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Electron Paramagnetic Resonance Studies of Di-tert-Butyl Nitroxide in Adamantane

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The EPR hyperfine coupling constants, linewidths, and rotational correlation times have been measured for di-*tert*-butyl nitroxide (DTBN) doped in adamantane. At low paramagnetic impurity concentrations, the nitrogen hyperfine coupling constant decreases from a_N = 16.7 ± 0.2 G to 15.8 ± 0.2 G, the linewidth increases from 0.57 ± 0.05 G to 1.0 ± 0.05 G, and the rotational correlation time decreases from 1.5×10^{-10} sec to 1.5×10^{-11} sec as the temperature is decreased from -20°C to -65°C. A plastic crystal to brittle crystal phase transformation occurs at -65°C. The hyperfine coupling constant remains constant, the linewidth goes through a maximum and decreases, and the rotational correlation time goes through a minimum and increases as the temperature is lowered through the phase transition. Rapid motion persists even at -130°C. No unequivocal evidence for anisotropic reorientation was found but the unusually large values of a_N may be attributed to an enhanced tumbling about the long axis of the molecule in the plastic crystal phase. Evidence for slow translational diffusion at low temperatures is observed.

INTRODUCTION

Adamantane, a hydrocarbon which is almost spherically symmetric ("globular"), may be regarded as a model substance for investigating the lattice dynamics of

molecular crystals.[1,2] In recent years inelastic scattering of slow neutrons,[3,4] nuclear magnetic resonance (NMR)[5,6] and heat capacity measurements[7] have provided information concerning the intermolecular forces of this substance in the solid phase.

Adamantane exists in two polymorphic forms, cubic (plastic phase) and tetragonal (brittle phase). At temperatures above -65°C, adamantane crystallizes as a face-centered cubic structure (space group $Fm3m\ (O_h^5)$).[8] At -65°C, the adamantane crystal transforms[7] from the face-centered cubic structure to the body-centered tetragonal structure (space group $P42_1c(D_{2d}^4)$).[9]

Thus far neutron spectroscopy has revealed the most detailed information about the lattice dynamics of adamantane.[3,4] These experiments suggests that in the cubic phase, the adamantane molecules undergo 90° rotational jumps between equilibrium orientations. The jump frequency at room temperature is approximately 10^{11} sec^{-1} and does not exhibit a strong temperature dependence. The jump frequency is in agreement with recent NMR studies,[5] however, contrary to the neutron scattering experiments, a strong temperature depen-

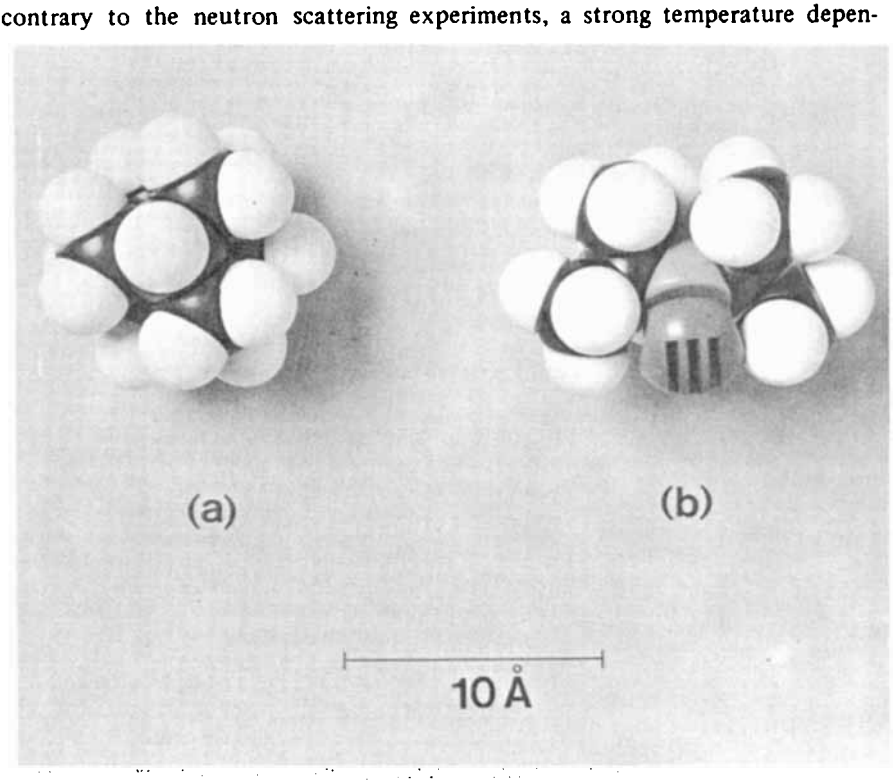

FIGURE 1 Pauling-Corey-Koltun models of (a) Adamantane and (b) DTBN. Note the similarity in size and shape between the two molecules.

