1980

Solid State Phase Transitions and Molecular Reorientation in Ortho-Carborane and Para-Carborane: An Isomer Effect

Peter A. Beckmann
Bryn Mawr College, pbeckman@brynmawr.edu

Amos J. Leffler

Solid state phase transitions and molecular reorientation in *ortho*- and *para*-carborane: An isomer effect

Peter Beckmann

Department of Physics, School of Graduate Studies, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010

Amos J. Leffler

Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085

The proton nuclear spin–lattice relaxation times at 30 MHz have been measured for *ortho*- and *para*-carborane between 170 and 310 K and between 210 and 320 K, respectively. *Para*-carborane undergoes solid–solid transitions at about 300 and 238 K while the *ortho* isomer shows only one transition at about 265 K. The details of the phase transitions are discussed and molecular reorientation in the isomers is compared.

I. INTRODUCTION

Nuclear spin relaxation is a very useful technique for the study of molecular reorientation and solid–solid phase transitions in molecular solids. Nuclear spin relaxation rates depend on the strengths of spin–lattice interactions and on the modulations of these interactions by the various molecular motions. An analysis of the motions furnishes information concerning molecular potentials. If a phase change occurs, the *inter*molecular interactions also change, causing spin–lattice relaxation rates to change at the same time. The molecules of interest in the present work are the *ortho* and *para* isomers of carborane, $B_{10}C_2H_{12}$, which is a nearly regular icosahedron. The three isomers shown in Fig. 1 are the *ortho* isomer with carbons adjacent, the *meta* isomer with a boron atom between the two carbons, and the *para* isomer in which the carbons are at opposite sides of the icosahedron.[1] In the present study, proton spin–lattice relaxation times, T_1, have been measured in *ortho*-carborane between 170 and 310 K and in *para*-carborane between 210 and 320 K. One phase transition has been observed in the *ortho* isomer and two phase transitions have been observed in the *para* isomer This work is a continuation of an earlier study[2] in which the *ortho* isomer was investigated.

Nuclear spin relaxation rates are rarely, by themselves, sufficient to determine the details of molecular structure and must be supplemented by structural methods such as x-ray diffraction. A primary deficiency of relaxation measurements is that if the motions are complex they give only average or "effective" potentials and motion parameters. Often, neutron scattering experiments[3–7] complement the nuclear spin relaxation studies but in the present case, the large capture cross section of ^{10}B renders such experiments impossible.

In Sec. II we briefly review the relevant spin–lattice relaxation theory and in Sec. III the proton spin–lattice relaxation experiments are discussed. An analysis of the data is presented in Sec. IV and the possible interpretations are discussed in Sec. V. The paper is summarized in Sec. VI.

II. RELAXATION THEORY

A. General review

The general theory of nuclear spin relaxation that results from the modulation of the nuclear dipole–dipole interaction can be found in standard references.[8–10] This general theory has been applied to *ortho*-carborane.[2] The protons interact with protons and ^{11}B and ^{10}B isotopes and both *intra*- and *inter*molecular interactions must be taken into account. The result, based on certain approximations discussed previously,[2] is that the relaxation rate, T_1^{-1}, takes on the form of weighted sums of Lorentzians, i.e., sums of terms of the form $A\tau/(1+\omega^2\tau^2)$. The angular frequencies involve the proton Larmor frequency and sums and differences of the proton and boron Larmor frequencies. The weights, A, involve nuclear dipole–dipole matrix elements or,
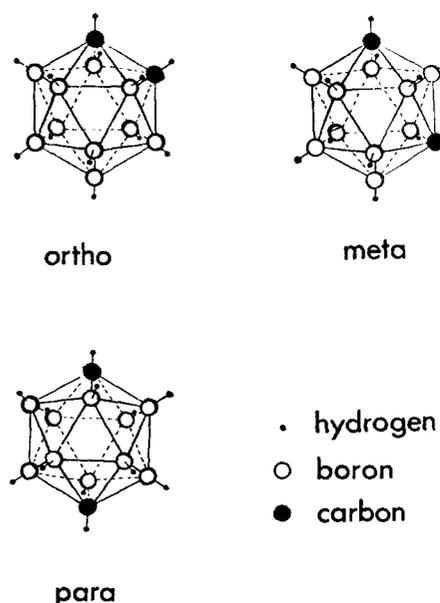

ortho   meta

para

. hydrogen
○ boron
● carbon

FIG. 1. The three isomers of carborane $B_{10}C_2H_{12}$; *ortho*, *meta*, and *para*. The ten borons and the two carbons from an icosahedron.

0021-9606/80/084600-08$01.00

equivalently, the appropriate second moments which can be calculated from known structures or reasonable approximations. The detailed formula for the *intra*molecular contribution to T_1^{-1} is[2]

$$(T_{1H}^{intra})^{-1} = (2\gamma_H^2/3)(\Delta M_{HH}^{intra})$$

$$\times [\tau(1 + \omega_H^2 \tau^2)^{-1} + 4\tau(1 + 4\omega_H^2\tau^2)^{-1}]$$

$$+ (\gamma_H^2/2)(\Delta M_{HB}^{intra}\{\tau[1 + (\omega_H - \omega_B)^2 \tau^2]^{-1}$$

$$+ 3\tau[1 + \omega_H^2\tau^2]^{-1} + 6\tau[1 + (\omega_H + \omega_B)^2\tau]^{-1}\} , \qquad (1)$$

where $\omega_H/2\pi$ is the proton Larmor frequency, $\omega_B/2\pi$ is the boron Larmor frequency, and γ_H is the proton gyromagnetic ratio. ΔM_{HH}^{intra} is the change in the proton second moment caused by the molecular reorientation modulating the proton–proton dipolar interactions, and ΔM_{HB}^{intra} is the change in the proton second moment caused by modulation of the proton–boron dipolar interactions. Since Eq. (1) deals with *intra*molecular contributions to T_{1H}, both second moment terms involve dipolar interactions within a single molecule. The ΔM_{HB}^{intra} must be understood to include properly weighted separate terms for the two boron isotopes. The *inter*molecular contributions to T_1 have the same form as Eq. (1) except that the second moments are those for dipolar interactions on different molecules.

