

44

[Reprinted from the Journal of Physical Chemistry, 76, 2871 (1972).]
Copyright 1972, by the American Chemical Society and reprinted by permission of the copyright owner.

Nitrogen and Boron Spin-Lattice Relaxation in Borazole¹

by George M. Whitesides,* Steven L. Regen,² John B. Lisle, and Robert Mays

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received January 7, 1972)

Publication costs assisted by the National Institutes of Health

The observed line shapes of the ¹H nuclear magnetic resonance spectra of neat borazole and of borazole in toluene-*d*₆, dimethyl-*d*₆ sulfoxide, chloroform-*d*, and cyclohexane-*d*₁₂ solutions are dominated by broadening due to the electric quadrupole-dependent nuclear spin-lattice relaxation of nitrogen and boron. Comparisons of observed spectra for borazole with those calculated for varying values of the nitrogen and boron spin-lattice relaxation rates establish that a parameter $f = [\tau(eq)^2]_{\text{B}}/[\tau(eq)^2]_{\text{N}}$ characterizing the relative response of the boron and nitrogen nuclei to rotational diffusion (eq 3) is indistinguishable from unity ($f = 1.0 \pm 0.1$) over a range of experimental conditions in these media. These observations are rationalized satisfactorily by eq 1 and provide empirical support for the usefulness of this equation in describing the influence of molecular motion on the rates of spin-lattice relaxation of quadrupolar nuclei. Spin-lattice relaxation of nitrogen is more rapid than that of boron in solutions containing the stable free radical di-*tert*-butylnitroxyl, presumably due to weak specific interactions between the borazole molecule and the nitroxyl radical. Combination of spin-lattice relaxation times inferred from the ¹H spectra of borazole with an estimate of its mean rotational correlation time in solution leads to approximate values for the quadrupole coupling constants: $(e^2qQ/h) \cong 7.6 \pm 2.9$ MHz (¹⁰B); 3.6 ± 1.3 MHz (¹¹B); 1.4 ± 0.5 MHz (¹⁴N).

Introduction

The determination of spin-lattice relaxation times for quadrupolar nuclei is a technique of increasing importance in the study of molecular motions in solution.³⁻⁵ Interpretation of these relaxation time measurements in terms of molecular motions rests on the assumption that relaxation is dominated by quadrupolar interactions and that contributions from dipole-dipole, anisotropic shielding, and spin-rotation interactions are unimportant. With this assumption,

equations having the form of eq 1 are used to relate re-

$$\frac{1}{T_{1X}} = \left(\frac{3}{40}\right) \left(\frac{2I+3}{I^2(2I-1)}\right) \left(\frac{e^2qQ}{\hbar}\right)^2 \left(1 + \frac{\eta^2}{3}\right) \tau_{\text{RX}} \quad (1)$$

laxation times to molecular motion. Here T_{1X} is the

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 4032), and to the National Institutes of Health (Grant No. GM-16020) for support of this research.

(2) A. D. Little Fellow, 1969-1970.

spin-lattice relaxation time of nucleus X, I is the nuclear spin of X, eQ is the electric quadrupole moment of the nucleus, $eq = \partial E/\partial z = \partial^2 V/\partial z^2 = V_{zz}$ is the principal component of the electric field gradient tensor at the nucleus, $\eta = [V_{xx} - V_{yy}]/V_{zz}$ is the asymmetry parameter describing the deviation of the electric field gradient tensor from axial symmetry, and τ_X , at the simplest level of interpretation, is a mean correlation time characterizing the power spectrum of the electric field gradient fluctuations at the nucleus that are effective in inducing magnetic dipole transitions.^{6,7}

The assumptions underlying this equation are undoubtedly tenable in the great majority of studies in solutions of normal viscosities, and the equation appears to have very generally applicable form. However, despite theoretical expansions of τ_X in terms of other microscopic parameters, particularly the components of the rotational diffusion tensor,³ the physical interpretation to be placed on this correlation time remains vague, depending significantly on the model chosen to generate the power spectrum of the electric field fluctuations resulting from molecular motion. In particular, the relative usefulness of inertial and diffusional models for molecular reorientation, and the interpretation of the "microscopic" viscosities commonly used in the diffusional treatments,^{4,8-10} are not clear. Further, although there is some agreement that for most nonionic molecules the *major* contributions to the field gradient fluctuations responsible for spin-lattice relaxation arise from the reorientation of the molecule containing the quadrupolar nucleus being observed, rather than from motions of other molecules in solution,³ the influence of relatively weak *intermolecular* interactions on the relaxation behavior of quadrupolar nuclei has not been thoroughly explored.

