing factor k.

The ASIS data in benzene, $\Delta\tau_{BC}$ (column 2, Table I), are then compared with the effective charges, Q_e, for all 19 hydrogen types using the linear relationship in eq 4 where A and B are the usual slope and intercept constants.

$$Q_e = A(\Delta\tau_{BC}) + B \quad (4)$$

Combining eq 3 and 4 gives

$$Q + k\Sigma Q_{nn} = A(\Delta\tau_{BC}) + B \quad (5)$$

For example, eq 5 for H(2) and H(1) of 1,6-$C_2B_4H_6$ becomes:

$$-0.07 + k(+0.05 + 0.05 - 0.07 - 0.07) = A(-3) + B$$

$$+0.05 + k(-0.07 - 0.07 - 0.07 - 0.07) = A(+37) + B$$

Using the benzene-induced shifts for the 19 comparison points the best linear correlation (Figure 4) is found when $k = 0.31$, $A = 1.83 \times 10^{-3}$, and $B = -9.16 \times 10^{-2}$.

$$Q + 0.31\Sigma Q_{nn} = 1.83 \times 10^{-3}(\Delta\tau_{BC}) - 9.16 \times 10^{-2} \quad (r = 0.93) \quad (6)$$

The high correlation coefficient ($r = 0.93$) for this approach is very satisfying; and the fractional (0.31) charge contribution of each nearest neighbor hydrogen emerging from a best fit to the 19 equations appears very reasonable.

Similar approaches both with and without the use of the nearest-neighbor term, $k\Sigma Q_{nn}$, have been taken for the shifts observed in hexafluorobenzene where it is found that a direct comparison between $\Delta\tau_{HC}$ (Table I, column 3) and Q gives a direct linear relationship of

$$Q = 1.86 \times 10^{-3}(\Delta\tau_{HC}) - 1.50 \times 10^{-2} \quad (r = 0.75) \quad (7)$$

The negative slope of eq 7 in hexafluorobenzene (cf. with the positive slope found in benzene, eq 2 and Figure 3) is expected based on the previously derived theory of ASIS effects. When nearest-neighbor effects are taken into account the best fit becomes

$$Q + 0.31\Sigma Q_{nn} = -2.04 \times 10^{-3}(\Delta\tau_{HC}) - 5.78 \times 10^{-2} \qquad (r = 0.85) \qquad (8)$$

An improvement in the correlation coefficient, r, is again observed when taking the "nearest neighbor" approach but the overall correlation is not as good as in the benzene case, eq 6. It is satisfying, however, to find the derived value of $k = 0.31$ in eq 8 is the same as that found in eq 6. One would not necessarily expect such perfect agreement, for the geometrical considerations of nearest-neighbor effects on collision complexes with the solute would probably not be identical for the two solvents hexafluorobenzene and benzene.

As cited in the Experimental Section, both $\Delta\tau_{BC}$ and $\Delta\tau_{HC}$ values are obtained by comparing the cage-compound ^1H NMR chemical shifts in the aromatic solvent with the shifts found when cyclohexane is the solvent. From previous studies cyclohexane seems to be as good or as poor as any other standard "nonaromatic" solvent.[23] In this regard we found it convenient to develop an approach which avoids the use of a nonaromatic solvent and in which the shift observed in benzene is directly compared with the shift observed in hexafluorobenzene, $\Delta\tau_{BH}$ (Table I, column 4). Since these two aromatic solvents generally cause shifts in opposite directions, this approach has the advantage of larger absolute shifts (column 4 values average 1.73 times larger than those in column 2 and 2.07 times larger than those in column 3) with approximately no significant change in experimental error. A direct linear comparison of $\Delta\tau_{BH}$ with the MO derived charge Q gives

$$Q = 9.02 \times 10^{-4}(\Delta\tau_{BH}) - 3.12 \times 10^{-2} \qquad (r = 0.80) \qquad (9)$$

When nearest-neighbor effects, eq 5, are taken into account, the best linear fit is

$$Q + 0.31\Sigma Q_{nn} = 1.01 \times 10^{-3}(\Delta\tau_{BH}) - 7.56 \times 10^{-2} \qquad (r = 0.91) \qquad (10)$$

The small difference in correlation indices between eq 10 and eq 6 is probably not significant and so use of either relationship is recommended over that of eq 8.