The reorientation frequency, τ^{-1}, is usually assumed to have a simple Arrhenius dependence on temperature, i.e.,

$$\tau^{-1} = \tau_\infty^{-1} \exp(-E_a/RT) , \qquad (2)$$

where R is the gas constant, τ_∞^{-1} is a temperature independent frequency, and E_a is an activation energy. Molecular reorientation is further discussed in Part B of this section.

At high temperatures $\tau \ll \omega^{-1}$ while at low temperatures $\tau \gg \omega^{-1}$. Under these conditions Eq. (1) predicts that $\ln T_1$ vs T^{-1} is linear with slopes of $+E_a/R$ and $-E_a/R$, respectively, and intercepts which involve τ_∞ and the weights A. A phase transition is characterized by a discontinuous change in E_a, τ_∞, or both. This in turn manifests itself in discontinuous changes in T_1, the slope of $\ln T_1$ vs T^{-1} or both.

B. Molecular reorientation

In general, Eq. (2) is valid for the case when the coupling between the molecule and the lattice is strong. In this case, molecular reorientation takes place each time the molecule has sufficient thermal energy to overcome the potential barrier. In general, systems which have many reorientation axes will not have a single activation energy. An icosahedron has six C_5 axes, ten C_3 axes, and fifteen C_2 axes. The barrier for reorientation about any one axis may involve a potential which, when plotted as a function of angle, exhibits minima of different heights. The theoretical groundwork for this situation has been developed[11,12] and has been shown to apply to *trans*, *trans*-muconodintrile which has only a single reorientation axis with different well depths.[13] A similar approach may be useful for the carborane system since the localized atomic charges may interact differently with neighboring molecules.

An alternative possibility is one in which there is a single activation energy for each reorientation axis but different barriers are associated with different axes. The approach in this case is to treat the problem in terms of reorientations superimposed on reorientations. The theoretical groundwork for this situation has been developed for the case of tertiary butyl groups[14] and has been used to interpret relaxation measurements in 4-methyl-2, 6-ditertiary butyl phenol.[15]

These models, discussed further in Sec. IV, all predict that more than one value of τ will appear in the relaxation equations.

III. THE PROTON SPIN–LATTICE RELAXATION EXPERIMENTS

Proton spin–lattice relaxation times were measured with the standard 180-t-90 pulse sequence using a homemade 30 MHz pulsed spectrometer. Temperature was regulated by varying the flow of cold nitrogen gas and measured with a thermocouple. The sample, contained in a glass tube, filled the coil volume of approximately 1 cm^3 and extended about 0.3 cm outside of the top of the coil. The thermocouple was positioned inside of the sample chamber and was embedded in the portion of the sample outside of the coil.

The *ortho*-carborane was obtained from the Ventron Corporation while the *para*-carborane was furnished by Professor M. F. Hawthorne of the University of California at Los Angeles. Both were used without further purification.

Spin–lattice relaxation time measurements were made only after the temperature of the sample remained constant for 10 min. The temperature difference between successive measurements was never more than 3 K. All three phase transitions were traversed slowly at least twice in each direction. The resolution of the thermocouple was ± 0.1 K and the uncertainty associated with the calibration was ± 0.5 K. Over the temperature range of each transition the calibration uncertainty will be in the same direction and therefore will not affect the uncertainty of small differences in temperature. The quoted errors for small temperature differences have their origin (a) in the ± 0.1 K resolution uncertainty and, (b) in the measured temperature difference between the appropriate adjacent data points. The quoted errors for absolute temperatures have, in addition, (c) the ± 0.5 K calibration uncertainty.

The sample of *ortho*-carborane used in the present work was the same as that used in the previous study.[2]

