$$B_2H_6 + CF_3^+ \longrightarrow BF_3 + BCH_6^+ \qquad (4)$$

the species formed by replacing a boron atom in B_2H_6 with a C^+ ion. The heat of formation of this species is unknown. We have assumed that its heat of formation from BH_3 and CH_3^+ is equal to the heat of formation of the isoelectronic species, B_2H_6, from two BH_3 molecules.

The binding energy of $H_3BN(CH_3)_3$, relative to that of BF_3, is taken to be the energy of reaction 5. Although the heat of the formation of the gaseous tetramethylammonium ion apparently has not been recorded, it can be estimated from a Born–Haber cycle for tetramethylammonium nitrate. The sum of reactions 6, 7, and 8 is reaction 9, for which $\Delta H°$ is the

$$H_3BN(CH_3)_3 + CF_3^+ \longrightarrow BF_3 + N(CH_3)_4^+ \qquad (5)$$

$$\frac{3}{2}O_2(g) + N_2(g) + 4C(s) + 6H_2(g) \longrightarrow [(CH_3)_4N]NO_3(s) \qquad (6)$$

$$[(CH_3)_4N]NO_3(s) \longrightarrow N(CH_3)_4^+(g) + NO_3^-(g) \qquad (7)$$

$$NO_3^-(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + e^-(g) \qquad (8)$$

$$\frac{1}{2}N_2(g) + 4C(s) + 6H_2(g) \longrightarrow N(CH_3)_4^+(g) + e^-(g) \qquad (9)$$

heat of formation of the gaseous tetramethylammonium ion. Médard and Thomas[26] have determined $\Delta H°_6$ to be -80.8 kcal/mol. The value of $\Delta H°_7$ (117.2 kcal/mol) was estimated by the formula of Kapustinsky, which, for salts of univalent anions, is[27]

$$U = 287.2\left[\frac{n(n+1)}{(r_+ + r_-)}\right]\left[1 - \frac{0.345}{(r_+ + r_-)}\right]$$

where n is the charge on the cation and r_+ and r_- are the cationic and anionic radii. The radius of the tetramethylammonium ion (2.43 Å) was calculated from the lattice constants for the chloride, bromide, and iodide salts[28,29] and the halide ionic radii,[30] and the nitrate ion radius was taken as 2.10 Å.[27] A previously calculated value of $\Delta H°_8$ (89.0 kcal/mol[27]) was used. The resulting value for the heat of formation of $N(CH_3)_4^+(g)$ is 125.4 kcal/mol.

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Structure and Dynamics in Metal Tetrahydroborates. I. Nuclear Magnetic Resonance Studies of Zirconium and Hafnium Tetrakis(tetrahydroborates)

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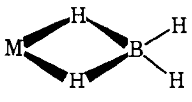
Abstract: The identical temperature dependence of the pmr spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ is due to the variable rate of ^{10}B and ^{11}B quadrupolar spin–lattice relaxation. Intramolecular rearrangement processes are still rapid at $-80°$. Quantitative analysis of the spectra as a function of solution viscosity yields results at least partially in accord with the hydrodynamic model for molecular reorientation, though inertial effects are also probably operative. Within experimental error, both molecules have the same nuclear quadrupole coupling constants, which are estimated to be: ^{10}B, 3.5 ± 0.6 MHz; ^{11}B, 1.7 ± 0.3 MHz, and the same activation energies for molecular reorientation, 3.1 ± 0.1 kcal/mol.

A number of transition metal hydroborate compounds are now known,[1] which, unlike their more familar salt-like alkali metal cogeners, possess characteristics typical of covalent molecules (solubility in nonpolar solvents, high volatility). These molecules are of interest in that they may serve as simple models for numerous organometallic systems of multicenter metal–ligand interactions. Their structural, chemical, and dynamical properties may also shed light on the nature of the hydrogen-transfer process both in borohydride reductions and in transition metal catalyzed hydrogenations. Finally, these molecules are of interest in that they appear to undergo a rapid, degenerate permutation of bridging and terminal hydrogen atoms,[1] possibly making them some of the most rapid fluxional[2] molecules yet discovered.

Studies of transition metal tetrahydroborates have been complicated by a number of factors. A structural problem has always existed in distinguishing between bidentate (A) and tridentate (B) bonding configurations. The difficulty in locating hydrogen atoms near a heavy metal has impaired the accuracy of X-ray diffraction studies[3,4] employed to completely resolve problems of this sort in the solid state. To date, the full potential of infrared and Raman spectroscopy as structural tools in these systems has not been realized. Nuclear magnetic resonance spectroscopy of metal



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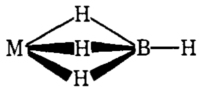

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tetrahydroborate systems, rather than resolving structural and dynamical problems, has been the greatest source of confusion and controversy. The proton magnetic resonance spectra of all known metal tetrahydroborates exhibit a single kind of boron hydride proton,[1] rather than the expected separate resonances expected for terminal and bridging hydrogens. The observed temperature dependence in nmr spectra has been attributed at various times to, among other processes, the slowing of a bridge–terminal exchange process,[5] "virtual decoupling,"[6a] and "thermal decoupling."[6b] We felt that a thorough, quantitative study of tetrahydroborate nmr spectra was required before any secure conclusions could be drawn regarding *both* structure and dynamics in solution.

In this paper, we present studies on tetrakis(tetrahydroborate) complexes of zirconium, Zr(BH$_4$)$_4$, I, and hafnium, Hf(BH$_4$)$_4$, II. Because the zirconium compound has been subjected to more extensive structural characterization[3,7] than any other transition metal tetrahydroborate, and because of its high symmetry and relatively simple geometry, it is an ideal model for spectroscopic examination. After briefly indicating how the solution structure of the molecule may be established from vibrational considerations, we will quantitatively discuss the nature of boron quadrupole spin–lattice relaxation and how it affects the nmr spectra. Employing line-shape analysis methods, significant information can be derived concerning the microdynamical behavior of the molecules in solution and the electronic distribution in the metal–ligand bond. Our data also allows us to say something about the nature and rate of the fluxional process which permutes bridge and terminal hydrogens.

Experimental Section

Synthetic. The compounds for this study were prepared from anhydrous ZrCl$_4$ or HfCl$_4$ and LiBH$_4$ using the procedure of James, *et al.*,[8] and were sublimed twice. The compounds were obtained as colorless, volatile crystalline solids, melting just above room temperature; they are extremely sensitive, smoking in air and detonating on contact with water. Thus, all manipulations were carried out *in vacuo* or under prepurified nitrogen, with rigorous exclusion of air and moisture. All glassware was oven dried before use, and tetrahydroborates were stored under nitrogen at −20°.

