ond side arm equipped with a quartz epr tube, and a third side arm with a glass break-seal to allow the introduction of oxygen. The Pyrex visible cells were fabricated from square tubing supplied by Ace Glass Co. and had a cutoff near 30 × 10^3 cm^{-1}.

A freezing point depression method with a modified apparatus described by Choi, Firth, and Brown[32] was used for molecular weight measurements. A Leeds and Northrup Model 8163 platinum-resistence thermometer and Leeds and Northrup Model 8069 ER thermometer bridge and Model 9838 nanovolt detector were used for temperature measurements. The molal freezing point constant 4.75[33] was used.

Commerical elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., and by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach uber Engelskirchen, West Germany. Laboratory chloride analyses were by the Volhard method and titanium was determined gravimetrically as TiO_2.[34]

Acknowledgment. Support of National Science Foundation Grant GP-11526 is gratefully acknowledged.

Registry No. C_5H_5N, 110-86-1; $TiCl_3$, 7705-07-9; O_2, 7782-44-7; $Ti_2Cl_6O \cdot 4C_5H_5N$, 51364-53-5.

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Notes

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Quadrupole-Induced ^1H-$^{10,11}B$ Spin Decoupling in Carboranes. Correlation of Decoupling Efficiency with Molecular Volume

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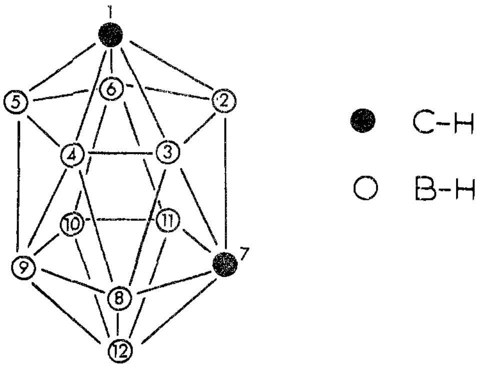
In applying dynamic nuclear magnetic resonance (dnmr) spectroscopy to elucidation of the structure and molecular dynamics of boron hydrides, two fundamentally different types of rate process may effect changes in the spectrum.[2] One process involves intramolecular or intermolecular chemical exchange and the other interconversion between ^{10}B ($I = 3$) and ^{11}B ($I = {}^3/_2$) spin states induced principally by boron quadrupolar relaxation.[3] Previous investigations of the ambient temperature ^{11}B nmr spectra of carboranes and carborane derivatives indicate clearly that the hydrogens are not scrambling.[2] This report concerns a variable-temperature ^1H nmr study of carboranes and halocarboranes in which ^1H-$^{10,11}B$ spin decoupling is observed at low temperatures. Although the decoupling efficiency correlates well with molecular volume, *i.e.*, the greater the molecular volume the higher the temperature at which decoupling occurs,[3] increasing molecular dipole moment also accompanied increasing molecular volume for the compounds studied and may provide additional mechanisms for $^{10,11}B$ nuclear spin relaxation.

Examination of the ^1H dnmr spectrum (60 MHz) of *m*-carborane [**1**; 1,7-dicarba-*closo*-dodecaborane(12)] in 50% CD_3OD-50% CD_3COCD_3 (v/v) at −21° (Figure 1) revealed a spectrum similar to that observed at room temperature with a sharp C-H resonance superimposed on the diffuse B-H peaks. Upon lowering the temperature, the B-H spectrum coalesced and then sharpened into a broad singlet resonance of approximate lorentzian line shape (Figure 1). This spectral behavior is very analogous to that reported for *o*-carborane [**2**; 1,2-dicarba-*closo*-dodecaborane(12)][4] and is best rationalized in terms of increasing viscosity and lower temperatures rendering boron quadrupole-induced ^1H-$^{10,11}B$ spin decoupling more efficient.[2] It is evident at −134° (Figure 1) that all of the ^1H chemical shifts in **1** are very similar and much smaller than the ^1H-^{11}B spin-spin coupling constants [$J(^1H, ^{11}B) = 148$-177 Hz].[5] Indeed, successive irradiation at the nmr resonant frequencies of the various boron atoms in **2** at room temperature produced respective decoupled ^1H resonances all having very similar chemical shifts. In addition to the B-H resonances in **1**, the C-H peak also sharpens markedly at lower temperatures (Figure 1) indicating the loss of small coupling of ^{11}B to the C-1 and C-7 protons at low temperatures.