This paper describes measurements of the temperature, viscosity, and solvent dependence of the spin-lattice relaxation times of the nitrogen and boron atoms of borazole, obtained by examination of the ¹H nmr line shapes of this substance. These measurements were intended to search for deviations of the experimental relaxation times from the behavior expected from an equation having the form of eq 1 and to help to define, in an empirical sense, the sensitivity of quadrupole relaxation rates to the intermolecular and environmental effects that are presently impractical to include in theoretical discussion. Borazole was chosen for the subject of this study because the presence of two chemically distinct¹¹ quadrupolar nuclei in a single rigid molecule of high symmetry provides an opportunity to circumvent some of the uncertainties inherent in eq 1 by focusing attention on *comparison* of the magnitudes of nitrogen and boron spin-lattice relaxation rates rather than on the *absolute* magnitudes of these rates. Thus, on the basis of eq 1, the spin-lattice relaxation times of, *e.g.*, ¹¹B and ¹⁴N should be related by eq 2.¹² We assume at the outset that the term con-

$$\frac{T_{1,^{14}\text{N}}}{T_{1,^{11}\text{B}}} = \left(\frac{4}{15}\right) \left(\frac{\tau_{^{11}\text{B}}}{\tau_{^{14}\text{N}}}\right) \left(\frac{e^2qQ_{^{11}\text{B}}}{e^2qQ_{^{14}\text{N}}}\right)^2 \left(\frac{3 - \eta^2_{^{11}\text{B}}}{3 + \eta^2_{^{14}\text{N}}}\right)$$

taining the asymmetry parameters η in this equation can be neglected. The magnitudes of these terms are not known for borazoles; however, for most organic compounds η is sufficiently small that η^2 is less than 0.1.¹² Thus, in all probability, the contributions from $\eta_{^{11}\text{B}}$ and $\eta_{^{14}\text{N}}$ could individually be safely neglected in eq 2; the error introduced by setting equal to unity the *quotient* that constitutes the last term in this equation is undoubtedly well within the final experimental uncertainty in this work ($\sim \pm 10\%$ for the ratio $T_{1,^{14}\text{N}}/T_{1,^{11}\text{B}}$; *vide infra*). Thus, since the nuclear quadrupole moments Q are known quantities,^{13,14} eq 2 can be rewritten in more compact form (eq 3). It is not prac-

$$\frac{T_{1,^{14}\text{N}}}{T_{1,^{11}\text{B}}} = 1.64 \left(\frac{\tau_{^{11}\text{B}}}{\tau_{^{14}\text{N}}}\right) \left(\frac{eq_{^{11}\text{B}}}{eq_{^{14}\text{N}}}\right)^2 = 1.64f \quad (3a)$$

$$f = \frac{[\tau(eq)^2]_{\text{B}}}{[\tau(eq)^2]_{\text{N}}} \quad (3b)$$

tical to make a reliable *a priori* estimate of the ratio $(eq_{\text{B}}/eq_{\text{N}})^2$; however, it is possible to estimate the ratio $\tau_{\text{B}}/\tau_{\text{N}}$. The nitrogen and boron nuclei occupy symmetry-equivalent positions in the borazole skeleton.

(3) Review: W. T. Huntress, Jr., *Advan. Magn. Resonance*, **4**, 2 (1970); *J. Chem. Phys.*, **48**, 3524 (1968); R. A. Dwek and R. E. Richards, *Discuss. Faraday Soc.*, **43**, 196 (1967); J. A. Pople, *ibid.*, 192 (1967).

(4) T. T. Bopp, *J. Chem. Phys.*, **47**, 3621 (1967); T. D. Alger and H. S. Gutowsky, *ibid.*, **48**, 4625 (1968); R. K. Harris and N. C. Pyper, *Mol. Phys.*, **20**, 467 (1971); and references in each.

(5) R. P. Hangland, L. Stryer, T. R. Stengle, and J. D. Baldeschwieler, *Biochemistry*, **6**, 498 (1967); R. G. Bryant, *J. Amer. Chem. Soc.*, **89**, 2496 (1967); Ch. Brevard and J. M. Lehn, *ibid.*, **92**, 4987 (1970).

(6) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, Chapters VII and VIII; C. P. Slichter, "Principles of Magnetic Resonance," Harper and Row, New York, N. Y., 1963, Chapters 5 and 6.

(7) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43**, 4107 (1965), and references therein.

(8) E. W. Randall and D. Shaw, *Spectrochim. Acta, Part A*, **23**, 1235 (1966); D. W. Aksnes, S. M. Hutchinson, and K. J. Packer, *Mol. Phys.*, **14**, 301 (1968); M. Arnold and K. J. Packer, *ibid.*, **10**, 141 (1966); C. Deverell, D. J. Frost, and R. E. Richards, *ibid.*, **9**, 564 (1965).

(9) W. A. Steele, *J. Chem. Phys.*, **38**, 2404 (1963); P. S. Hubbard, *ibid.*, **53**, 985 (1970); S. G. Brush, *Chem. Rev.*, **62**, 513 (1962); A. Bondi, *J. Amer. Chem. Soc.*, **88**, 2131 (1966).

(10) D. E. Woessner, *J. Chem. Phys.*, **40**, 2341 (1964); K. T. Gillen and J. H. Noggle, *ibid.*, **52**, 4905 (1970); W. B. Moniz and H. S. Gutowsky, *ibid.*, **38**, 1155 (1963); H. Shimizu, *ibid.*, **40**, 754 (1964).