All solvents were dried by storage over Davison 4A Molecular Sieves. Then, where possible, they were distilled under nitrogen from sodium–potassium alloy–benzophenone just prior to use. If distillation was not possible, the solvents were either freeze–thaw degassed and trap-to-trap distilled *in vacuo* or were thoroughly saturated with nitrogen.

Spectroscopic. Infrared spectral measurements were made of the compounds as solutions in dry, degassed Nujol. Both Zr(NH$_4$)$_4$ and Hf(BH$_4$)$_4$ are moderately soluble in this solvent, and it was found to be far easier to record spectra in Nujol solutions between flat sodium chloride plates, then to fill infrared cavity cells. The tetrahydroborates also appear to react with sodium chloride, and the Nujol solutions react at a considerably reduced rate. As a precaution, repeated scans were made to monitor any spurious peaks which might be growing in due to decomposition or reaction. Spectra were recorded on Beckman IR-9 and IR-10 infrared spectrophotometers and were calibrated with polystyrene film.

Nuclear magnetic resonance spectra were recorded on Varian T-60 and A-60 (60 MHz), and Bruker HFX-90 (90 MHz) spectrometers. Samples were prepared by either of two methods. For qualitative experiments, solutions were prepared in Schlenk apparatus and were transferred by syringe to serum-stoppered nmr tubes. For quantitative work, the solid tetrahydroborates were loaded inside a glove bag into tared sample tubes equipped with serum caps, and after the filled tube had been weighed, carefully measured amounts of the proper solvent were added *via* syringe. This afforded accurately known concentrations for dilution studies.

All data for accurate line shape analysis were recorded on the Bruker HFX-90 instrument. Spectra were recorded at a maximum amplitude and minimum possible sweep width. Calibration was achieved by measuring the distance to the locking signal with a Hewlett-Packard 5216A electronic counter. Temperature control was accomplished wih the Bruker B-ST 100/700 temperature control unit, which had been previously calibrated with a Wilmad low-temperature thermometer. Temperatures are considered accurate to ±1° with a temperature fluctuation of less than 0.2° over the course of a spectrum (500 sec).

Temperatures of spectra obtained with the A-60 instrument were calibrated with the same Wilmad thermometer.

Treatment of Nmr Data. To determine the influence of ^{11}B and ^{10}B spin–lattice relaxation on the proton line shapes, theoretical spectra were generated by computer for different values of the spin–lattice relaxation time. The problem was treated as a multisite exchange process in which proton sites resonating in the presence of the different boron spin states (^{11}B (81.2% abundant), $m = {}^3/_2, {}^1/_2, -{}^1/_2, -{}^3/_2$; ^{10}B (18.8% abundant), $m = 3, 2, 1, 0, -1, -2, -3$, where m is the nuclear spin angular momentum quantum number) are exchanged as the quadrupolar nuclei make transitions between these states ($\Delta m = \pm 1, \pm 2$). The spin–spin coupling constants $J_{^{10}\text{B}-\text{H}}$ and $J_{^{11}\text{B}-\text{H}}$ are the effective chemical shifts between the different proton sites. The proton line width in the absence of "exchange" was taken to be that of internal tetramethylsilane, 0.30 Hz. Since line width broadening in all accessible temperature regions is in such an excess of 0.30 Hz, we feel that this assumption does not significantly affect the accuracy of our results.

Computation was performed on a CDC 6400 digital computer with a local version of the program EXCNMR, originally written by Professor George M. Whitesides of M.I.T. We are grateful to Professor Whitesides and Mr. W. J. Ehmann for a listing. This program computes the line shapes using the formalism of Kubo and Sack.[9] The calculation requires as input a matrix of exchange probabilities among the various sites, which is multiplied by the overall rate constant for exchange, $1/\tau$, where τ is the mean residence time at a site. For nuclei with quadrupole moments, probabilities for transitions between spin states are given by eq 4 and 5 (later in the text). These equations can be used to calculate the elements of the exchange matrix, since they give the probability of exchange betwen sites and the overall rate of spin–lattice relaxation ($1/T_1$).

To include the effects of coupling to *both* ^{10}B and ^{11}B for a rigorous treatment, it was necessary to compute a spectrum for a case with only ^{10}B coupling, and for one with only ^{11}B coupling, to scale the relative areas of these spectra, and to add the spectra within the program to produce a Calcomp plot which was the sum of the separate spectra. Ignoring the 18.8% abundant ^{10}B spectrum[22] was found to be a poor approximation, especially in the regions where collapse of the multiplet structure is appreciable. The relative spin–lattice relaxation times of ^{11}B and ^{10}B are dictated by eq 2 and 3 (given later), and, assuming that their eq and τ_c are the same, are calculated to be

$$T_{1(^{11}\text{B})} = 0.651 T_{1(^{10}\text{B})}$$

Hence, for line shape analysis, spectra were computed, with this ratio held constant, varying T_1 until an acceptable visual match was achieved with the experimental spectra.

The Arrhenius plots yielding the activation parameters for molecular reorientation were computer fitted by the method of least squares.

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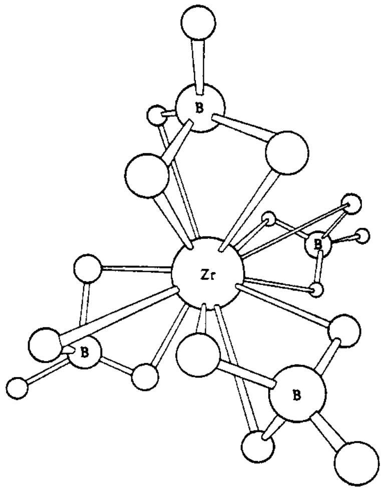

Figure 1. The structure of I, $Zr(BH_4)_4$.

Viscosity data for toluene were taken from the work of Whitesides and Mitchell.[10]

Structural Considerations

The structure of $Zr(BH_4)_4$ has been determined both by an X-ray diffraction study[3] at −160° and by electron diffraction in the gas phase.[7] The two determinations are in substantial agreement, and the results are illustrated in Figure 1. The zirconium atom is tetrahedrally coordinated to four tetrahydroborate groups bound in a tridentate manner. The Zr–B–H_t vector, where H_t is the single terminal hydrogen of a tetrahydroborate group, rigorously constitutes a threefold rotation axis of the molecule. This structure is unusual in that it is the only well-supported case of a tridentate borohydride–transition metal molecule.[1]

The vibrational spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ were of interest for several reasons. First, it was necessary to know if the two molecules were structurally similar, to aid in analysis and comparison of the nmr spectra. Secondly, though the solid-state and gas-phase structures were fairly well established (the rigorous T_d symmetry found in the X-ray structure assumed no disorder), we were anxious both to confirm the previous conclusions and to determine whether this structure persisted in solution, where nmr studies were to be made. We present here only a portion of our infrared and laser Raman results,[11] as they pertain to the choice between structures A and B.