dence for the rotational jump frequency was also observed. Clearly further work is required on the temperature dependence of the molecular reorientation. In the tetragonal phase, the dynamics of the adamantane molecules can best be described as a superposition of the vibrations of the molecular center of masses and the librations of the molecules.

Further studies of molecular motion in the frequency domain 10^9 to 10^{12} sec^{-1} should be quite interesting. Electron paramagnetic resonance (EPR) studies of nitroxide spin probes have proved to be quite useful for studying molecular motion in this frequency regime [10] in numerous studies in liquids. Not much work has been reported on the EPR of nitroxide in solids. In one experiment, [11] the free radical di-*tert*-butyl nitroxide (DTBN) was fully immobilized in a crystal while in another, [12] DTBN in thiourea exhibited anisotropic rotation. In this work, we describe experiments in which the EPR of the stable free radical DTBN, doped into adamantane is measured at various temperatures. This radical was chosen from the available nitroxides because it is similar in size (Fig. 1) and molecular weight to adamantane and can be incorporated into the adamantane crystal lattice. Rapid motion is observed over a wide temperature range. The DTBN molecule is slightly elongated thus the interesting possibility exists that enhanced rotation about the long axis, sometimes referred to [12] as "y-axis anisotropy", occurs.

EXPERIMENTAL

EPR spectra were recorded with a JEOL JES-3BX X-band spectrometer using 100 KHz magnetic field modulation. The amplitude of the field modulation was adjusted to a low value in order to prevent line distortion. The microwave power incident on the cavity was approximately 1 mw which prevented line broadening and distortion due to signal saturation. The magnetic field sweep was calibrated with an NMR gaussmeter combined with a Hewlett-Packard frequency counter. Variable temperature studies were accomplished using a homemade gas-flow cryostat capable of regulating the temperature to within ±1°C. Measurements at liquid nitrogen temperatures were made in an immersion Dewar. Helium gas was bubbled through the liquid nitrogen above the position of the sample lowering the temperature of the liquid nitrogen to approximately 73°K and thus preventing nitrogen bubbling.

Adamantane (Aldrich Chemical Company, Puriss grade) and di-*tert*-butyl nitroxide (Eastman Kodak Company) were used without further purification. The samples were prepared in the following manner: (a) 1.0000 gram of adamantane was dissolved in 20.0 cc n-pentane ("Baker Analyzed" Reagent) at room temperature, (b) 1.5 $\mu\ell$ of di-*tert*-butyl nitroxide was added to the adamantane-pentane solution and thoroughly mixed, (c) the sample was cooled in an

ice bath for 1 hour, and (d) the solution was then brought to room temperature and the solvent was stripped off by blowing air (at room temperature) over the sample. The polycrystalline material was uniformly powdered in a mortar and pestle and then sealed in quartz tubes. The EPR measurements either were taken immediately or the samples were stored at 77°K until they were measured at a later time.