IV. DATA ANALYSIS

A. Phase transitions

The temperature dependence of T_1 for both isomers is shown in Fig. 2. The *ortho* isomer exhibits a phase transition at about 265 K. Previous calorimetric[16] and proton spin relaxation studies[2] of the *ortho* isomer report transition temperatures of 277 ± 3 and 274 ± 2 K, respectively. The *para* isomer shows two phase transitions, one in the vicinity of 300 K and the other in the
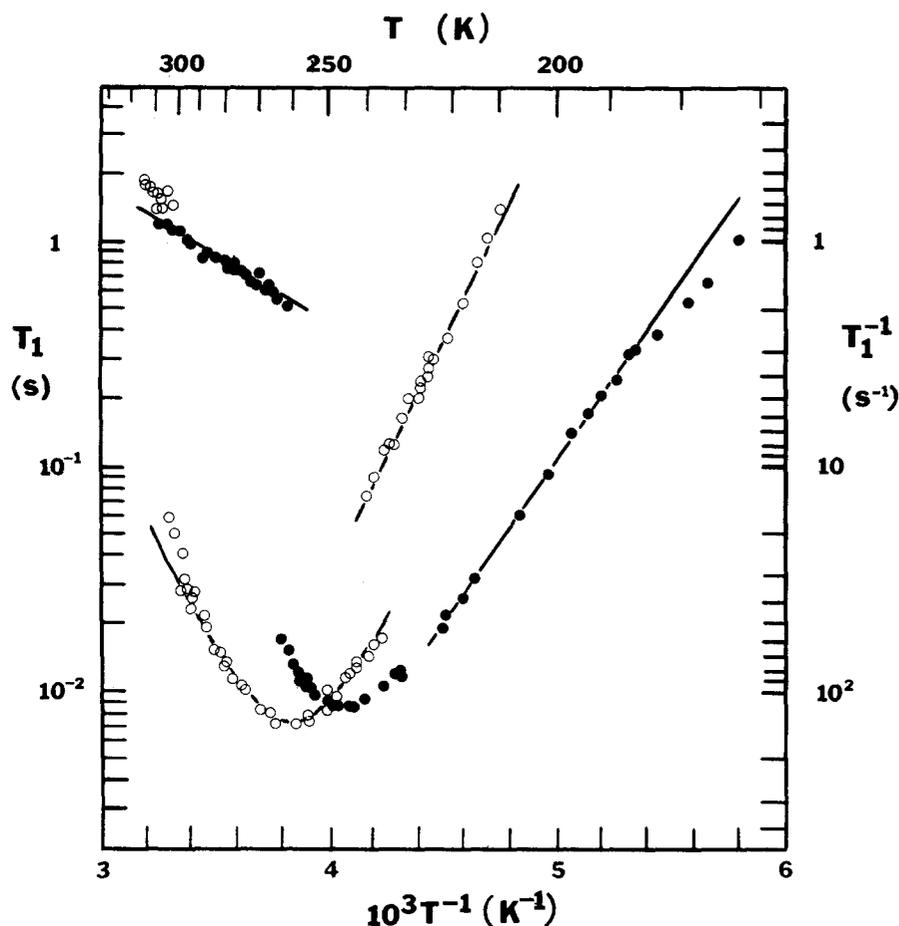
FIG. 2. Spin–lattice relaxation time T_1 vs temperature T. The experimental data is indicated by open circles for *para*-carborane and by closed circles for *ortho*-carborane. The solid lines are discussed in the text. The details in the regions of the three phase transitions are shown in Figs. 3, 4, and 5.

vicinity of 238 K. The two transitions have been confirmed by differential scanning calorimetry measurements kindly done by Dr. D. W. Breakey of the Perkin–Elmer Corporation.

Careful measurements of the spin–lattice relaxation times were made in the vicinity of each of the transi-

tions. These are shown in Figs. 3–5. The high temperature phases have been designated I, the low temperature *ortho* phase and the medium temperature *para* phase are called II, and the low temperature *para* phase is called III. The relaxation curves were observed to be non exponential in the vicinity of the I–II transition in the *ortho* isomer and in the vicinity of the II–III
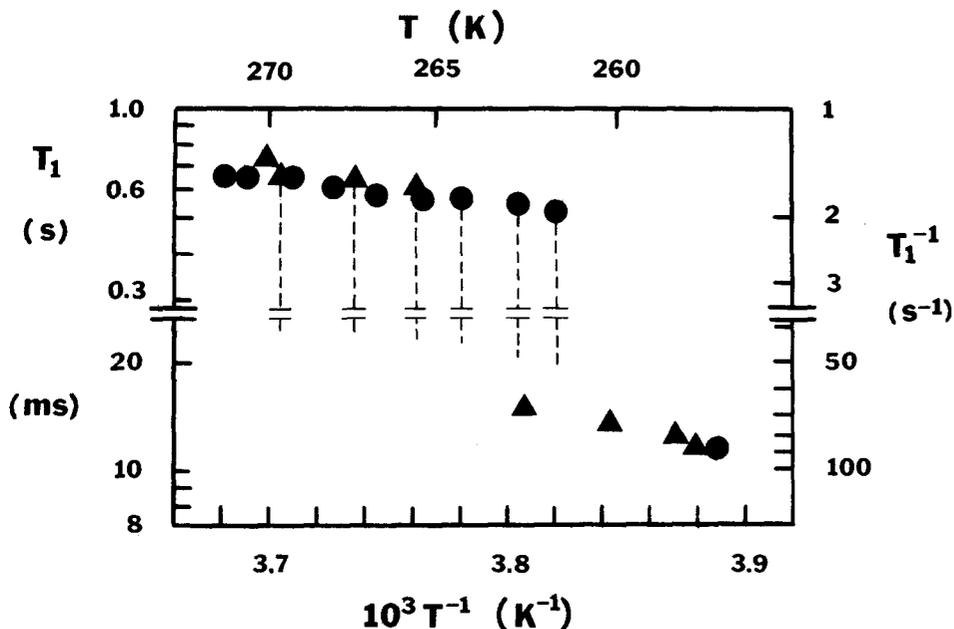