Hydrogen Charges Obtained from ASIS Effects. There is no reason to suppose that the available MO-derived charge, Q, is a more accurate reflection of relative hydrogen charge than $\Delta\tau$(ASIS). Once the relationships in eq 2 and 6–10 became available, it was intriguing to calculate a Q(ASIS) for each hydrogen using $\Delta\tau$ values only. This could have the effect of "averaging out" imperfections in Q derived from MO theory. In the approach that avoids "nearest neighbor" effects the charges are given in columns 7, 9, and 11 (Table I) as obtained (eq 2, 7, and 9) from ASIS effects observed in benzene (BC), hexafluorobenzene (HC), and a combination of both (BH), respectively. The trends in Q(ASIS) within each compound are, not unexpectedly, in reasonable agreement with the hydrogen charges, Q, obtained from the molecular orbital approach. The only reversals are seen for H-B(3) and H-B(1) of 2,4-$C_2B_5H_7$ and H-B(2) and H-B(1) of $B_{10}H_{14}$. In the case of 2,4-$C_2B_5H_7$ it is interesting to note, however, that electrophilic substitution onto the cage borons favors the 1- over the 3-position,[24] and for decaborane, the magnitude of the charge reversal is not alarming.

In an approach that takes into account nearest-neighbor effects of the kind mentioned above, a set of charges, Q_d(ASIS) (column 8, Table I), can be derived using eq 6 and the measured $\Delta\tau_{BC}$ values given in column 2. For example, the ASIS derived hydrogen charge values for 1,6-$C_2B_4H_6$ are calculated from the two equations [note: $Q_d(\text{ASIS})_{BC}$ is abbreviated to Q in these equations]:

$$Q_{H(1)} + 0.31[4Q_{H(2)}] = 1.83 \times 10^{-3}(+37) - 9.16 \times 10^{-2}$$

$$Q_{H(2)} + 0.31[2Q_{H(2)} + 2Q_{H(1)}] = 1.83 \times 10^{-3}(-3) - 9.16 \times 10^{-2}$$

$$\therefore Q_{H(1)} = +0.096$$

$$Q_{H(2)} = -0.097$$

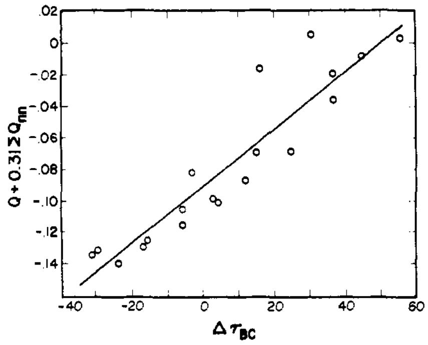

Figure 4. Plot of $Q + 0.31\Sigma Q_{nn}$ vs. $\Delta\tau_{BC}$; see eq 6.

Q_d(ASIS) in columns 10 and 12 are derived in the same fashion using the $\Delta\tau$ values given in columns 3 and 4 and the relationships shown in eq 8 and 10, respectively. The Q_d(ASIS) trends within each compound in each of columns 8, 10, and 12 are in very good agreement with the MO derived charge, Q (column 5). The one exception in column 8 appears to be the reversal of H-B(5) and H_μ-B(4,5) in $C_2B_4H_8$ but it is to be noted that chemical shifts for H-B(5) overlap with the more intense H-B(4) in each solvent making it difficult to obtain very precise $\Delta\tau$ values. The same charge reversal, H-B(5) vs. H_μ-B(4,5), is found in column 10 along with several other reversals (cf. column 10 with column 5); however, the correlation ($r = 0.85$) is poorer for eq 8, used to derive $Q_d(\text{ASIS})_{HC}$, than for eq 6 and 10, which are used to derive $Q_d(\text{ASIS})_{BC}$ (column 8) and $Q_d(\text{ASIS})_{BH}$ (column 12). It is perhaps satisfying though, that the only charge reversals are for those hydrogen pairs which, by the previous MO-derived charges calculations, are immediately adjacent in the hydrogen charge spectrum of each of the cage compounds. In the case of $Q_d(\text{ASIS})_{BH}$, column 12, the trends within each compound correspond perfectly with Q with the minor exception of H-B(5) and H_μ-B(4,5) or $C_2B_4H_8$.