(11) For a review of borazoles, see H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. II, Wiley, New York, N.Y., 1966, pp. 174-434; O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, **93**, 5066 (1971), and references therein.

(12) For examples, see C. T. O'Konski, "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 11.

(13) The values of the nuclear quadrupole moments used in this paper are (in esu cm²) $eQ(^{14}\text{N}) = 1.56 \times 10^{-26}$,^{13a} $eQ(^{10}\text{B}) = 8.04 \times 10^{-26}$,^{13b} $eQ(^{11}\text{B}) = 3.86 \times 10^{-26}$.^{13b}

(14) (a) C. T. O'Konski and T. Ha, *J. Chem. Phys.*, **49**, 5354 (1968); see also C. C. Lin, *Phys. Rev.*, **119**, 1027 (1960); (b) H. Schaefer, R. Klemm, and F. Harris, *ibid.*, **176**, 49 (1968).

In consequence, in the absence of association between borazole and other components of the solution, the diffusional motion of boron and nitrogen nuclei with respect to the external magnetic field should be identical. Thus, the ratio τ_B/τ_N , at the simplest level of interpretation, would be expected to be unity.

The technique used to determine relaxation times in this work yields simultaneous measurements on nitrogen and boron, two nuclei having magnetic dipole transitions at different frequencies [$\nu_0(^{14}\text{N}) = 4.33$ MHz, $\nu_0(^{11}\text{B}) = 19.25$ MHz at 14 kG], and characterized by different chemical shift anisotropies and dipole-dipole interactions with other spins in the solution. Since comparison of the ratio of the relaxation times of these two nuclei should serve to reduce the importance of several possible types of experimental error, small contributions to relaxation rates from sources other than the fairly restricted set covered by eq 1 might be detectable in borazole that would be difficult to detect in other compounds. Thus, in particular, fluctuations in the magnitude of the parameter f (eq 3b) on changing solution composition, viscosity, or temperature should be attributable either to a failure of eq 1, or to the influence of specific intermolecular association between solvent and the boron or nitrogen nuclei, since eq 1 clearly implies that f should be invariant to the nature of the medium in the absence of intermolecular association effects.

The influence of quadrupole relaxation on the ^1H nmr spectrum of borazole and its analogs has been discussed previously.¹⁵

Results

The ^1H nmr spectrum of a sample of neat borazole containing a small amount of benzene as an internal resolution standard at -8° consists of a triplet arising from protons bonded to ^{14}N [$J(^1\text{H}, ^{14}\text{N}) = 54 \pm 2$ Hz] centered at δ 5.47, superimposed on a quartet due to protons on ^{11}B [$J(^1\text{H}, ^{11}\text{B}) = 135 \pm 3$ Hz, δ 4.43]; the expected septet due to protons on ^{10}B ($\sim 19\%$ natural abundance) is obscured by the more intense ^{11}B - H resonances (Figure 1). Lowering the temperature of the sample to -72° results in partial collapse of the NH and BH signals to broad superimposed singlets. Although complete collapse cannot be observed in samples composed mainly of borazole because these samples freeze at $\sim -55^\circ$, samples in dimethyl- d_6 sulfoxide (DMSO- d_6 , 68% v/v) show two relatively sharp peaks at -62° . Samples of borazole in toluene- d_6 could be cooled to -80° before freezing; spectra at these low temperatures resemble those observed for 68% borazole in DMSO- d_6 . The line widths characteristic of all of these spectra were never sufficiently narrow to permit observation of ^1H - N - B - ^1H , ^1H - B - ^{14}N , or ^1H - N - ^{11}B spin-spin coupling, although partial decoupling indicated that two bond heteronuclear couplings were not important: thus, the ^1H nmr spectrum