A number of partial or complete vibrational analyses have been performed on B_2H_6,[12] $Al(BH_4)_3$,[13] $Zr(BH_4)_4$,[14] $Be(BH_4)_2$,[15] and BH_4^- [16] employing isotopic substitution together with high-resolution infrared and Raman spectroscopy. From these it is possible to assign a number of diagnostic bands to vibrations of the MBH_4 moiety. In particular, the terminal B–H stretches occur as strong bands in the infrared at *ca.* 2450–2600 cm^{-1}. The coupling of these vibrations between different BH_4 groups is expected to be very small, especially when they are attached to heavy metals. For bidentate tetrahydroborates, A, the symmetric and antisymmetric stretching vibrations of the terminal BH_2 moiety appear in the infrared as two sharp bands with a splitting of *ca.* 60–80 cm^{-1}, whereas tridentate tetrahydroborates, B, are expected to exhibit only a single terminal B–H stretch. This simple criterion has frequently been overlooked in structure assignments.

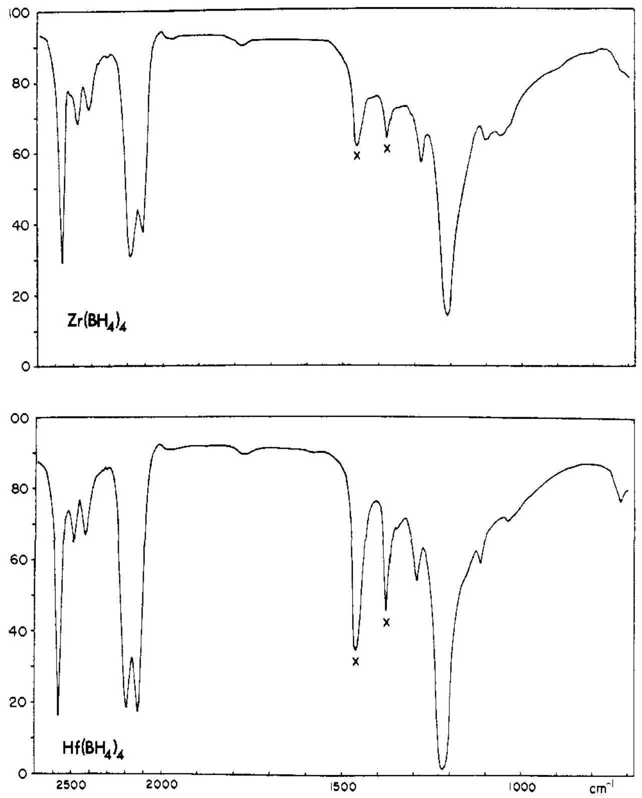

Figure 2. Infrared spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ as solutions in Nujol. The bands due to Nujol are marked X.

Figure 2 presents the solution infrared spectra of I and II. First, it should be noted that the spectra are nearly identical, which is strong evidence that the structures are very similar. The simplicity of the solution spectra is in accord with the structure shown in Figure 1. In particular, only one sharp band is observed in the terminal B–H stretching region, as expected. Thus, the hafnium complex has approximately the same geometry in solution as the zirconium complex, and this geometry is that shown in Figure 1, *i.e.*, the tridentate tetrahedral structure found in the gas phase[7] and in the solid state.[3]

Nuclear Magnetic Resonance Studies

The room-temperature pmr spectrum of $Zr(BH_4)_4$ dissolved in toluene-d_8 is shown at the bottom of Figure 3. The large quartet, the splitting of which is identical at 60 and 90 MHz, is attributed to coupling of four magnetically equivalent boron hydride protons bound to boron-11 ($I = {}^3/_2$), while the smaller peaks are due to a superimposed septet due to splitting of protons bound to boron-10 ($I = 3$). There is no evidence of

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"virtual coupling" which would be seen if there were substantial spin–spin coupling between protons and/or borons on different BH_4 groups attached to zirconium. The pmr spectrum of $Hf(BH_4)$ is nearly identical with that of the zirconium compound, the only difference being that the center of the multiplet is shifted *ca.* 1 ppm to lower field. Table I presents the relevant spectral data for the two compounds, which is in accord with but more complete than that reported by James, *et al.*[8] It should be noted that all the boron hydride lines are quite broad compared to those of the C_6D_5-CD_2H multiplet.

Table I. Nmr Data for I and II[a]

	Compound	
	$Zr(BH_4)_4$	$Hf(BH_4)_4$
δ^b	510.0 ± 2.0	410.1 ± 2.0
$J_{^{11}B-H}$	90.0 ± 0.3	88.6 ± 0.4
$J_{^{10}B-H}$	30.0 ± 0.2	29.6 ± 0.2

[a] All data in hertz for 0.5 *M* toluene-d_8 solutions. [b] Shift to high field of internal benzene.

Figure 3 also shows the temperature dependence of the $Zr(BH_4)_4$ pmr spectrum. It is quite evident that a symmetrical collapse of the entire spectrum takes place on cooling, which is not caused by loss of resolution due to increased viscosity or crystallization (see the $C_6D_5CD_2H$ multiplet). The variable-temperature behavior of $Hf(BH_4)_4$ is virtually identical with that of the zirconium compound. Furthermore, the line shapes at 60 MHz are the same within experimental error as those observed at 90 MHz. A dilution study also revealed that the spectral changes were independent of concentration over a 3.5-fold range, indicating the unimolecularity of the process.

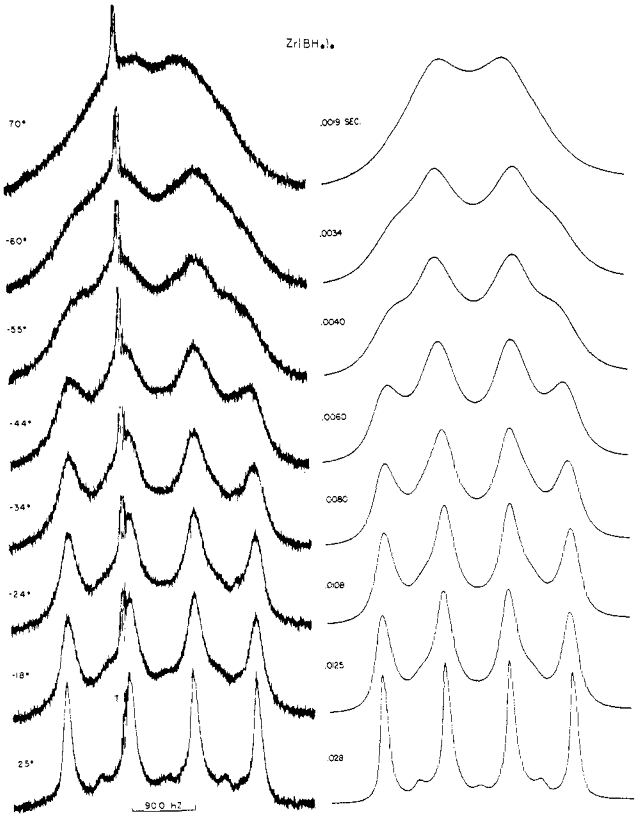

Figure 3. Left: variable-temperature 90-MHz pmr spectra of $Zr(BH_4)_4$ dissolved in toluene-d_8. The peak marked T is due to traces of $C_6D_5CD_2H$. Right: computed spectra for various ^{11}B spin–lattice relaxation times, T_1.