FIG. 3. T_1 vs T in the vicinity of the I–II phase transition in *ortho*-carborane. Note that one decade is omitted on the abscissa between the T_1 values in the two phases. The circles and triangles denote decreasing and increasing temperature, respectively. The vertical dashed lines indicate nonexponential relaxation indicative of both phases being present. The lengths of the dashed lines have no significance.
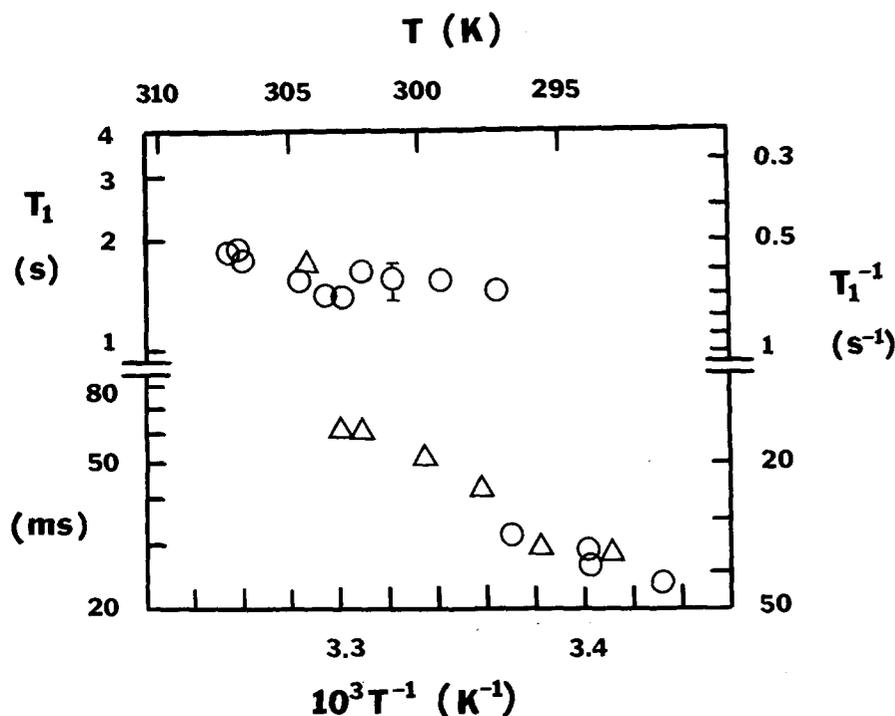
FIG. 4. T_1 vs T in the vicinity of the I–II phase transition in para-carborane. Note that one decade is omitted in the abscissa between the T_1 values in the two phases. The circles and triangles denote decreasing and increasing temperature, respectively. The relaxation was always exponential to within the accuracy of the experiment.

transition in the para isomer indicating that both phases are present.[17,18] Further, the physical size of a region of a given phase must be large enough that the protons in one region do not interact with the protons in another region, in which case spin diffusion would give rise to a single T_1. Although these nonexponential relaxation curves could be fitted by the sum of two exponentials, the method of measurement permitted an accurate determination of either the long or short components of T_1 due to the large differences in value. For the II–III transition in the para isomer, T_1 changes by a factor of about 5 while in the I–II transition of the ortho isomer T_1 changes by a factor of about 30. Nonexponential relaxation is indicated by dashed vertical lines in Figs. 3 and 5. The lengths of these lines have no significance. We are not able to say whether the coexistence of the two phases is an equilibrium situation or whether the transitions, once started at a given temperature, proceed very slowly. (However, see below for further comment.) The spin–lattice relaxation in the vicinity of the I–II transition of the para isomer shown in Fig. 4 was always exponential within experimental error.

On the basis of the temperature difference between successive measurements, the calibration uncertainty of the thermocouple, and the temperature resolution of the thermocouple, values for the transition temperatures and the coexistence ranges are shown in Table I. In each case the listed transition temperature was taken as the midpoint of the coexistence range.

Although the previous T_1 measurements[2] in the ortho isomer were less precise than those reported here, the temperature was varied more slowly and no clear evidence of nonexponential relaxation was observed in the vicinity of the I–II transition. As stated previously, T_1 above and below the transition changes by a factor of about 30. In the pulsed NMR experiments, if one

chooses a repetition period which is long compared with the short T_1 (phase II) but short compared with the long T_1 (phase I), then the "equilibrium" signal will be that due to the protons in phase II molecules and the protons in phase I molecules will remain saturated. In this case, the relaxation will be exponential with a T_1 in-
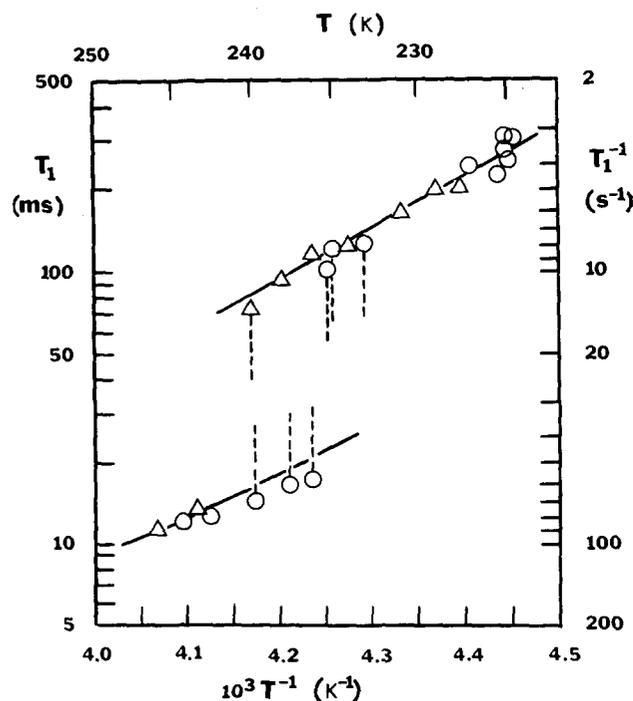

FIG. 5. T_1 vs T in the vicinity of the II–III phase transition in para-carborane. The circles and triangles denote decreasing and increasing temperature, respectively. The vertical dashed lines indicate nonexponential relaxation indicative of both phases being present. The lengths of the dashed lines have no significance.