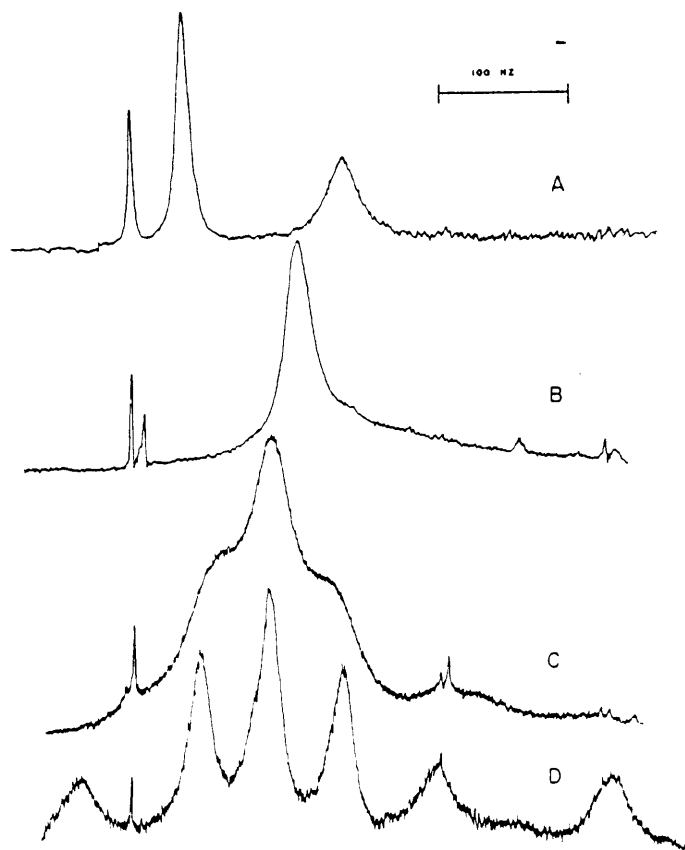


Figure 1. ^1H nmr spectra at 60 MHz of (A) borazole in DMSO- d_6 (68% v/v) at -62° , (B) borazole in toluene- d_6 (33% v/v) at -80° , (C) borazole (neat) at -72° , and (D) borazole (neat) at -8° . The sharp line at low field in each spectrum is the benzene used as an internal line width standard.

of neat borazole at 30° showed that no significant change in the shape of the lines comprising the H - ^{14}N triplet accompanied collapse of the H - ^{11}B quartet on irradiation at the boron resonance frequency.

The difference in the appearance of the borazole spectra in neat samples and in toluene and DMSO solution are primarily a reflection of the differences in viscosities of these samples, rather than of sample temperatures.¹⁶ The Gierer and Wirtz modification of the Stokes equation provides a fairly satisfactory empirical relation between the temperature and bulk viscosity of the sample, dimension of solvent and solute molecules, and the nmr rotational correlation times of the solute (eq 4).¹⁷ This equation contains the assumptions that

(15) H. Watanabi, T. Torani, and M. Ohtsuru, *Mol. Phys.*, **14**, 367 (1968). A recent paper by E. K. Mellon, B. M. Coker, and P. B. Dillon, *Inorg. Chem.*, **11**, 852 (1972), describes an investigation of the nmr spectrum of borazole closely related to that described in this article.

(16) See G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 2245 (1969), for a discussion of this point.

(17) A. Gierer and K. Wirtz, *Z. Naturforsch. A*, **8**, 532 (1953); D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **7**, 515 (1964). See R. A. Assink, J. DeZwaan, and J. Jonas, *J. Chem. Phys.*, **56**, 4975 (1972), for a recent experimental investigation of certain of the assumptions underlying this treatment.

one correlation time is sufficient to describe the rotational behavior of the solute and that the difference between the macroscopic and "microscopic" viscosities can be taken into account by the "microviscosity factor" of $1/6$.¹⁷

$$\tau_X = \frac{r_{\text{solute}}\tau_s}{6r_{\text{solvent}}} = \frac{(r_{\text{solute}})(V_{\text{solute}})\eta}{6kT(r_{\text{solvent}})} \quad (4)$$

Here r_{solute} and r_{solvent} are hard-sphere radii for solute and solvent molecules (cm), τ_s is the Stokes correlation time (sec), V_{solute} is the hard-sphere "volume" of the solute, and η is the macroscopic solution viscosity (poise). On the basis of this equation, τ_X should depend on both η and T ; however, in practice, the change in sample viscosity η on changing temperature is normally much larger proportionately than the change in the reciprocal temperature; hence, the spectra of Figure 1 illustrate primarily the influence of solution viscosity on the spin-lattice relaxation rates of ^{11}B and ^{14}N of borazole.

Relaxation rates for boron and nitrogen were extracted from the experimental spectra using a procedure outlined previously¹⁶ by treating the relaxation processes responsible for the collapse of the ^{14}NH , ^{11}BH , and ^{10}BH multiplets separately as equivalent to chemical exchange between equally populated sites separated in frequency by $m_I J_{X,H}$, corresponding to the $(2I + 1)$ substates of m_I of a nucleus having spin I . The appropriate transition rates between the m_I substates are given by eq 5-7.¹⁸

$$k_{m,m\pm 1} = k_{m+1,m} = \frac{(2m \pm 1)^2(I + m \pm 1)(I \mp m)}{2T_{1X}(2I - 1)(2I + 3)} \quad (5)$$

$$k_{m,m\pm 2} = k_{m\pm 2,m} = \frac{(I \mp m)(I \mp m - 1)(I \pm m + 1)(I \pm m + 2)}{2T_{1X}(2I - 1)(2I + 3)} \quad (6)$$

$$k_{m,m} = \sum_{m' \neq m} k_{m,m'} \quad (7)$$

With these equations, the calculation of the amplitude of the proton signal at frequency ω for any values of $T_{1,^{14}\text{N}}$, $T_{1,^{11}\text{B}}$, and $T_{1,^{10}\text{B}}$ is reduced to the solution of eq 8.