As mentioned above, the temperature dependence of the $Zr(BH_4)_4$ spectrum has been attributed[5a] to the slowing down of the intramolecular exchange process which permutes bridge and terminal hydrogens. We shall now demonstrate, by several lines of reasoning, that this explanation is incorrect. First, the field independence of the line shapes is contrary to what would be expected for an exchange process where the exchanging sites had an appreciable chemical shift difference. Also, the fact that the line shape collapse is symmetrical is not in accord with the fact that eventually chemically shifted resonances with relative areas of 3:1 must "freeze out." This leaves only the possibility that the terminal and bridging hydrogens have nearly identical chemical shifts and that the gross changes in line shape at intermediate rates of exchange arise from differences in magnitudes and/or signs of coupling constants and how they are averaged. First, there is no *a priori* reason to expect the bridging hydrogens attached to a transition metal, an environment which is known to induce large paramagnetic shifts of protons,[17] to have almost the same resonance frequency as a terminal hydrogen. The shift in the average BH resonance position (over 1 ppm) on going from zirconium to hafnium (Table I) is most reasonably explained by just this type of chemical shift change at the bridging hydrogens, induced by the metal. Also, it should be noted that there is usually a considerable difference in chemical shift between bridging and terminal hydrogens in the boron hydrides[18] (4.6 ppm in diborane[19]). Even if it is assumed that the bridging and terminal hydrogens fortuitously have the same chemical shift, employing what are reasonable values for the B–H coupling constants taken from the boron hydrides[18] ($J_{BH_t} \approx 2.5_{BH_b}$, and both coupling constants having the same sign), it is still not possible to rationalize the observed spectral behavior in terms of an exchange process since one would anticipate that upon lowering the temperature, the ^{11}B quartet would partially collapse and spread outward, rather than inward as observed. This is because the room-temperature J_{B-H} value is a weighted average of the two slow-exchange limit coupling constants, one of which must be larger than the average fast-exchange limit coupling constant. Additionally, numerous studies on other systems have shown it unlikely that the rates of fluxional processes will be identical for different metals in the same group of the periodic table. The most relevant example here is that of the dynamic π-allyl systems $M(h^3\text{-}C_3H_5)_4$, M = Zr, Hf, where the rates are greatly different (Hf ≫ Zr).[20] Thus, the postulate of a bridge–terminal exchange process as the sole cause of the slowing temperature dependent spectral changes is unten-

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able, and it will be shown that this exchange process is very rapid even at −80°.

The observed spectral behavior *is* in accord with the temperature-dependent "washing-out" of boron–hydrogen spin–spin coupling due to quadrupoler-induced transitions of the boron nuclei among their various spin states. This will have the phenomenological effect of "decoupling" the boron nucleus from the protons. The factors governing the spin–lattice relaxation of nuclei with quadrupole moments are understood theoretically, as are their manifestations in the magnetic resonance spectra of nuclei spin–spin coupled to them.[21] A brief discussion of the theory will be presented to explain the temperature dependence of the $M(BH_4)_4$ spectra and, on a more general level, to illustrate how significant information can be derived from the quantitative analysis of the nmr spectra of protons coupled to a relaxing quadrupolar nucleus.

In solution, a very efficient relaxation mechanism for nuclei with spin $I > {}^1/_2$ is one in which the quadrupole moment interacts with the electric field gradient at the nucleus, which is fluctuating due to rapid molecular reorientation. In the extreme narrowing region, *i.e.*, in which $\omega_0{}^2\tau_c{}^2 \ll 1$, where ω_0 is the frequency of a transition of the quadrupolar nucleus and τ_c is the correlation time characterizing the molecular tumbling responsible for quadrupole relaxation, the nuclear spin–lattice relaxation time is given by

$$\frac{1}{T_1} = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}(1+\eta^2/3)(e^2qQ/h)^2\tau_c \tag{1}$$

where I = nuclear spin, η = the asymmetry parameter at the quadrupolar nucleus, eq = the field gradient at the quadrupolar nucleus, eQ = the nuclear quadrupole moment of the nucleus, and e^2qQ = the nuclear quadrupole coupling constant. For the particular cases of $Zr(BH_4)_4$ and $Hf(BH_4)_4$, the structural data[3,7,11] show rigorous axial symmetry at the boron so that $\eta = 0$. Hence, for boron-10 ($I = 3$) and boron-11 ($I = {}^3/_2$)

$$\frac{1}{T_{1\,^{10}\mathrm{B}}} = \frac{3}{200}\left(\frac{e^2qQ}{h}\right)^2\tau_c \qquad Q = 0.074 \times 10^{-24}\ \mathrm{cm}^2 \tag{2}$$

$$\frac{1}{T_{1\,^{11}\mathrm{B}}} = \frac{1}{10}\left(\frac{e^2qQ}{h}\right)^2\tau_c \qquad Q = 0.0355 \times 10^{-24}\ \mathrm{cm}^2 \tag{3}$$

where the nuclear quadrupole moments are as given. Thus, it can be seen that two factors will govern the rate of spin-lattice relaxation of the boron nuclei. The magnitude of the quadrupole coupling constant, proportional to the field gradient at boron in the particular molecule, will determine how strongly the quadrupole moment couples to the fluctuations which are capable of inducing the relaxation. The rotational correlation time, characterizing how rapidly the molecule is undergoing reorientation in solution, also controls the rate of spin–lattice relaxation. Generally, the larger the molecule, the longer the correlation time.