1

Examination of the ^1H dnmr spectra (60 MHz) of 9,12-dibromo-1,2-dicarba-*closo*-dodecaborane(12) or **3** in 50% CD_3OD-50% CD_3COCD_3(v/v) at −20° (Figure 2) revealed a typical spectrum. Lowering the temperature resulted in the expected spectral sharpening due to quadrupole-induced ^1H-$^{10,11}B$ spin decoupling (Figure 2). Very similar behavior was observed for 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane-(12) and 8,9,10,12-tetrabromo-1,2-dicarba-*closo*-dodecaborane(12) in 50% CD_3OD-50% CD_3COCD_3 as illustrated respectively in Figures 3 and 4.

Although the solvent impurity peaks (*e.g.*, CHD_2COCD_3) have been subtracted from Figures 1-4, it was observed that the CHD_2 ^1H dnmr pentet of either solvent impurity coalesced at about the same temperature (~−110°) in all four

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[1] Alfred P. Sloan Research Fellow, 1971-1974; Camille and Henry Dreyfus Teacher-Scholar, 1972-present.

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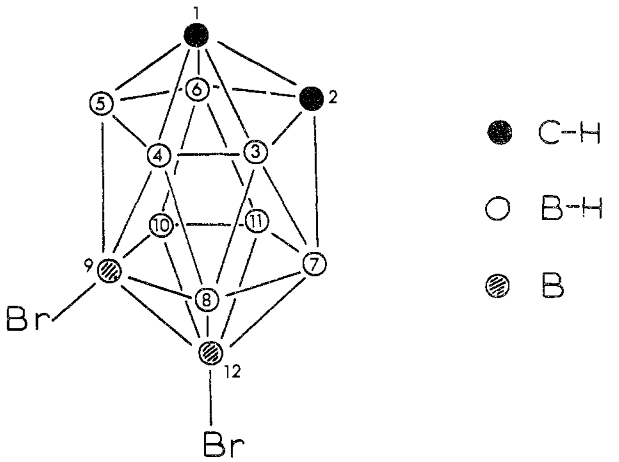

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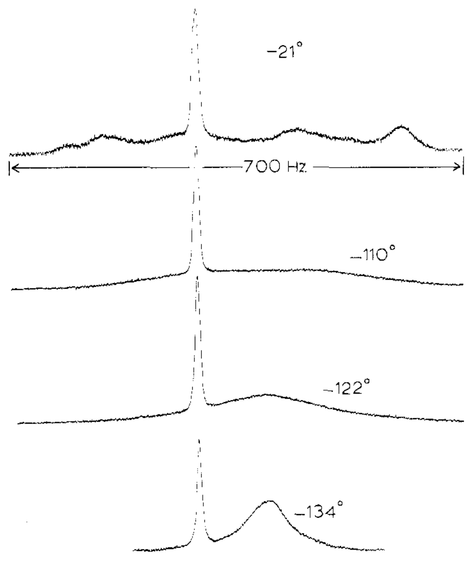

Figure 1. The ^{1}H dnmr spectra (60 MHz) of 1,7-dicarba-*closo*-dodecaborane(12) in 50% CD_3OD-50% CD_3COCD_3 (v/v). Solvent impurity peaks due to CHD_2OD, CD_3OH, and CHD_2COCD_3 have been subtracted from the spectra for clarification of presentation.

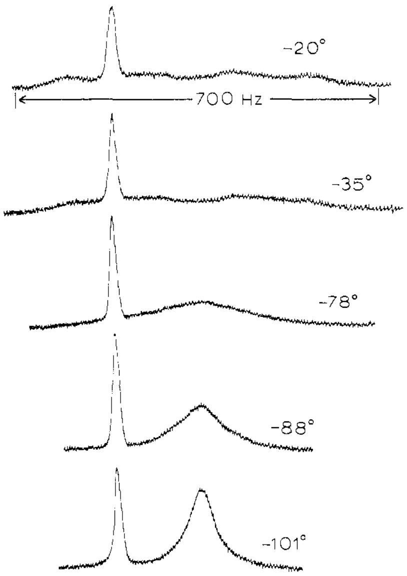

Figure 2. The ^{1}H dnmr spectra of 9,12-dibromo-1,2-dicarba-*closo*-dodecaborane(12) in 50% CD_3OD-50% CD_3COCD_3 (v/v) with solvent impurity peaks subtracted.

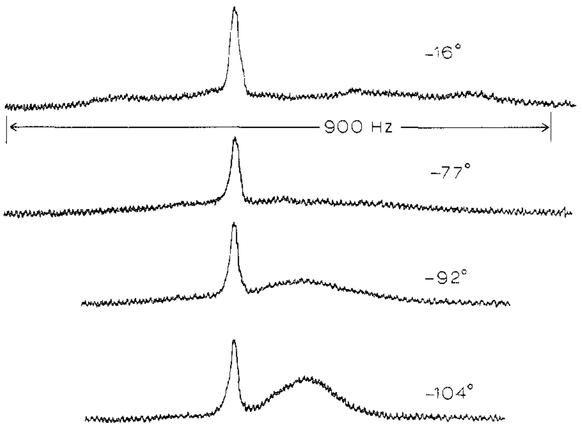

Figure 3. The ^{1}H dnmr spectra (60 MHz) of 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane(12) in 50% CD_3OD-50% CD_3COCD_3 (v/v) with solvent impurity peaks subtracted.