$$I(\omega) \propto \text{Re}\left\{\left(\frac{1}{3}\right)\mathbf{I} \cdot [\mathbf{i}\omega_{^{14}\text{N}} + \mathbf{R}_{^{14}\text{N}} + (1/T_{1,^{14}\text{N}})\mathbf{K}_{^{14}\text{N}}]^{-1} \cdot \mathbf{I}\right\} + \left(\frac{1}{4}\right)0.81\mathbf{I} \cdot [\mathbf{i}\omega_{^{11}\text{B}} + \mathbf{R}_{^{11}\text{B}} + (f/T_{1,^{11}\text{B}})\mathbf{K}_{^{11}\text{B}}]^{-1} \cdot \mathbf{I}\right\} + \left(\frac{1}{7}\right)0.19\mathbf{I} \cdot [\mathbf{i}\omega_{^{10}\text{B}} + \mathbf{R}_{^{10}\text{B}} + (f/T_{1,^{10}\text{B}})\mathbf{K}_{^{10}\text{B}}]^{-1} \cdot \mathbf{I}\right\} \quad (8)$$

Here, *e.g.*, $\omega_{^{14}\text{N}}$ is a diagonal matrix whose elements are the values $(m_I J_{N,H} - \omega_N - \omega)$; $\mathbf{R}_{^{14}\text{N}}$ is a diagonal matrix whose elements describe the widths of the NH lines in the absence of quadrupole relaxation; and the matrix $(1/T_{1,^{14}\text{N}})\mathbf{K}_{^{14}\text{N}}$ contains the transition rate constants obtained from eq 5-7, describing the transfer of

magnetization between the various NH resonances under the influence of ^{14}N relaxation.¹⁹ The influence of unresolved $^1\text{HNB}^1\text{H}$ couplings on the ^1H line shapes was approximated by assuming a line width in the absence of relaxation that was uniformly 10 Hz broader than the observed width of the benzene internal resolution standard (typically 3 Hz in nonviscous solutions and 5 Hz in $\text{DMSO}-d_6$ at -62°). The relative isotopic abundances of ^{14}N , ^{11}B , and ^{10}B (1.00:0.81:0.19) were taken into account by appropriate adjustment of intensities. The multiplicative factor f in eq 8 was used to adjust the fit of calculated to observed spectra independently for NH and BH resonances; it can be interpreted as the deviation of the ratio of relaxation times at ^{11}B and ^{14}N from the value calculated in eq 3 (eq 9).

$$\left(\frac{T_{1,^{14}\text{N}}}{T_{1,^{11}\text{B}}}\right)_{\text{obsd}} = f \left(\frac{T_{1,^{14}\text{N}}}{T_{1,^{11}\text{B}}}\right)_{\text{calcd}} = 1.64f \quad (9)$$

Calculated spectra were obtained from eq 8 using standard computer routines.^{19,20} Representative spectra illustrating the dependence of the proton line shapes on the spin-lattice relaxation times are given in Figure 2; chemical shifts used in these calculations were obtained in neat borazole. Relaxation times characterizing the experimental spectra were obtained by visual fitting of spectra calculated by varying the boron and nitrogen relaxation times to these spectra; variations in chemical shifts and in the assumed proton T_2 (as inferred from the benzene line width) with temperature were taken into account.

By varying viscosity and/or temperature, the ^1H spectrum of borazole could be easily adjusted in a medium of interest to give spectra at any point between the limits in which NH and BH couplings were fully resolved or collapsed. For determinations of f (eq 8 and 9) it was found most convenient to compare calculated and experimental spectra in the region in which the NH and BH resonances were single, broad lines. Comparisons were carried out by varying $T_{1,^{14}\text{N}}$ to give the best fit between calculated and experimental shapes for the NH line and then calculating several complete spectra for several values of f centered around $f = 1.0$. Three representative theoretical spectra are compared with the experimental spectrum of borazole in $\text{DMSO}-d_6$ at -44° in Figure 3. In this instance, $f = 1.0$ ap-

(18) Numerical values for these rate constants are given in eq 4-6 (for $I = 1$) and 4-4 (for $I = 2$) of ref 7, and $I = 3$ in J. Bacon, R. J. Gillespie, J. S. Hartman, and U. R. K. Rao, *Mol. Phys.*, **18**, 561 (1970). They will not be reproduced here. For discussions of the limitations of this computational procedure, see N. C. Pyper, *ibid.*, **21**, 977 (1971), and references therein.

(19) For reviews of techniques, see C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965).

(20) Calculations were carried out using a version of the program NMRCTL (*cf.* J. K. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1971). Matrix inversions were carried out using procedures based on the routine ALLMAT (*cf.* G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969); R. E. Schirmer, J. H. Noggle, and D. F. Gaines, *ibid.*, **91**, 6240 (1969); R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.*, **49**, 2455 (1968)).