The effect of the boron spin–lattice relaxation on the proton spectrum can now be described. Using ^{11}B as an example, at a slow spin–lattice relaxation rate, the pmr quartet observed can be thought of as due to protons resonating in the presence of the four possible boron spin states, $+{}^3/_2$, $+{}^1/_2$, $-{}^1/_2$, $-{}^3/_2$. As the spin–lattice relaxation time decreases, the lifetimes of the boron nuclear spin states decrease and, as in a site-exchange process, proton coupling to the boron nucleus begins to "wash out."[22] If the lifetimes become sufficiently short, the protons are unable to distinguish which boron state they are "seeing," and no coupling information is evident. The probability of transitions between the spin states of the quadrupolar nucleus ($\Delta m = \pm 1, \pm 2$) is given by[21]

$$k_{m,m\pm1} = k_{m\pm1,m} = \frac{(2m \pm 1)^2(I \pm m + 1)(I \mp m)}{2T_1(2I-1)(2I+3)} \tag{4}$$

$$k_{m,m\pm2} = k_{m\pm2,m} = \frac{(I \mp m)(I \mp m - 1)(I \pm m + 1)(I \pm m + 2)}{2T_1(2I-1)(2I+3)} \tag{5}$$

where m is the nuclear spin angular momentum. For a solution of a given compound, the temperature-dependent spectral changes will be due almost entirely to changes in τ_c.[23] Specifically, it is frequently observed (*vide infra*) that $\tau_c \propto \bar{\eta}/T$, where $\bar{\eta}$ is the macroscopic viscosity of the solution and T is the temperature. Lowering the temperature of the solution increases the correlation time both as an inverse function of T and, for most solutions, by increasing $\bar{\eta}$. The result is a very rapid rate of spin–lattice relaxation for the quadrupolar nucleus. No slowing intramolecular exchange process is required to produce a rather elaborate spectral temperature dependence.

Computer simulation[10,22] was next employed to determine if quadrupolar relaxation effects were sufficient to explain the observed spectra. It was desired to achieve a very accurate simulation so that the effect of temperature and viscosity on T_1 and τ_c could be studied and the boron quadrupole coupling constant estimated (*vida infra*). All studies of this sort have made the physically reasonable assumption that in diamagnetic systems such as those under discussion, short relaxation times of the magnitude observed can only arise if quadrupole coupling is the dominant mechanism of nuclear spin–lattice relaxation.[21] Allerhand has shown this to be the case for several boron hydrides.[24] Moniz and Gutowsky were able to demonstrate for ^{14}N compounds that competing relaxation mechanisms such as intramolecular dipole–dipole and spin–rotational interactions made only small contributions.[25] Likewise, broadening of the proton resonance *via* relaxation due to "modulation" of the ^{10}B–H and ^{11}B–H scalar interaction should be small.[21a,26] Thus, calculations of the proton line

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(22) R. J. Gillespie and J. W. Quail, *Can. J. Chem.*, 42, 2673 (1964).

(23) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London, 1969, Chapter 8.

(24) A. Allerhand, J. D. Odom, and R. E. Moll, *J. Chem. Phys.*, **50**, 5037 (1969).

(25) (a) W. B. Moniz and H. S. Gutowsky, *ibid.*, **38**, 1155 (1963). (b) Assuming a B–H distance of 1.2 Å and a relatively small ^{11}B quadrupole coupling constant of 0.5 MHz, the dipolar contribution in I and II can be shown to be quite small. However, the gyromagnetic ratios of ^{10}B and ^{11}B are larger than for ^{14}N,[25c] and the dipolar contribution is probably somewhat larger than that calculated in ref 25a for ^{14}N–H. (c) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965, p 590.

(26) J. P. Kintzinger and J. M. Lehn, *Mol. Phys.*, **54**, 133 (1968).

shapes as a function of boron T_1 can be made with the reasonable assumption that boron quadrupolar effects will dominate the observed spectral changes.

The proton line shapes for I and II were computed by a well-accepted method which treats the problem as a multisite exchange process.[21c,10,27] To ensure a complete line-shape analysis, the effects of *both* ^{11}B and ^{10}B coupling were included, by digitally superimposing the two sets of separately calculated, scaled spectra (see Experimental Section for details). As is evident in Figure 3, agreement between experimental and theoretical spectra is good.[28] This implies that quadrupolar effects are responsible for the spectral changes and that the intramolecular rate process is still rapid (probably greater than 10^4 sec^{-1}) at $-80°$. Efforts to reach lower temperatures have been frustrated by solubility problems and the great reactivity of these compounds toward most solvents.

Supplemental studies were carried out in similar solvents of varying viscosity, while holding the temperature constant. Since frequently $\tau_c \propto \bar{\eta}/T$, we wish to demonstrate that the most convenient way for chemists to routinely identify effects due to quadrupolar relaxation is by varying the viscosity of nmr sample solutions. Figure 4 shows room-temperature pmr spectra of I dissolved in perfluoropentane and Fluorolube. Infrared studies confirmed that no appreciable reaction takes place between the solvent and $M(BH_4)_4$ compounds in the course of several hours. Qualitatively (more quantitative experiments are discussed below), these solutions differed greatly in viscosity, and it can be seen that T_1 has been reduced dramatically on changing to more viscous Fluorolube solutions. We consider it highly unlikely that the rate of an internal rearrangement process would be so sensitive to viscosity.

It can be seen from eq 1 that knowledge of both T_1 and τ_c would allow calculation of the boron nuclear quadrupole coupling constants in I and II. Since these quantities are related to the electric field gradient at the boron nucleus, information about the bonding and electronic structure is obtainable. For molecules such as I and II, which are relatively complex and which probably have small quadrupole coupling constants ($\lesssim 5$ MHz), few convenient methods are available to measure e^2qQ/h.[29] Indeed, direct measurement of T_1 by various nmr techniques (*e.g.*, line-shape analysis,[10] pulsed methods[25a]) combined with an accurate estimate of τ_c may be the only practical way of obtaining these data in solution. The line-shape analysis method of studying quadrupole relaxation, which we used here, offers the great advantage to chemists that it utilizes the same instrumentation and software commonly employed for other dynamic nmr studies.

Computation of τ_c requires a model to best describe the tumbling of molecules in solution. At present, there is some controversy concerning how to derive the most realistic correlation time and how to most accurately describe the microdynamical behavior of solutions in general. Fortunately, the form of eq 1 is such that the error in e^2qQ/h will only reflect the square root of the error in τ_c. It will be seen that the high symmetry of I and II simplifies most calculations of τ_c, probably ensures that reasonably accurate quadrupole coupling constants can be estimated, and allows some qualitative conclusions to be drawn about the mechanism of the spin–lattice relaxation process.

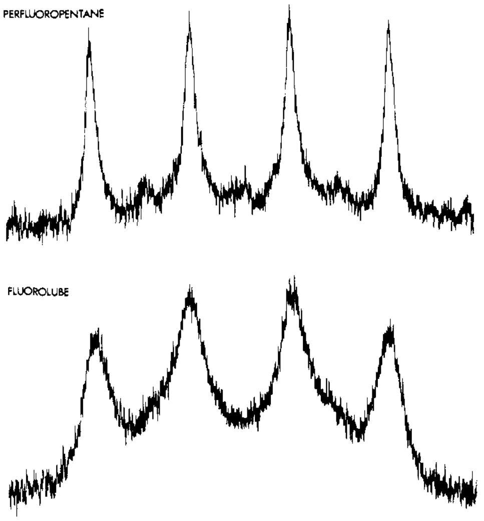

Figure 4. Room-temperature proton nmr spectra at 90 MHz of $Zr(BH_4)_4$ solutions as a function of viscosity. The concentration of $Zr(BH_4)_4$ and the line width of internal benzene were approximately the same in the two samples.