TABLE I. Characteristic temperatures and temperature ranges for the solid–solid phase transitions in *ortho*- and *para*-carborane. All temperatures are in K.

	Temperature increasing		Temperature decreasing		
Transition	Transition temperature	Coexistance range	Transition temperature	Coexistance range	Hysteresis
I–II (*ortho*-carborane)	267.3 ± 2.5	5.9 ± 2.1	262.4 ± 2.5	5.7 ± 2.1	4.9 ± 4.0
I–II (*para*-carborane)	303.3 ± 1.6	none	297.0 ± 0.9	none	6.3 ± 1.5
II–III (*para*-carborane)	241.0 ± 3.6	2.9 ± 3.2	235.4 ± 6.2	11.7 ± 5.8	5.6 ± 8.8

dicative of phase II. If this were the case, the transition would appear to be at a higher temperature than observed in this study which may explain the higher reported temperature in Ref. 2. It should be pointed out that the linewidth change and the break in the T_1 plot as a function of temperature for ^{11}B as reported in Ref. 2 were very close to the proton T_1 discontinuity reported there. From the relatively long coexistence temperature range in the II–III phase transition of the *para* isomer in the decreasing direction compared to the increasing direction, it is concluded that kinetics plays an important role.

B. Activation energies

Realistic expressions for T_1 as a function of temperature which follow from the various models discussed in Sec. II would require structural information and potential calculations as input. However, meaningful qualitative conclusions can be drawn from simple fits to the data if it is consistent with the assumption of a single correlation time, τ. Fits of the data with this assumption are shown in Fig. 2 and the resulting activation energies are given in Table II.

In *ortho*-carborane in phase I ($\omega\tau \ll 1$) $\ln T_1$ is proportional to T^{-1} and a linear least squares fit gives $E_a = 12$ kJ/mol. Using Eq. (1) with *inter*molecular second moment values gives the further information $\tau_\infty = 2.8 \times 10^{-13}$ s. All that can be stated about phase I of *para*-carborane is that it is consistent with this value of E_a but with a very large uncertainty. In phase III of *para*-carborane ($\omega\tau \gg 1$) $\ln T_1$ is also proportional to T^{-1} and a linear least squares fit gives $E_a = 40$ kJ/mol. Similarly, for the *ortho* isomer between 185 and 225 K, an E_a value of 27 kJ/mol was found. The anomaly below 185 K in *ortho*-carborane is discussed later. A least squares fit for the *para* isomer in phase II is not possible because the I–II and II–III transitions occur before the short and long correlation time limits are reached. We show a fit with an E_a of 40 kJ/mol only to indicate that the data for *para*-carborane is consistent with the same activation energy in phases II and III. If this value of E_a in phase II in *para*-carborane was changed by 10%, a visually equally successful fit can be found but the fit is visually poorer if E_a is changed by 15% from 40 kJ/mol. Data points within the transition hysteresis regions (like the four highest temperature data points in phase II of *para*-carborane) were not used in any of the fits. In the vicinity of the T_1 minimum in phase II of *ortho*-carborane, different values of E_a for the high

and low temperature sides were found in agreement with earlier work.[2] In the temperature region just below the T_1 minimum, E_a is consistent with the low temperature value of 27 kJ/mol and in the temperature region between the I–II phase transition and the T_1 minimum, E_a is consistent with the phase II and III values of 40 kJ/mol for *para*-carborane.

V. DISCUSSION

A. *Inter*molecular interactions

The most unexpected result of this work is the difference in the behavior of the two isomers in the low temperature phases, especially the existence of a second phase transition in the *para* isomer. We are interested in those aspects of the *inter*molecular interactions that will be different for the two isomers or, equivalently, those which depend on the relative positions of the carbon atoms. *Ortho*-carborane has a molecular electric dipole moment of 4.4 D.[19,20] Whereas the more symmetric *para*-carborane has no dipole moment[19] it will have a molecular electric quadrupole moment. Kitaigorodsky[21] has analyzed the relative contributions to *inter*molecular potentials from dipole and quadrupole moments and has shown, in general, that the latter makes a very much smaller contribution than the former. However, the quadrupolar interaction in the *para* isomer must be considered, at least at lower temperatures, in light of there being no dipole moment.

Another possible difference between the two isomers may involve the differences in the pairwise sums of electrostatic interactions. Recent analyses of *inter*molecular interactions[21–25] have been based on the atom–atom approach in which the van der Waals interactions between all atoms in each of two molecules are

TABLE II. Activation energies of *ortho*- and *para*-carborane (in kJ/mol)[a] in the different phases.

Phase	*para*-carborane	*ortho*-carborane
I	~12	12
II (temperatures above T_1 minimum)	40	~40
II (temperatures below T_1 minimum)	40	27
III	40	...

[a] 1 kJ/mol = 0.24 kcal/mol = 10.4 meV/molecule.

summed up. Monte Carlo type computer programs have been devised to allow computation of the most stable arrangements between molecules in arrays by altering the orientation of neighboring molecules relative to one central molecule. Unfortunately there are presently no available interaction parameters between boron and other atoms and so this could not be done in the present work. Furthermore, very recent work[26-29] indicates that the atom–atom method is deficient in treating electrostatic interactions and in many cases the latter are comparable in magnitude to the former. With these limitations it is possible only to draw qualitative conclusions concerning the difference in the behavior of the two isomers.