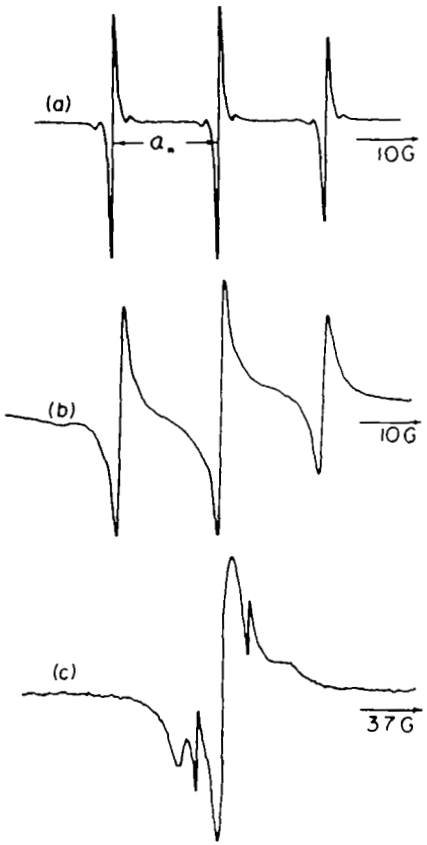

FIGURE 2 First derivative EPR spectra of DTBN in adamantane at (a) T = -20°C, (b) T = -130°C, and (c) T = -150°C. The measurement of the hyperfine coupling constant a_N is indicated as well as the field sweep in (c) is a factor of 3.7 times as large as the field sweep in (a) and (b). The difference in the peak to peak intensities in the high field (M_I = -1), intermediate field (M_I = 0) and low field (M_I = 1) hyperfine lines is due to differences in the linewidths, ΔHpp (M_I).

RESULTS

EPR spectra of DTBN in adamantane are shown in Figure 2 at -20°C (Figure 2a), -130°C (Figure 2b), and -150°C (Figure 2c). Note that the magnetic field sweep is a factor of 3.7 larger in Figure 2c. The spectra in the temperature range from room temperature to -130°C are typical for a rapidly reorienting nitroxide showing isotropic hyperfine coupling to the ^{14}N nucleus. [13] The lines are quite sharp, much like nitroxide spectra observed in liquids. At 77°K, a typical polycrystalline spectrum due to immobilized nitroxide radicals is observed. [13] Figure 2c shows that at -150°C a population of both rapidly reorienting and immobilized nitroxide radicals are present in the adamantane matrix.

Many samples, especially those prepared with large amounts of DTBN showed a broad underlying spectrum in addition to sharp lines even when studied at room temperature. Samples stored for a period of time or samples heated both show a conversion of the sharp spectra to the broad underlying spectra indicating that solute segregation [14] and its attendant electron-electron dipolar broad-

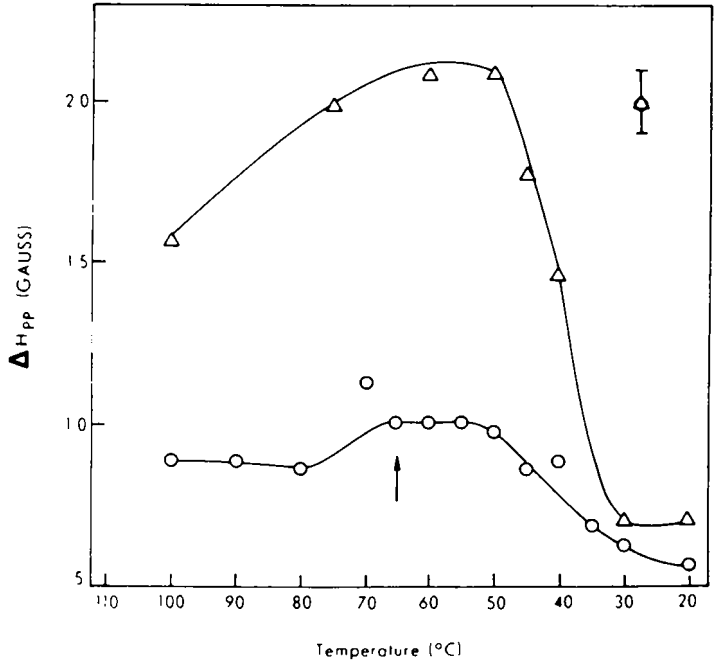

FIGURE 3 EPR linewidths ΔHpp($M_I = 0$) vs. temperature for DTBN in adamantane for a fresh sample, Δ; and an "aged" sample, O. See text. The plastic to brittle phase transition temperature is denoted by the arrow. The lines are smooth curves through the data.

ening occurred. The absence of the underlying spectrum was a criterion for the selection of the samples used in this study.