Relative H_μ Acidities. It is already known that bridge hydrogen acidity follows the order: $B_{10}H_{14} > B_5H_9$.[25] Bridge hydrogens in the present study number only three, but it is interesting to note that the relative positive charge assigned to each from the various ASIS derived approaches (columns 7–12) as well as Q_{MO} all result in $H_\mu(B_{10}H_{14}) > H_\mu(B_5H_9) > H_\mu(C_2B_4H_8)$. This would imply that $C_2B_4H_8$ is the least acidic of the three but the usual word of caution should be mentioned in that this ignores the relative stabilities of the conjugate anions, and, as is already known, H_μ of $C_2B_4H_8$ is more easily removed as H^+ than is the more positive HC[26] although greater positive charge appears, from both MO calculations and ASIS derived Q values, to reside on the latter.

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The Effect of Charge upon Mobility. A Critical Examination of the Zwanzig Equation

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Abstract: The diffusion coefficients of a homologous series of tetraalkyltins (Me_4Sn, Et_4Sn, Pr_4Sn, Bu_4Sn), tetraethylmethane, and carbon tetrachloride in acetrontrile, ethanol, 2-propanol, and 1-butanol at 25 °C, and in acetone, methanol, and 1-octanol at 10 and 25 °C, have been determined using the Taylor dispersion technique and the Gouy interferometer. Deviations from the predictions of Stokes' law as large as a factor of 4 are observed in some cases. Comparison of the diffusion coefficient for tetraalkyltins with ionic mobilities for the tetraalkylammonium ions allows the dielectric friction coefficient of the Zwanzig equation to be determined directly. It is found that the theory overestimates this effect by as much as a factor of 10.

Traditionally, ionic mobilities have been discussed in terms of deviations from Stokes' law. Although there are a number of unresolved problems associated with using continuum theory to describe the hydrodynamic behavior of small ions, Stokes' law has nevertheless been widely applied in detecting solvent structural effects[1] and in calculating hydration numbers.[2]

In addition to the hydrodynamic frictional force implicit in Stokes' law, Born,[3] Fuoss,[4] and Zwanzig[5] have shown that a more complete description of ionic mobility also requires the inclusion of a dielectric frictional force. The Zwanzig theory provides reasonable qualitative agreement in the sense that it predicts curves similar in shape to those observed experimentally. However, the quantitative agreement is poor possibly because the Zwanzig equation is in essence a correction to Stokes' law.

The question of the validity of Stokes' law when applied to small solutes can be answered experimentally by diffusion measurements. To this end, we have measured the diffusion coefficients of a number of symmetrical tetraalkyltins in a variety of solvents. These data permit the hydrodynamic friction coefficient to be determined directly. Since these neutral compounds are similar in size and shape to tetraalkylammonium ions, a comparison of their transport behavior allows the effect of charge upon mobility to be directly ascertained. In addition, the diffusion data allow the dielectric friction coefficient to be determined experimentally and compared to that predicted by the Zwanzig equation.

Experimental Section

Apparatus. Except where noted, the diffusion data were obtained using the Taylor dispersion technique. In this method, a small sample (10 μL) of a dilute solution (~1–3% by weight) is injected into the solvent as it flows through a capillary tube. Taylor[6] has shown that provided that the flow is laminar, the combination of flow and diffusion results in a Gaussian distribution of the solute along the tube. For liquids, the diffusion coefficient can be determined from the expression[7]

$$D = \frac{0.2310 r^2 t_R}{(W_{1/2})^2} \tag{1}$$

where D is the binary diffusion coefficient, r is the radius of the capillary tube, t_R is the residence time of the solute in the tube, and $W_{1/2}$ is the eluted peak width at half its height.

The solvent flow through the capillary is controlled by a Cheminert metering pump, Model CMP-2V. The pumping rate was adjusted so that the average volume flow was 0.5 cm/s or less. We have used two capillary tubes, a 200-ft long stainless steel tube of 0.02-in. diameter and a 300-ft long stainless steel tube of 0.03-in. diameter (Superior Tube Co.). An injection port located at the top of the capillary tube contained a silicone rubber septum coated with Teflon (Unimetric Corp.) which allowed the sample to be injected directly into the capillary with a microsyringe. At the other end of the capillary, the solute dispersion peak was detected with a Waters differential refractometer Model R401 and recorded with a chart recorder. The capillary tubing was placed in a constant temperature bath which was controlled to ±0.01 °C. The temperature of the differential refractometer cell was controlled by circulating water from the bath through it.

In our preliminary experiments, the fluid flow was controlled by