The most striking difference between the two isomers, in addition to the third phase in *para*-carborane, is that the I–II transition temperature in *para*-carborane occurs 30° higher than in the *ortho* isomer despite the presence of the large dipole moment in the latter. If we make the reasonable assumption that all of the individual atom–atom and electrostatic interactions referred to above are the same in both isomers then we are forced to conclude that the molecular dipole moment in the *ortho* isomer destabilizes the low temperature phase allowing the transition to the high temperature phase to occur at a lower temperature. Theoretical calculations[30] have indicated that the carbon atoms have a more negative charge than do the boron atoms. This situation will result in a stronger *inter*molecular interaction between carbon and hydrogen atoms and could lead to an alignment of the *para* isomer. In the case of the *ortho* isomer, the most favorable arrangement does not seem clear since if two molecules align themselves for maximum electrostatic interaction there cannot be a strong interaction between this pair of molecules and the surrounding neighbors. It is probable that there is not a favored arrangement for the *ortho* isomer resulting from the *inter*molecular electrostatic interaction thus accounting for the lower transition temperature between phases.

B. Molecular reorientation

In the discussion of molecular reorientation in the various phases we make use of the proton and boron second moment calculations and experimental values.[2,16] The observed second moment values in both phases I and II of *ortho*-carborane are very much less than the calculated rigid lattice value. In phase I (below the onset of translational diffusion at 470 K [16]) the observed second moment value is 0.71 G^2 while in phase II (above 220 K) the observed second moment value is 1.1 G^2.[16] Below this temperature the second moment increases rapidly and at 175 K has a value of about 18 G^2 compared with the rigid lattice value of 34 G^2. Previous measurements[2] have shown that although there is only a small change in the proton second moments at the transition temperature, there is a very sizeable [11]B linewidth change at the transition. Also, the decrease in intensity due to the disappearance of the satellite transitions (3/2–1/2 transitions) indicate that the reorientation in phase II must be anisotropic.[2] The proton linewidths do not change significantly,[2,16] probably be-

cause the reorientation in phase II is rapid enough to prevent proton line broadening. No linewidth data is available for the *para* isomer but the similarity of the T_1 data of the two isomers suggests that it would be similar to the *ortho* isomer in the neighborhood of the phase transition.

The crystal structure of *ortho*-carborane (and *meta*-carborane) at 298 K in phase I is consistent with a face-centered-cubic structure[16] and it is reasonable to assume the same structure for the *para* isomer in this phase. The activation energy of 12 kJ/mol is in agreement with rapid isotropic reorientation as discussed earlier.[2,16]

Below the I–II transitions, but on the high temperature side of the T_1 minimum, both isomers have activation energies, E_a, of 40 kJ/mol. The activation energy for *para*-carborane remains essentially temperature independent as the temperature is decreased through the II–III phase transition at 238 K down to the lowest temperature measured. In contrast, the activation energy for *ortho*-carborane changes gradually with temperature until the low temperature value of 27 kJ/mol is reached at about 230 K. (See Fig. 2 and Table II.) Such asymmetry in E_a has been observed in a variety of systems.[13,31-33] The fact that there is an asymmetry in E_a for the *ortho* isomer but not the *para* isomer suggests that the orientation in *ortho*-carborane is more anisotropic than in *para*-carborane in phase II. The T_1 minima for C_5, C_3, and C_2 reorientations occur at progressively lower temperatures.[2,34] In *ortho*-carborane the reorientation about one C_2 axis does not reorient the electric dipole vector, reorientation about the three adjacent C_3 axes introduce only a slight "wobble" in this vector and so on. Thus the reorientation about certain axes may become faster, relative to other axes, as the temperature is decreased and if the reorientations have different barrier heights, the effective activation energy will change. This is consistent with the observed change in E_a if C_2 reorientation becomes more important than, say, C_5 reorientation as temperature is lowered.

The value of T_1 at its minimum is about 20% greater in *ortho*-carborane (8.5 ms) than in *para*-carborane (7.2 ms). This also suggests that the reorientation in the former is more anisotropic,[2,35] if it is assumed that the unknown crystal structure for both isomers is the same. At present all that is known is that the crystal structure of phase II is not face-centered-cubic.[36]

Of the models discussed qualitatively in Sec. II, the one that assigns well depths of different heights for the potentials is worthy of mention even though we shall see that it probably does not apply in this case. In the case of a threefold barrier with two of the three minima a height ΔE above the third, it has been shown[13] that for the case $\Delta E \gg kT$, T_1 is increased by the factor $\exp(\Delta E/kT)$. We mention this example because some rotation axes in the carboranes might have potential well minima of different depths due solely to the small differences in carbon and boron interactions with neighboring molecules as discussed previously. This model

also predicts an asymmmetric T_1 minimum but in the opposite direction than is observed in *ortho*-carborane; i.e., this model predicts a higher E_a on the low temperature side of the T_1 minimum. The model also suggests a departure from the usual $(T_1)_{min} \propto \omega$. From the previous experiments at 10 and 20 MHz[2] and the 30 MHz experiments reported here it can be seen that to within experimental error, $(T_1)_{min} \propto \omega$.