In Figure 2, the linewidths as measured between points of maximum slope (ΔHpp) are noted to vary with temperature. The variation of ΔHpp with temperature is given in Figure 3. The linewidths are found to depend also on DTBN concentration and sample history. At lower concentrations of DTBN, the linewidth is narrower and after storing a sample for two weeks at 77°K in the dark the linewidth is narrower. We call the latter sample the "aged" sample. Quantitative measurements of ΔHpp vs concentration of DTBN were not attempted because of the difficulty in determining the final concentration of radical *in* the adamantane. The linewidths of DTBN in the aged sample vs temperature are shown in Figure 3 also. Both samples show the same qualitative behavior; increasing linewidth with decreasing temperature from -30°C to near the phase transition at -65°C at which point the linewidth passes through a maximum and decreases slightly. The arrow in Figure 3 shows the temperature at which the phase transition occurs.

Aging the sample also decreases the intensity of the sharp spectrum by a factor of $\sim$50 and as mentioned above introduces a broad underlying spectrum. Since the intensity of the EPR spectrum is proportional to the concentration, then the narrowing of the EPR lines is easily understood as being due to lowering of the effective radical concentration. Both the fact that the broad underlying spectrum increases with time indicative of segregation of DTBN from the matrix and the fact that the EPR lines narrow indicative of a lower effective radical concentration are in full accord with a model in which DTBN molecules that are near one another in a fresh sample diffuse together.

The three hyperfine lines in both Figures 2a and 2b have slightly different linewidths and this accounts for the fact that the peak heights of the three lines are unequal. Linewidth variation among the hyperfine lines may be due to (a) long ($> 10^{-11}$ sec) rotational correlation times of the DTBN molecule or (b) the superposition of spectra due to two populations of DTBN, each exhibiting slightly different hyperfine coupling constants and g-values. Both of these possibilities result in an excess broadening of the high field line.[15] The latter possibility is discussed in the Discussion section.

If we assume that the unequal linewidths result from hindered rotation then we may estimate the correlation time from the spectra. The rotational correlation time may be computed from the linewidths of the three hyperfine lines if isotropic reorientation is assumed. This correlation time, roughly the time required for the radical to reorient by 1 radian is given by[16]

$$\tau_c = K[\Delta Hpp(1) + \Delta Hpp(-1) - 2\Delta Hpp(0)] \qquad (1)$$

where $\Delta Hpp(M_I)$ is the linewidth of the M_I component of the hyperfine triplet. Now, K is a quantity that depends on the radical and the matrix. For DTBN, the

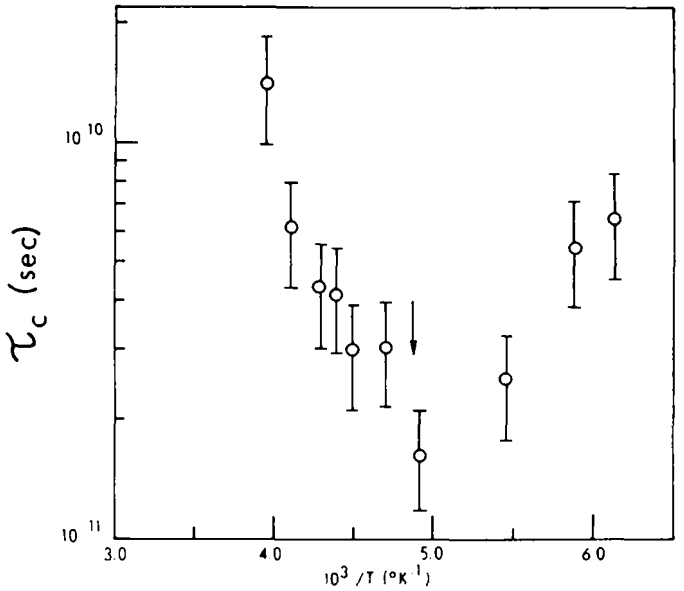

FIGURE 4 Rotational correlation times τ_C as a function of T^{-1} for an "aged" sample of DTBN in adamantane. The phase transition temperature is marked by the arrow.

value of $K = 7.1 \times 10^{-10}$ G^{-1} sec if parameters from single crystal work [11] are employed, while $K = 5.7 \times 10^{-10}$ G^{-1} sec if parameters derived from the 77°K spectrum in this work are used. Neither procedure is exactly correct because the two environments are different from the environment of the plastic crystal. We use the latter value in this work noting that *relative* values of τ_c would be unaffected. The variation of τ_c with temperature computed using Eq. (1) and the experimental linewidths is shown in Figure 4 for an aged sample. The values of τ_c for the fresh sample are uniformly larger as is obvious from the fact that the linewidths are broader. As we discuss below, the broader lines in the fresh sample are most likely due to exchange or dipolar interactions between the tumbling spins, thus the rotational correlation times derived from aged samples are more meaningful quantitatively. Nevertheless, we do find that the qualitative behavior of τ_c in the fresh sample is similar to that in Figure 4 where τ_c decreases with decreasing temperature, goes through a minimum at the phase change temperature, and then increases. The arrow in Figure 4 shows the temperature of the plastic to brittle phase transition.