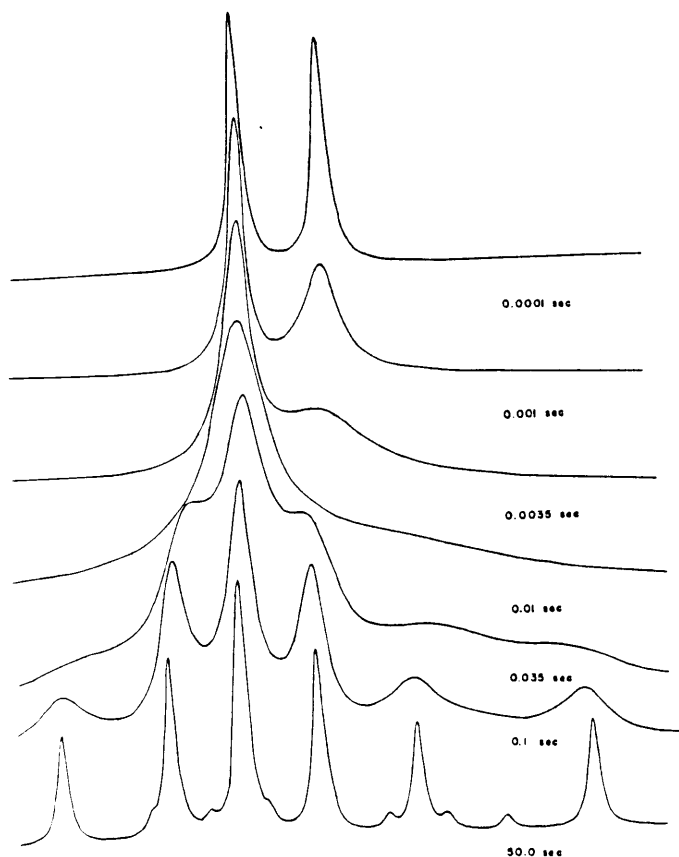


Figure 2. Calculated ^1H nmr line shapes for borazole as a function of a uniform relaxation time T_1^0 . The individual relaxation times are related to T_1^0 by the following expressions: $T_{1,^{15}\text{N}} = T_1^0/6.73$; $T_{1,^{10}\text{B}} = T_1^0/11.06$; $T_{1,^{11}\text{B}} = T_1^0/7.20$.

pears to give better agreement between calculated and experimental line shapes than $f = 1.1$ or $f = 0.90$. The results of similar experiments in several other media are summarized in Table I.

Table I: Values of f (Eq 8) for Borazole in Several Solvents

Solvent (concn. v/v)	f	Temp. $^{\circ}\text{C}$
Neat	1.0 ± 0.1	-37
DMSO- d_6 (68%)	1.0 ± 0.1	-44
CDCl_3 (44%)	1.0 ± 0.1	25
Toluene- d_6 (33%)	1.0 ± 0.1	-11
Cyclohexane- d_{12} (42%)	1.0 ± 0.1	25
CCl_4 (60%) with added di- <i>tert</i> -butylnitroxyl ^a	0.17 ± 0.08	25

^a The concentration of nitroxyl radical was $\sim 5\%$.

The significant conclusion to be drawn from these data is that $f = 1$ in a variety of "typical" solvents within the limits of the experimental technique ($\sim \pm 10\%$). Thus, these data provide support for the contention that eq 1 does provide a useful functional relationship between the molecular motions charac-

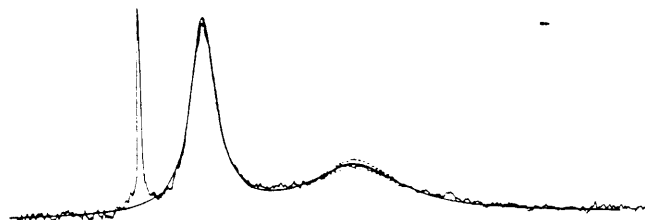


Figure 3. Comparison of the observed spectrum of borazole in DMSO- d_6 (68% v/v) at -44° with spectra calculated assuming the following values of f (eq 7): $f = 1.0$ (—); $f = 1.1$ (---); and $f = 0.9$ (····). The single resonance downfield from the NH line is benzene used as an internal line width standard.

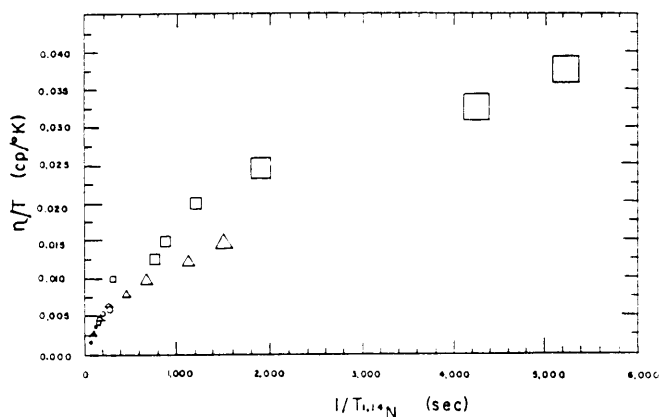
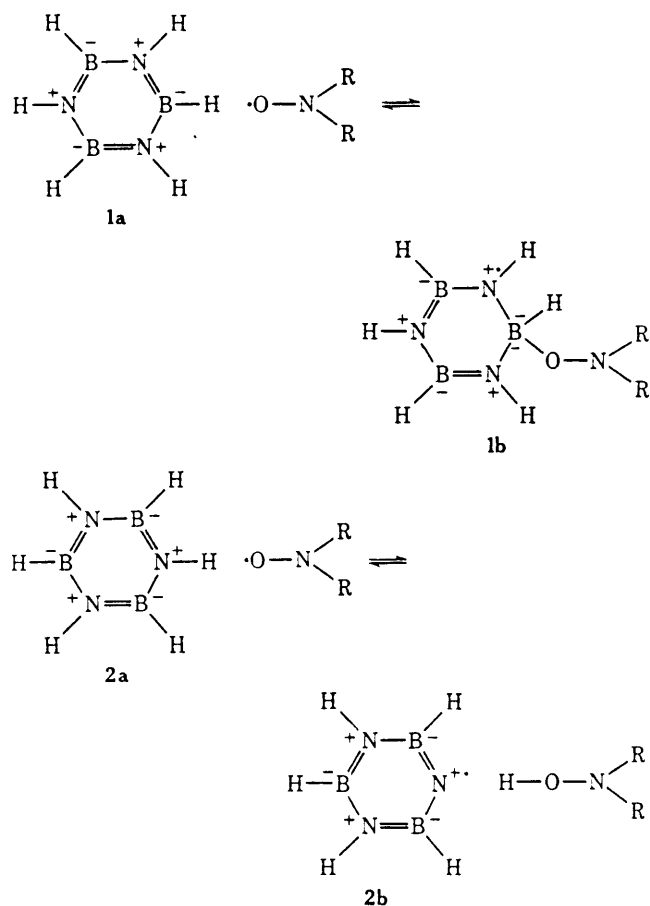