Further evidence for the more anisotropic reorientation in *ortho*-carborane than in *para*-carborane in phase II is given by a comparison of the NMR work on 9-bromo-*meta*-carborane[35] and on *ortho*-diarsadecaborane ($As_2B_{10}H_{10}$).[37] In the former the value of the proton T_1 at the minimum at 30 MHz is about 15 ms (approximately twice that of *ortho*- and *para*-carborane) indicating more anisotropic reorientation as one might expect when a proton is replaced by a bromine. Similar arguments can be made from the results of linewidth measurements and $As_2B_{10}H_{10}$ (in which As replaces C–H in carborane) is found to be intermediate between 9-bromo-*meta*-carborane and *ortho*-carborane.

Phase III of *para*-carborane has no counterpart in the *ortho* isomer. The reorientation in this phase is in the long correlation time limit ($\tau\omega \gg 1$) at the Larmor frequency of 30 MHz. Although little is known beyond this, the fact that it has the same activation energy as phase II below $(T_1)_{min}$ suggests that there must be a relation between the reorientations in the two phases.

C. Phase transitions

We propose that the I–II phase transition in both isomers involves, in addition to the structural change from face-centered-cubic to an unknown structure, a partial alignment of the molecules from the disordered lattice[16] in phase I. The aligning force is due to the *inter*molecular or atom–atom potential and is partially offset by the dipole moment in the *ortho* isomer. At this point it is not known whether the phase II structures, which are presently being investigated, are the same in both isomers and therefore a more detailed discussion is unwarrented. In the II–III transition in *para*-carborane at 238 K there must be another interaction coming into play. One possible candidate is the *inter*molecular quadrupole interaction discussed previously. Thus the II–III transition in *para*-carborane at about 238 K may correspond to the onset of a long range ordering of quadrupoles. Although this occurs in solid hydrogen it is surprising that such an effect would manifest itself at the relatively high temperatures of interest in the present case. Further discussion of phase III of *para*-carborane must await second moment measurements to determine the degree of anisotropy of the motion.

In Fig. 2, the solid line for *ortho*-carborane at low temperatures is based on the data in the range 185 K $< T < 225$ K. There is a significant departure from this line at temperatures below 185 K. The behavior is characteristic of either an additional relaxation mechanism coming into play[31] or another phase transition. One possible mechanism is that of cooperative motion involving pairs of molecules. Although probably always present,[16] it is only at low temperatures where ordinary

molecular reorientation is less effective, that relaxation from such a process would manifest itself. In this temperature region, the observed second moment is increasing rapidly with decreasing temperature[16] which tends to support such a hypothesis. We note, however, that phase transitions involving discontinuities in E_a but very small discontinuities in T_1 have been observed.[38,39] Finally we note that a small anomaly in the calorimetry of *ortho*-carborane was found[16] at 165 K which is slightly lower than 173 K, the lowest temperature reported in the present work.

It is evident from the present discussion and all of the reported work on the carboranes that a detailed understanding of molecular reorientation in the carboranes is not possible without structural information on the low temperature phases. Even the rigid lattice second moment calculations[2,16] were based on the face-centered-cubic structure due to the lack of further information. A structural study of *para*-carborane is in progress and hopefully results will be forthcoming.

Ultimately the need is for *inter*molecular interaction calculations of the type that have appeared in the literature in recent years.[24-27,40] With this information a thorough spin–lattice relaxation analysis can be carried out. For example a theory[41] and a recent extension of that theory[42] based on the Ising model approach[43] have been presented for the tetrahedral NH_4^+ ion and applied to the BH_4^- ion.[18] Although the behavior of the carboranes is experimentally similar, the lack of structural information prevents application of a similar model. Finally, a very general nuclear relaxation theory based on a study of correlation functions and fluctuations near a structural phase transition has been given.[44]

VI. CONCLUSIONS

We have performed a study of the temperature dependence of the proton spin–lattice relaxation times in *ortho*- and *para*-carborane. For the two isomers the difference in behavior is striking. At high temperatures the molecules of both isomers reorient rapidly and isotropically on specific lattice sites. *Para*-carborane undergoes a phase transition at about 300 K and *ortho*-carborane a transition at about 265 K to as yet undetermined structures. The *para* isomer shows a constant activation energy for reorientation in the lower temperature phase while that of *ortho*-carborane decreases from a value similar to the *para* isomer just below the transition to a much lower value at the lowest temperatures measured. It is postulated that the molecular reorientation in the lower temperature phases in both isomers is more anisotropic than in the high temperature phases due to the relatively more effective interactions between molecules and the difference in behavior between the isomers is due to the large molecular dipole moment in the *ortho* isomer. The *para* isomer undergoes a second transition at 238 K and it is postulated that the molecular quadrupole moment may play a role in this transition. The reorentation in the low temperature phase of *ortho*-carborane is slightly more anisotropic than *para*-carborane at the same temperature on the basis of the T_1 values. The low temperature anomaly of *ortho*-

carborane in the vicinity of 185 K may result from the onset of another phase transition or it may be due to cooperative reorientations of pairs of molecules.

Comparing isomers of a substance can add significantly to the understanding of fundamental interactions in molecular solids since the structural differences correspond to switching certain interactions on or off. Such studies can involve the measurement of dielectric constants[45] and dielectric relaxation rates as well as nuclear spin relaxation rates.[46] A considerable amount of theoretical work is required to understand the *inter*-molecular potentials in the carboranes and it is hoped that this work will stimulate the appropriate investigations. Crystal structure data of the low temperature phases is needed and T_1 measurements in *ortho*-carborane should be extended to lower temperature in order to investigate the anomaly in the relaxation data. T_1 measurements in *meta*-carborane will be performed soon. These are important since *meta*-carborane is intermediate between *para*- and *ortho*-carborane in terms of molecular moments. As indicated in the introduction, neutron scattering experiments cannot be carried out on these compounds.