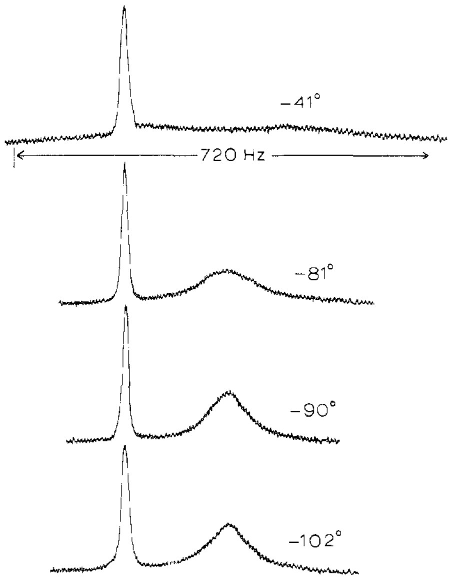

Figure 4. The ^{1}H dnmr spectra (60 MHz) of 8,9,10,12-tetrabromo-1,2-dicarba-*closo*-dodecaborane(12) in 50% CD_3OD-50% CD_3COCD_3 (v/v) with solvent impurity peaks subtracted.

dnmr samples indicating efficient deuteron ($I = 1$) quadrupole-induced ^{1}H-^{2}H spin decoupling. The observation that CHD_2 coalescence occurred at essentially the same temperature for all samples speaks for a very similar dependence of solution viscosity on temperature in all four cases which will be important in subsequent discussion.

A comparison of Figure 3 of ref 4 and Figure 1 herein with Figures 2-4 herein indicates a similar spread in the B-H resonances, *i.e.*, similar $J(^1H, ^{11}B)$ values. However, a perusal of the various figures indicates more efficient quadrupole-induced ^{1}H-^{11}B spin decoupling (as manifested by significant peak sharpening at higher temperatures) in the halocarboranes (Figures 2-4) as compared to the unsubstituted carboranes (Figure 1). For example, compare the spectrum at −101° in Figure 2 with that at −110° in Figure 1.

The efficiency of the observed ^{1}H-^{10,11}B spin decoupling will depend on the rate of ^{11}B or ^{10}B spin-state interconversion; the more rapid the spin-state interconversion, the more efficient the decoupling. Quadrupole relaxation may be assumed to provide the dominant mechanism for ^{11}B and ^{10}B spin relaxation.[2] The rate of ^{11}B or ^{10}B spin-state interconversion or the nuclear spin-lattice relaxation time (T_1) is a function of a number of parameters including the nuclear quadrupole coupling constant and an *inverse* function of the molecular correlation time (τ_c)[2,3] which may be considered a measure of the rate of molecular tumbling. Using a simple spherical model, τ_c can be expressed in terms of eq 1 in

$$\tau_c = 4\pi\eta a^3/3kT \tag{1}$$

which η is the viscosity, a is the radius of the sphere, k is Boltzmann's constant, and T is the absolute temperature.[6] In the four cases reported here, we may assume that η shows the same dependence on temperature (see above discussion) and any significant difference in spectral behavior is due most likely to a change in molecular volume ($4\pi a^3/3$; eq 1). As τ_c increases due to an increase in molecular volume, quadrupole-induced ^{10}B and ^{11}B spin-state interconversion becomes more efficient and ^{1}H-^{10,11}B spin decoupling occurs. It is clear from a consideration of eq 1 that τ_c will be greater for the larger halocarboranes than for the smaller unsubstituted carboranes. Thus, more efficient quadrupole-induced ^{1}H-^{10,11}B spin decoupling in the halocarboranes is manifested by spectral sharpening at higher temperatures (Figures 2-4) as compared to the unsubstituted compounds (Figure 1).