Figure 4. Plot of η/T as a function of $1/T_{1,^{15}\text{N}}$ for borazole in DMSO- d_6 (68% v/v) (\square); borazole in toluene- d_6 (33% v/v) (Δ); and borazole (neat) (\circ). Relaxation times for ^{11}B can be obtained from this plot using the relation $1/T_{1,^{11}\text{B}} = 1.64(1/T_{1,^{15}\text{N}})$.

terized by τ_X and the spin-lattice relaxation time of a quadrupolar nucleus and that other factors not included in eq 1 that might in principal contribute to T_1 apparently are not experimentally significant.

The one medium in which there is a significant deviation of f from unity is one composed of ca. 60% borazole in CCl_4 containing the stable free radical di-*tert*-butylnitroxyl, in which the ^{14}N is selectively relaxed.²¹ Whether the selective relaxation of ^{14}N is due to a σ -complex formation between a boron atom of borazole and nitroxyl radical (1) or hydrogen bonding between a proton bound to nitrogen and nitroxyl (2), both of which could selectively place the ^{14}N nuclei in close proximity to an unpaired electron, or to some other more complex mechanism, is not clear. However, it is pertinent to considerations of the utility of eq 1 that only a drastic change in medium (*i.e.*, addition of a paramagnetic species to the solution containing borazole) is capable of inducing an observable deviation of f from its expected value.^{22,23}

(21) Increasing the concentration of di-*tert*-butylnitroxyl broadens and collapses the NH resonances more rapidly than the BH resonances. Since the solvent viscosity is not appreciably changed by addition of nitroxyl, the deviation of f from unity thus appears to be due to a decrease in $T_{1,\text{N}}$ rather than an increase in $T_{1,\text{B}}$.



The Gierer-Wirtz equation (eq 4) predicts a linear relation between $1/T_{1,1N}$ (and $1/T_{1,1B}$) and η/T . This relation is only approximately obeyed by the relaxation time data obtained in this study (Figure 4): a plot of the reciprocal relaxation times *vs.* η/T shows a significant curvature. This curvature has the sense that would be expected if reorientation of borazole around its C_3 axis were faster than that around the C_2 axes. However, the presently available data are not sufficient to distinguish between a failure of the approximations underlying the Gierer-Wirtz equation¹⁷ and errors in the line shape analysis at the fast- or slow-exchange limits, due to neglect of spin-spin couplings, cross-relaxation effects, or other factors influencing line shapes.

Regardless, the observation that the relaxation data for borazole in toluene, DMSO, and borazole solutions fall approximately along a common curve provides support for the assertion that specific interactions between borazole and typical diamagnetic solvent molecules do not strongly influence the relaxation behavior of the former.

Keeping in mind the failure of the relaxation data obtained in this study to obey eq 4 in detail, these data can nonetheless be used in conjunction with eq 4 to obtain crude estimates of the quadrupole coupling constants of nitrogen and boron in borazole. To

evaluate the dimensional parameters contained in eq 4, borazole and toluene were assumed to be hard spheres: $r_{\text{borazole}} = 2.96 \text{ \AA}$ and $r_{\text{toluene}} = 3.09 \text{ \AA}$.²⁴⁻²⁶ Inserting these values and the experimentally determined viscosity of a 33% (v/v) solution of borazole in toluene (1.07 cP at -39°) into eq 4, the correlation time for reorientation τ_X is estimated to be $5.7 \times 10^{-12} \text{ sec}$;²⁷ this value, together with the experimental value for $T_{1,1N}$ in toluene at -39° ($= 5.5 \times 10^{-3} \text{ sec}$), yields values for the quadrupole coupling constants: $(e^2qQ/h) \cong 3.6 \pm 1.3 \text{ MHz}$ (¹¹B); $7.6 \pm 2.9 \text{ MHz}$ (¹⁰B); $1.4 \pm 0.5 \text{ MHz}$ (¹⁴N).²⁸⁻³¹