The nitrogen hyperfine coupling constant, a_N, varies with temperature as shown in Figure 5. Coupling constants in the fresh and the aged samples are similar, decreasing from 16.7 ± 0.2 G at -20°C to 15.8 ± 0.2 G at -65°C which is near the phase transition. The coupling constant is then rather constant below the phase transition, which is marked by the arrow.

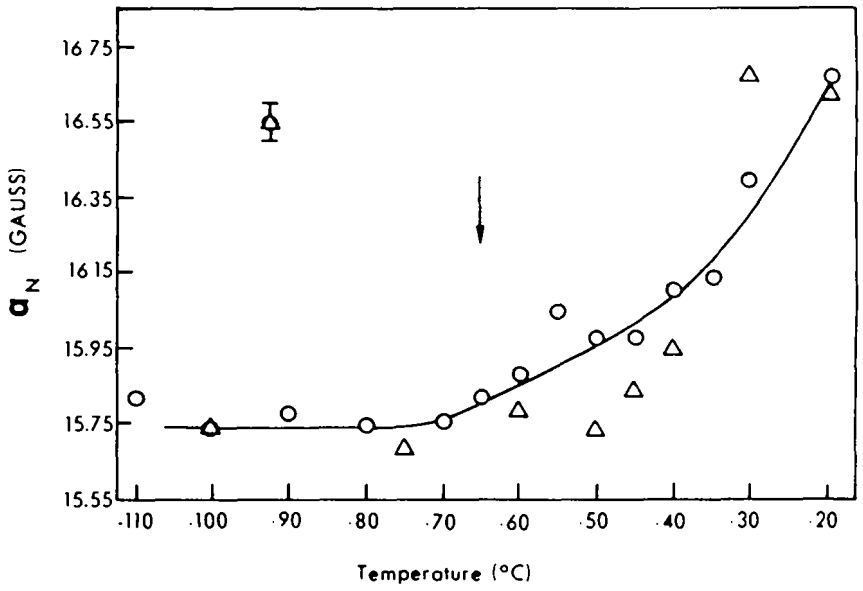

FIGURE 5 Nitrogen hyperfine coupling constants for DTBN in adamantane in a fresh sample, Δ; and an "aged" sample, O.The curve is a smooth curve through the data points for the "aged" sample.

DISCUSSION

The most striking observation in this work is that DTBN, a molecule very similar to adamantane, reorients quite rapidly even at temperatures as low as -110°C where $\tau_c \sim 6 \times 10^{-11}$ sec. Thus, if we make the plausible assumption that the DTBN molecules behave similarly to the adamantane molecules, the latter reorient as fast in a solid at -110°C as molecules of comparable size do in viscous liquids! We are unable to distinguish between a libration and a rotation in these experiments.

The variation of τ_c with temperature is very interesting but must be viewed with some caution for two reasons. First, the broadening of the EPR lines is concentration dependent. The main mechanisms for concentration dependent broadening are electron-electron dipolar interactions[17] and exchange interactions.[18] In a liquid, the latter would be expected to dominate and would lead to line broadening that was temperature dependent.[18] In a dilute solid, the dipolar contribution would be expected to dominate and would be relatively temperature independent.[17] In these unusual plastic crystals, we do not rule out exchange broadening and its attendant temperature dependence. Indeed Figure 3