Early calculations of τ_c[30] were based on the Stokes–Einstein hydrodynamic equation, which treated the tumbling molecule as a sphere rotating in a homogeneous medium of macroscopic viscosity $\bar{\eta}$, *i.e.*, the molecular rate of reorientation was supposed to be completely controlled by frictional forces

$$\tau_c = 4\pi\bar{\eta}a^3/3kT \qquad (6)$$

where a is the molecular radius, which is usually obtained from the molar volume assuming hexagonal closest packing of the molecules as hard spheres. Except for small, highly polar molecules, correlation times calculated by this method have been approximately one order of magnitude larger than those observed experimentally. Also, the equation in the form given above makes no provision for solutions. Gierer and Wirtz[31] have proposed a more satisfactory, modified Stokes equation, which employs an intuitively more satisfying "microviscosity,"[31] gives results in generally good agreement with experiment,[32,33] and is readily applicable to solutions

$$\tau_c = (a_{\text{solute}})(V_{\text{solute}})\bar{\eta}/6kT(a_{\text{solvent}}) \qquad (7)$$

where V_{solute} is the hard-sphere hexagonal closest

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(27) (a) M. Suzuki and R. Kubo, *Mol. Phys.*, **7**, 201 (1964); (b) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43**, 4107 (1965).

(28) (a) Our initial attempts at spectral simulation encountered some difficulty until it was discovered that the value given in a number of nmr textbooks (taken from a Varian table) for the quadrupole moment of ^{10}B was in error. An improved simulation was obtained with a correct value[28b] (given in eq 2). The spectral line shapes are sensitive to the ratio $T_{1\,^{11}\mathrm{B}}/T_{1\,^{10}\mathrm{B}}$, which in turn is proportional to $(Q_{^{10}\mathrm{B}}/Q_{^{11}\mathrm{B}})^2$, and the incorrect value of $Q_{^{10}\mathrm{B}}$ could thus be detected. (b) J. A. S. Smith, *J. Chem. Educ.*, **48**, 39 (1971); *cf.* R. K. Nesbet, *Phys. Rev. A*, **2**, 1208 (1970).

(29) Reference 23, Chapter 3.

(30) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(31) A. Gierer and K. Wirtz, *Z. Naturforsch., A*, **8**, 532 (1953).

(32) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **7**, 515 (1964).

(33) D. E. Woessner, B. S. Snowden, Jr., and T. E. Strom, *ibid.*, **14**, 265 (1968).

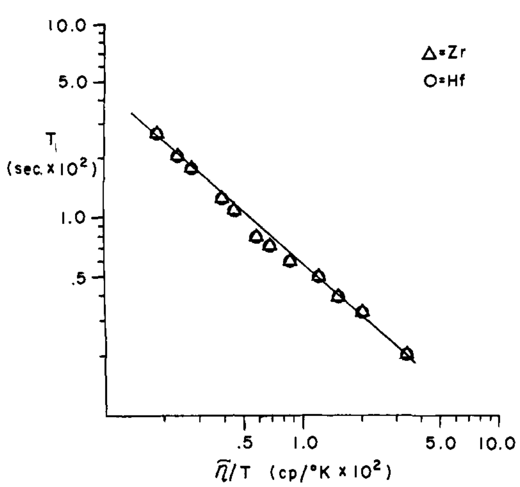

Figure 5. The dependence of the ^{11}B spin–lattice relaxation time on temperature and solution viscosity for toluene-d_8 solutions of I and II.

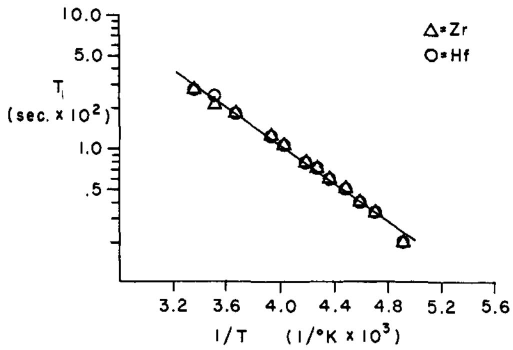

Figure 6. The temperature dependence of the ^{11}B spin–lattice relaxation time for toluene-d_8 solutions of I and II.

packed volume of the solute, and a_{solute} and a_{solvent} are radii as in eq 6. Another variant[34] of the hydrodynamic approach also yields results in reasonable agreement with experiment. An essential feature of all three treatments is that $\tau_c \propto \bar{\eta}/T$; hence, from eq 1, that $1/T_1 \propto \bar{\eta}/T$. We were anxious to test to what degree the boron spin–lattice relaxation in solution conforms to the Stokes hydrodynamic description of molecular reorientation, since the validity of the hydrodynamic description is a matter of some dispute.[35] For $1/T_1$ *vs.* $\bar{\eta}/T$ plots, it was desirable to know the viscosity of $M(BH_4)_4$ solutions at a number of temperatures. The extreme sensitivity of the solutions precluded an experimental determination, and published viscosities for pure toluene[10] were employed instead. That the spectral line shapes were invariant in the aforementioned dilution studies supports the assumption that the viscosity behavior of the relatively dilute (*ca.* 0.5 *M*) toluene solutions of I and II is approximated by the behavior of the pure solvent. Figure 5 shows that log–log plots of T_1 *vs.* $\bar{\eta}/T$ for both I and II are essentially linear over a fairly large range of temperature and viscosity; the two plots are also coincident within experimental error. These results are in accord with a model in which frictional forces play a large role in controlling molecular reorientation, *i.e.*, $1/T_1 \propto \bar{\eta}/T$.

Criticism of the Stokes frictional approach has come from a number of theoretical treatises[35,36] which indicate that the rotational inertia of the tumbling molecule must be considered in the calculation of τ_c. Various treatments have taken into account both inertial and hydrodynamic effects or solely inertial effects, depending on the derivation as well as the size and shape of the molecule. Steele[36b] has shown for approximately spheroidal, nonpolar molecules which do not interact strongly with the solvent, that τ_c should be fairly independent of frictional forces in molecular reorientation processes that are governed solely by inertial effects (the "inertial limit"[35]). If molecules I and II are assumed to be *approximately* spheroidal (*i.e.*, angular independence of the intermolecular potential function[36b]), then the strong viscosity dependence of T_1 seen in noncoordinating toluene[38] and fluorocarbons appears to be at variance with a purely inertial model.