An additional mechanism for ^{10}B and ^{11}B nuclear spin relaxation which must be considered involves direct intramolecular or intermolecular interaction of the nuclear spins with tumbling dipoles in solution.[3] Indeed, the significantly greater dipole moment for *o*-carborane ($\mu = 4.3$ D[7]) as compared to *m*-carborane ($\mu = 2.8$ D[7]) necessitates some consideration of this mechanism. Assuming an essentially spherical geometry for *o*- and *m*-carborane,[8] para B-C and B-B distances of 3.3 Å, B-H and C-H bond lengths of 1.1 Å, and a van der Waals radius for hydrogen of 1.2 Å, a molecular radius of 4.0 Å is calculated for *both* compounds. Thus, in applying eq 1 to *o*- and *m*-carborane at a given temperature, it may be assumed that η, a, and T have the same respective values for both compounds and, therefore, τ_c is the same for both species. Since all the ^{1}H chemical shifts in *o*- or *m*-carborane are essentially identical and the ^{1}H-^{10,11}B spin-spin coupling constants in both compounds are very similar,[2] the almost coincident coalesced ^{1}H nmr spectra for *o*-carborane at −108° (see ref 4, Figure 3) and *m*-carborane at −110° (Figure 1) reveal the boron nuclear spin relaxation rates for the two compounds to be quite close at essentially the same temperature. This observation is consistent with the calculated identical τ_c values (eq 1). If dipolar interactions were a significant factor in boron nuclear spin relaxation, very different spectra at a given temperature would be expected for these two compounds of different dipole moment. Thus, it may be assumed that under these experimental conditions boron quadrupolar relaxation provides the principal nuclear spin relaxation mechanism for boron nuclei in these two compounds.[3] It should be noted at this point that the ^{1}H nuclear spin relaxation rate should also be affected by dipolar interactions. However, the sharp carborane C-H resonances observed to very low temperatures (Figures 1-4) indicate that this effect is not very important in the temperature range of interest in this study and is consistent with our conclusions regarding the dominant mechanism of boron nuclear spin relaxation. A similar approach may be applied to 9,12-dibromo-*o*-carborane ($\mu = 7.2$ D[7a,9]) and 9,10-dibromo-*m*-carborane ($\mu = 5.4$ D[9]). In order to estimate "a" (eq 1) for the two dibromo compounds, the distances across all six pseudo-fivefold rotation axes were averaged assuming para B-C and B-B distances of 3.3 Å, B-H and C-H bond lengths of 1.1 Å, a B-Br bond length of 2.0 Å, and van der Waals radii for hydrogen and bromine of 1.2 and 1.95 Å, respectively. This results in an average molecular radius (a; eq 1) of 4.3 Å for both compounds. The higher nmr coalescence temperatures for the two dibromocarboranes (Figures 2 and 3) as compared to *o*- and *m*-carborane (Figure 1) are consistent with increasing molecular volume and increasing τ_c (eq 1). However, it should be noted that the nmr spectrum of 9,12-dibromo-*o*-carborane with the higher dipole moment sharpens at slightly higher temperatures (Figure 2) as compared to 9,10-dibromo-*m*-carborane (Figure 3). This observation may indicate an increasing importance of dipolar mechanisms for boron nuclear spin relaxation in these compounds of high dipole moment. An average radius of 4.7 Å is calculated for 8,9,10,12-tetrabromo-*o*-carborane. No dipole moment data are available although the higher coalescence temperature (Figure 4) as compared to *o*- and *m*-carborane is consistent with both increased molecular volume and dipole moment.

Thus, in any variable-temperature ^{1}H nmr study of carborane derivatives, increasing molecular volume will lead very likely to ^{1}H-^{10,11}B spin-spin coupling coalescence at increasing temperatures due to increasingly efficient ^{10,11}B nuclear spin relaxation.

Experimental Section

The dnmr spectra were recorded using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.[9] Heteronuclear spin decoupling was performed using an NMR Specialties SD-60B heteronuclear spin decoupler.

9,12-Dibromo-1,2-dicarba-*closo*-dodecaborane(12) and 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane(12) were prepared by the methods of Smith, Knowles, and Schroeder.[10] 8,9,10,12-Tetrabromo-1,2-dicarba-*closo*-dodecaborane(12) was prepared by an analogous procedure.

Acknowledgment. We are grateful for Public Health Service Research Grant No. CA12025-01 and to Olin Mathieson Chemical Corp. for samples of *o*- and *m*-carborane.

Registry No. **1**, 16986-24-6; **3**, 17702-36-2; 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane(12), 17032-20-1; 8,9,10,12-tetrabromo-1,2-dicarba-*closo*-dodecaborane(12), 20755-68-4; ^{10}B, 14798-12-0; ^{11}B, 14798-13-1.

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Synthesis and Magnetic Properties of Copper(II) Complexes of *N*-(Hydroxyalkyl)pyrrole-2-carboxaldimines

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Spin-spin coupling in polynuclear copper(II) complexes remains of considerable interest and significant developments have been reported. Bertrand and Kelley[1] have recently

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