Experimental Section

General. Nmr spectra were taken on Varian HA-100 and A-60 spectrometers equipped with V-6040 variable-temperature controller. Calibration of the temperature control unit was accomplished by measuring peak separations in methanol or ethylene glycol samples. Viscosities of neat borazole as a function of temperature were taken from the literature;²⁵ viscosities of borazole in toluene (33% v/v) and borazole in DMSO (68% v/v) were measured using a Cannon-Manning semi-

(22) Di-*tert*-butylnitroxyl forms relatively stable complexes with a number of Lewis acids.²³ Nucleophilic attack on borazole seems to involve the boron centers.¹¹

(23) B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 5170 (1969); W. Beck and K. Schmidther, *Chem. Ber.*, **100**, 3363 (1967); L. A. Krinitskays and S. Dobryakov, *Bull. Acad. Sci. USSR*, **3**, 558 (1966); B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 2169 (1969).

(24) The density of borazole at -39° is 0.904 g/cm^3 ;²⁵ the density of toluene at -39° is 0.921 g/cm^3 . Hard sphere radii were calculated assuming a closest packing relation between the hard spheres and the molar volume $= 0.74v_m = 4\pi r^3/3$.

(25) L. B. Eddy, H. Smith, Jr., and R. R. Miller, *J. Amer. Chem. Soc.*, **77**, 2105 (1955).

(26) E. D. Washburn, Ed., "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 29.

(27) For comparison, values of τ of 1.3 , 1.7 , and $2.4 \times 10^{-11} \text{ sec}$ have been determined for benzene-*d*₆ and benzene at $\sim 30^\circ$: D. E. Woessner and B. S. Snowden, *J. Chem. Phys.*, **52**, 1621 (1970); T. E. Bull and J. Jonas, *ibid.*, **52**, 4553 (1970); G. Bonera and A. Rigamonti, *ibid.*, **42**, 171 (1965); see also D. E. O'Reilly, *ibid.*, **53**, 850 (1970).

(28) The value of the coupling constant for ¹¹B is of interest in a qualitative estimation of the π -bond order of the N-B bond of borazole. Ring and Koski²⁹ have suggested that the π -bond order of B-N multiple bond can be determined by the expression $\pi_{B-N} = 1 - [e^2qQ/h]_{11B}/5.39$. Our estimate of the quadrupole coupling constant leads to $\pi_{B-N} = 0.33 \pm 0.13$, in rough agreement with previous estimates of this parameter (~ 0.5).^{30,31} The estimate of this parameter by Mellon, *et al.*,¹⁵ based on similar quadrupole coupling constants appears to be too high by a factor of 2.

(29) M. Ring and W. Koski, *J. Chem. Phys.*, **35**, 381 (1961). For other recent discussions pertinent to the electronic structure of borazole, see D. R. Armstrong and D. T. Clark, *Chem. Commun.*, 99 (1970); H. Bock and W. Fuss, *Angew. Chem., Int. Ed. Engl.*, **13**, 182 (1971); G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970); S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **49**, 312 (1968); K. E. Blick, J. W. Dawson, and K. Niedenzu, *Inorg. Chem.*, **9**, 1416 (1970); S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **19**, 1 (1970).

(30) R. W. Rector, G. W. Schaeffer, and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949); H. Watanabe, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, **82**, 3294 (1960).

(31) For a listing of representative ¹⁴N quadrupole coupling constants in heterocyclic compounds, see E. A. C. Lucken in "Physical Methods in Heterocyclic Chemistry," Vol. IV, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1971, Chapter 2.

micro viscometer modified for operation under a nitrogen atmosphere. The viscometer was calibrated against literature values for toluene³² (temperature, viscosity in cP): 24°, 0.560; 6°, 0.720; -12°, 0.970. Measured values for the solutions of borazole in toluene were 24°, 0.410; 6°, 0.532; -12°, 0.759. Values for solutions of borazole in DMSO were 24°, 1.17; 6°, 1.61; -12°, 2.47.

Borazole was prepared using a literature procedure³³ and was purified by three successive bulb-to-bulb distillations immediately before use. Samples for spectroscopic examination were prepared on a vacuum

line in flame-dried glassware using standard procedures.³⁴

Acknowledgment. We are indebted to Mr. Calvin Powell and Dr. Jeanne K. Krieger for extensive assistance with the computer programs used in this work.

(32) L. G. Belinskaya, *Uch. Zap., Mosk. Oblast. Pedagog. Inst.*, 33, 221 (1955); *Chem. Abstr.*, 52, 821i (1958).

(33) H. Watanabe and M. Kubo, *J. Amer. Chem. Soc.*, 82, 2428 (1960).

(34) Borazole is inert to oxygen, but sensitive to moisture: A. Stock and E. Pohland, *Chem. Ber.*, 59, 2215 (1926).