Activation parameters for molecular reorientation[35a] can be obtained from the equation

$$\tau_c = \tau_c{}^0 \exp(E_a/RT)$$

By plotting log T_1 *vs.* $1/T$, an Arrhenius plot is obtained with slope $-E_a/2.303R$, where E_a is the Arrhenius activation energy for molecular reorientation. Figure 6 presents such straight plots for I and II, and, within experimental error, the zirconium and hafnium data are coincident, with $E_a = 3.1 \pm 0.1$ kcal/mol. Thus, despite disparate masses (molecular weights: $Zr(BH_4)_4$, 150.6; $Hf(BH_4)_4$, 237.9), these molecules have about the same thermal barriers to reorientation processes leading to quadrupolar relaxation. Both the hydrodynamic and inertial models predict this type of behavior, since the dimensions of I and II[37] (hence, the molecular radii and volumes, as well as moments of inertia) must be very nearly the same. In accord with theory,[21] only the rotational motions are effective in quadrupolar relaxation processes. Thus, our results indicate that in this particular system, hydrodynamic effects are important in describing (if only phenomenologically) microdynamical solute–solvent behavior, and purely inertial models appear not to provide a complete description.

The above discussion suggests that correlation times and nuclear quadrupole coupling constants of reasonable accuracy can be calculated, starting from the equation of Gierer and Wirtz[31] (eq 7). The facts that I and II are nearly spherical and that the solute and solvent molecules have approximately the same sizes satisfies the derivation of eq 7, as does the evidence that I and toluene do not interact strongly.[38] For eq 7, the parameters a_{solute} and a_{solvent} were obtained by calculating the hard-sphere, hexagonal closest packing volumes (V_{solute}, V_{solvent}) from the molar volumes, V_m, using the relationship[31]

$$4\pi a^3/3 = 0.74V_m$$

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(34) G. J. Jenks, *J. Chem. Phys.*, **54**, 658 (1971).

(35) W. T. Huntress, Jr., *Advan. Magn. Resonance*, **4**, 1 (1970).

(36) (a) R. W. Mitchell and M. Eisner, *J. Chem. Phys.*, **33**, 86 (1960); (b) W. A. Steele, *ibid.*, **38**, 2404, 2411 (1963); (c) W. B. Moniz, W. A. Steele, and J. A. Dixon, *ibid.*, **38**, 2418 (1963); (*d*) H. Shimizu, *Bull. Chem. Soc. Jap.*, **39**, 2385 (1966).

(37) The effective ionic radii for Zr(IV) and Hf(IV) are nearly the same [R. D. Shannon and T. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969)], as are the single-bond metallic radii for Zr and Hf (L. Pauling, "The Chemical Bond," Cornell University Press, Ithaca, N. Y., 1967, Chapter 7).

(38) V. V. Volkov, K. G. Myakishev, and G. I. Bagryantsev, *Russ. J. Inorg. Chem.*, **15**, 996 (1970).

The molar volumes were obtained for I and II from the unit cell crystallographic data for I[3] (assuming I and II to be the same size) and for toluene, from the density.[39] The calculated τ_c's were combined in eq 1 with $1/T_1$ values obtained in the computer simulation, to yield estimates of e^2qQ/h. In order to gain some insight into the nature and magnitude of random errors which could be involved in this calculation, the quadrupole coupling constants were computed at a number of temperatures, using the appropriate T_1 and τ_c values.[40] The results are given in Table II, and the precision observed neglecting the region of high viscosity and low temperature (where large errors are possible) is surprisingly good. We estimate the ^{11}B nuclear quadrupole coupling constants in I and II to be 1.7 ± 0.3 MHz.

Table II. Nuclear Quadrupole Coupling Constant Data for I and II

Compound	Temp, °C	τ_c, sec[a]	e^2qQ/h, MHz ^{11}B	e^2qQ/h, MHz ^{10}B[b]
I	25	3.29×10^{-12}	1.67	3.48
II	25	3.29×10^{-12}	1.67	3.48
I	−10	6.17×10^{-12}	1.70	3.54
II	−10	6.17×10^{-12}	1.70	3.54
I	−40	1.27×10^{-11}	1.71	3.56
II	−40	1.27×10^{-11}	1.71	3.56
I	−60	3.53×10^{-11}	1.46	3.04
II	−60	3.53×10^{-11}	1.46	3.04

[a] Calculated from eq 7. [b] Calculated from the relationship $Q_{^{10}B}/Q_{^{11}B} = 2.08$.

A detailed analysis of the e^2qQ/h data would require more exact structural information and a series of compounds for comparison purposes. Some qualitative conclusions can be drawn. First, the size of the coupling constant is relatively large. Though extensive data[41] are not available for four-coordinate boron, it appears that in I and II there is little contribution from an ionic resonance hybrid such as

$$M^+ \; BH_4^-$$

in which e^2qQ/h is expected to be nearly zero. For borates in which boron is bonded to four oxygen atoms, solid-state e^2qQ/h values typically fall in the range 50–700 KHz,[42] even when there is substantial deviation of the BO_4 moiety from tetrahedral symmetry. In H_3BCO, e^2qQ/h (in the gas phase) is 1.55 ± 0.08 MHz.[43] For alkali metal tetrahydroborates[44] and tetrafluoroborates[44c] solid-state coupling constants are invariably less than 200 KHz, even in cases of low site symmetry. Our results are thus consistent with the covalent nature of I and II. One explanation for the size of the field gradient at boron may be that there is considerable direct interaction between the transition metal and boron. This is in accord with structural data,[7] where the zirconium to bridging hydrogen distance, 2.21 (0.04) Å, is only slightly shorter than the zirconium to boron distance, 2.31 (0.01) Å. The fact that the quadrupole coupling constants for I and II are, within experimental error, the same is not surprising, in view of the numerous similarities in zirconium and hafnium chemistry.[45]

Finally, some discussion of the fluxional bridge–terminal hydrogen exchange process is appropriate. This process was found to be rapid ($1/\tau \gtrsim 10^4$) at −80°. It has been suggested[5d,8] that bidentate tetrahydroborates could scramble bridge and terminal hydrogens *via* a monodentate structure. We feel a more plausible pathway could involve a tridentate $\rightleftharpoons$ bidentate interconversion which would be general for all known tetrahydroborates of structure A or B. Tridentate molecules could equilibrate the two types of hydrogens *via* a higher energy bidentate configuration; in a complementary fashion, molecules with a ground-state bidentate structure could populate a tridentate geometry to execute the interconversion process. The two cases occupy similar but inverted reaction coordinates.