ACKNOWLEDGMENTS

[1] R. N. Grimes, *Carboranes* (Academic, New York, 1970).
[2] A. J. Leffler, M. N. Alexander, P. L. Sagalyn, and N. Walker, J. Chem. Phys. **63**, 3971 (1975).
[3] P. S. Goyal and B. A. Dasannacharya, J. Phys. C **12**, 209 (1979).
[4] Chr. Steenbergen, L. A. de Graaf, L. Bevaart, J. Bartolomé, and L. J. de Jongh, J. Chem. Phys. **70**, 1450 (1979).
[5] J. Töpler, R. D. Richter, and T. Springer, J. Chem. Phys. **69**, 3170 (1978).
[6] J. Vanderhaeghen, W. Wegener, S. Hautecler, and L. Van Gerven, Physica B **95**, 163 (1978).
[7] Y. Fujii, S. Hoshino, and T. Sakuma, J. Phys. Soc. Jpn. **45**, 175 (1978).
[8] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).
[9] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1961).
[10] C. P. Slichter, *Principles of Magnetic Resonance*, 2nd Ed. (Springer-Verlag, New York, 1978).
[11] D. C. Look and I. J. Lowe, J. Chem. Phys. **44**, 3437 (1966).
[12] J. E. Anderson, J. Magn. Reson. **11**, 398 (1973).
[13] M. Polak and D. C. Ailion, J. Chem. Phys. **67**, 3029 (1977).
[14] M. B. Dunn and C. A. McDowell, Mol. Phys. **24**, 969 (1972).
[15] P. A. Beckmann, C. I. Ratcliffe, and B. A. Dunell, J. Magn. Reson. **32**, 391 (1978).
[16] R. H. Baughman, J. Chem. Phys. **53**, 3781 (1970).
[17] W. Mandema and N. J. Trappeniers, Physica **76**, 123 (1974).
[18] A. Trokiner, H. Theveneau, and P. Papon, J. Chem. Phys. **69**, 742 (1978).
[19] A. W. Laubengayer and W. R. Rysz, Inorg. Chem. **4**, 1513 (1965).
[20] R. Maruca, H. Schroeder, and A. W. Laubengayer, Inorg. Chem. **6**, 572 (1967).
[21] A. I. Kitaigorodsky, *Molecular Crystals and Molecules* (Academic, New York, 1973).
[22] A. Gavezzotti and M. Simonetta, Acta Crystallogr. Sect. A **31**, 645 (1975).
[23] C. A. Fyfe and D. Harold-Smith, J. Chem. Soc. Faraday Trans. II 7, 645 (1975).
[24] A. I. M. Rae and R. Mason, Proc. Roy. Soc. A **304**, 487 (1968).
[25] D. E. Williams, J. Chem. Phys. **47**, 4680 (1967).
[26] F. Mulder and C. Huiszoon, Mol. Phys. **34**, 1215 (1977).
[27] L. Carozzo, G. Coronghu, C. Petrongolo, and E. Clementi, J. Chem. Phys. **63**, 787 (1978).
[28] F. L. Hirshfeld and K. Mirsky, Acta Crystallogr. Sect. 5, 366 (1979).
[29] P. H. Smit, J. L. Derissen, and F. B. van Duijneveldt, J. Chem. Phys. **67**, 274 (1977).
[30] M. F. Guest and I. H. Hillier, Mol. Phys. **26**, 435 (1973).
[31] P. A. Beckmann and S. Clough, J. Phys. C 10, L231 (1977).
[32] H. S. Gutowsky and S. Albert, J. Chem. Phys. **58**, 5446 (1973).
[33] L. Niemelä and E. Ylinen, Phys. Lett. A **31**, 369 (1970).
[34] E. N. Ivanov, Phys. Status Solidi **42**, 453 (1970).
[35] A. J. Leffler, M. N. Alexander, and P. L. Sagalyn, J. Chem. Phys. **65**, 2650 (1976).
[36] T. H. Doyne (private communication).
[37] A. J. Leffler, M. N. Alexander, and P. L. Sagalyn, J. Chem. Phys. **67**, 844 (1977).
[38] A. Watton, E. C. Reynhardt, and H. E. Petch, J. Chem. Phys. **69**, 1263 (1978).
[39] D. E. Woessner and B. S. Snowden, Jr., J. Chem. Phys. **47**, 378 (1967).
[40] D. E. Williams, Acta Crystallogr. Sect. A **28**, 84 (1972).
[41] K. H. Michel, J. Chem. Phys. **58**, 142 (1973).
[42] R. G. Petschek and B. I. Halperin, Phys. Rev. B **19**, 166 (1979).
[43] R. J. Glauber, J. Math. Phys. (N. Y.) **4**, 294 (1963).
[44] G. Bonera, E. Borsa, and A. Rigamonti, Riv. Nuovo Cimento **2**, 325 (1972).
[45] A. H. White and W. S. Bishop, J. Am. Chem. Soc. **62**, 8 (1940).
[46] A. M. I. Ahmed, R. G. Eades, T. A. Jones, and J. P. Llewellyn, J. Chem. Soc. Faraday Trans. II 68, 1316 (1972).