If the rate of an intramolecular rearrangement process is sufficiently rapid to render the local correlation time of a quadrupolar nucleus comparable to or less than that of the entire molecule, it may be possible to detect that process[21b,46] and to derive a rough estimate of the local correlation time. One restriction is that the local process involve substantial reorientation of the field gradient at the quadrupolar nucleus, with respect to both the molecular framework and the static magnetic field. This is because the quadrupolar relaxation mechanism requires fluctuation of the field gradient, and the local correlation time must be small enough not to be swamped by the tumbling of the entire molecule (*e.g.*, a spinning $-CH_2D$ group attached to a large, aromatic hydrocarbon[46b,c]). For metal tetrahydroborates such as I and II, local "spinning in place" of the BH_4 group does not involve rearrangement of the field gradient, and the relaxation time of the boron nuclei would be controlled by the tumbling of the entire molecule. A number of intramolecular mechanisms are conceivable in which the bridge–terminal interchange process is coupled with a reorientation of the M–B vector (as in a rearrangement of the coordination geometry about the metal). However, with the limited number of data at hand, all that can be concluded is that the T_1 *vs.* $1/T$ plot (Figure 6) gives no indication that more than one rate process is occurring for I or II, as might be evidenced by a pronounced nonlinearity.

Conclusions

The molecules $Zr(BH_4)_4$, I, and $Hf(BH_4)_4$, II, possess nearly identical structures in solution, *i.e.*, the tridentate structure shown in Figure 1. This structure, however, is not rigid and even at −80° there is a rapid, intramolecular interchange of bridge and terminal hydrogens. The reported temperature dependence of the pmr spectra of I and II is due predominately, if not

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(39) "International Critical Tables," Vol. VII, McGraw-Hill, New York, N. Y., 1930, p 218.

(40) Nuclear quadrupole coupling constants in solution are not expected to exhibit an appreciable temperature dependence.[23]

(41) Reference 23, p 261.

(42) (a) K. C. Lal and H. E. Petch, *J. Chem. Phys.*, **43**, 1834 (1965); (b) H. M. Kriz and P. J. Bray, *J. Magn. Resonance*, **4**, 76 (1971).

(43) W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

(44) (a) T. Tsang and T. C. Farrar, *J. Chem. Phys.*, **50**, 3498 (1969); (b) G. W. Ossman and J. W. McGrath, *ibid.*, **47**, 5452 (1967); (c) A. H. Silver and P. J. Bray, *ibid.*, **32**, 288 (1960).

(45) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 913.

(46) (a) M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965); (b) Ch. Brevard and J. M. Lehn, *J. Amer. Chem. Soc.*, **92**, 4987 (1970); (c) Ch. Brevard, J. P. Kintzinger, and J. M. Lehn, *Chem. Commun.*, 1193 (1969).

entirely, to the variable rate of ^{10}B and ^{11}B quadrupole relaxation, which progressively "washes out" the boron–hydrogen spin–spin coupling. The boron spin-lattice relaxation follows an $\tilde{\eta}/T$ dependence, which implicates hydrodynamic (frictional) effects in the description of molecular reorientation leading to quadrupole relaxation, though inertial effects are also probably operating. Computation of the molecular correlation time based on a hydrodynamic model allows a reasonably accurate estimation of the nuclear quadrupole coupling constants, which are identical for I and II: ^{10}B, 3.5 ± 0.6 MHz; ^{11}B, 1.7 ± 0.3 MHz. These values indicate the metal–ligand bonding deviates significantly from an ionic description, and are qualitatively in accord with the covalent properties of the molecules. The Arrhenius activation energies for molecular reorientation are, within experimental error, the same for $Zr(BH_4)_4$ and $Hf(BH_4)_4$, 3.1 ± 0.1 kcal/mol. There is no evidence that an intramolecular rearrangement process is rapid enough to compete with molecular tumbling as a mechanism for quadrupolar relaxation.

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Reaction of Tetrasulfur Tetranitride with Strained Olefins[1]

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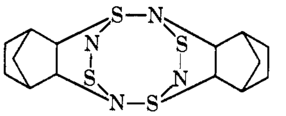
Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05401. Received July 8, 1971

Abstract: Tetrasulfur tetranitride has been shown to undergo cycloaddition reactions with strained, rigid bicyclic olefins such as norbornene and other [2.2.1] bicyclic systems. The nmr, ir, and mass spectra of the resulting bis cycloadducts indicate that the norbornyl unit is bonded to S_4N_4 through the nitrogen atoms and has the exo-cis stereochemistry. Total exchange in solution of one norbornyl unit for another was demonstrated, and competition experiments enabled the establishment of a relative reactivity sequence.

The study of the chemistry of tetrasulfur tetranitride, S_4N_4, has revealed an intriguing and complex pattern of structure and reactivity.[2–4] Tetrasulfur tetranitride has been shown to undergo Lewis acid–base, redox, and ring contraction reactions. Becke-Goehring and Schwarz have reported some novel adducts which are formed from S_4N_4 and norbornene, norbornadiene, and cyclopentadiene in an apparent cycloaddition reaction.[5] They proposed a 1,4-cycloaddition wherein the olefin is bonded to alternate sulfur and nitrogen atoms, as in **1**. However, no convincing evidence was presented to support this proposed structure. Josey has shown that the interaction of S_4N_4 with substituted acetylenes leads to 1,2,5-triadiazoles;[6] this suggests attack solely on nitrogen (as in **2**) as a possibility for the olefin system. Recent MO calculations coupled with orbital symmetry considerations suggest attack solely on sulfur (as in **3**).[7] Since, with the exception of the work of Becke-Goehring and Schwarz, cycloaddition reactions are unknown for inorganic heterocycles which contain multiple bonds, such as S_4N_4, we have investigated this system in order to establish the effect of reaction conditions on the nature of the product, the type of olefin capable of undergoing this reaction, and the structures of the products.



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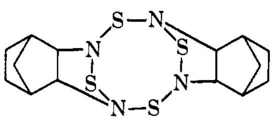

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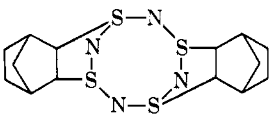

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Experimental Section

Materials. Tetrasulfur tetranitride[8] and 2,3-trithianorbornane, $C_7H_{10}S_3$,[9] were prepared by published procedures. All other reactants and solvents were available commercially and used without further purification.

Measurements. The 60-MHz proton nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer and the 100-MHz nmr spectra on a JEOL MH-100 spectrometer. All nmr spectra were run in deuteriochloroform with TMS as an internal standard. Mass spectra were obtained with a Perkin-Elmer RMU-4 mass spectrometer operating at 70 eV and 130°. Infrared spectra were recorded on Perkin-Elmer Model 51 and Beckman Model 5A (CsBr) spectrophotometers. Raman spectra were recorded on a JEOL JRS-S1 Laser Raman spectrometer using an Ar-ion laser. Photolysis reactions were carried out using

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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

[2] M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 207 (1959).

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[5] M. Becke-Goehring and R. Z. Schwarz, *Z. Anorg. Allg. Chem.*, **296**, 1 (1958).

[6] A. D. Josey, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Division of Organic Chemistry, p 14.

[7] R. Gleiter, *J. Chem. Soc. A*, 3174 (1970).

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