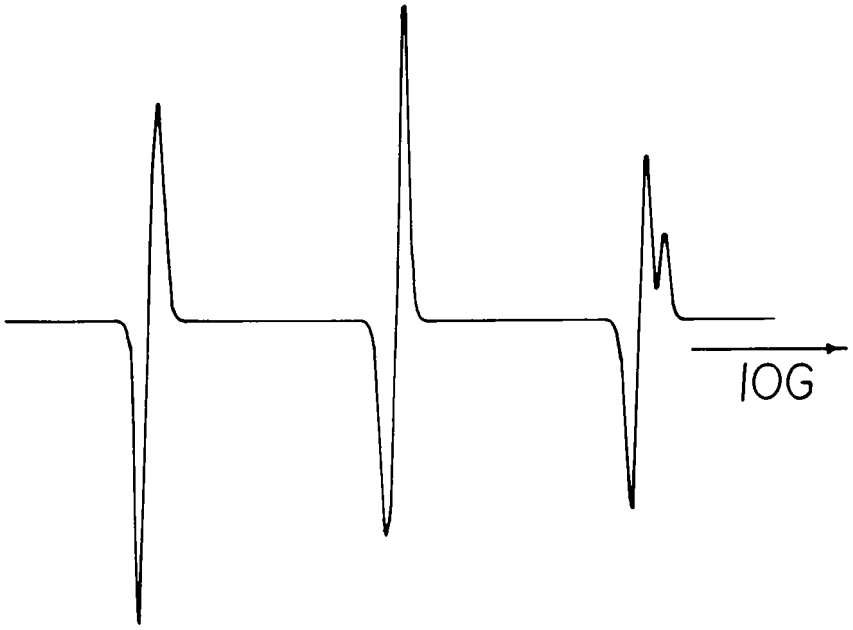

FIGURE 6 Simulated composite spectrum due to two magnetic sites for DTBN in adamantane. Site one has $a_N = 16.7$ G, $\Delta Hpp = 0.57$ G and site two has $a_N = 15.8$ G, $\Delta Hpp = 1.0$ G. There is 15% (doubly integrated area) of the former and 85% of the latter.

indicates that the concentration dependent broadening *is* temperature dependent. The question arises: Is the factor of 50 lower in concentration in the aged sample low enough to neglect concentration effects? The answer is very likely yes because $\Delta Hpp = 0.57$ G observed at T = -20°C is very near the limit of $\Delta Hpp = 0.5$ G due to the unresolved hyperfine coupling of the unpaired electron to the t-butyl protons in the DTBN.[19] The lineshape is measured to be very nearly Gaussian at T = -20°C which is consistent with the linewidths being dominated by unresolved hyperfine coupling.[19] We note that the variation in linewidth with temperature in the aged sample is a factor of 2 and, even if we assume that all of this variation is a result of having too large a concentration, then the variation of τ_c would be different by a factor of 2. The measured variation of τ_c is over more than a decade. Thus we conclude that exchange broadening may be operative in this unusual solid, but that in the aged sample, the contribution to the τ_c temperature profile is no more than 20% and probably much less.

We have been unsuccessful in carrying out experiments in which substantially smaller concentrations were used because of signal to noise problems.

The second difficulty in interpreting the temperature variation of τ_c is that

the superposition of two nitroxide spectra of similar a_N and g-values can give a composite spectrum that appears very much the same as Figure 2a and 2b.[15] We entertain this possibility for two reasons. The spectrum in Figure 2c shows that there are two populations of DTBN at low temperatures and too, the variation of a_N with temperature is unusual (Figure 5). In a liquid, the isotropic hyperfine coupling constant of DTBN is found to vary with the static dielectric constant, D_S, of the solvent[20] and this dependence holds in the frozen solvents as well.[14] The variation in a_N from $\sim$16.7 – 15.8 G is difficult to understand from a dielectric constant point of view because these values reflect a change in the D_S from 50 to 17 using data from water-ethanol mixtures to calibrate a_N vs D_S.[21] To our knowledge, D_S has not been measured in adamantane over this temperature range but it would be very surprising if D_S is larger or if D_S varies very much with temperature. Thus we must consider the possibility that the observed spectrum is composed of two spectra having coupling constants $a_{N_1} = 15.8$ G and $a_{N_2} = 16.7$ G and that the relative amounts of these vary with temperature. Figure 6 shows a simulation of the spectrum with 85% of the former and 15% of the latter. The linewidths were chosen to be the experimental linewidths at T = –65°C and T = –20°C respectively. In Figure 6 and in simulations over the entire range of the relative amounts of the two spectra, using several linewidth values, the high field line is always resolved into two lines contrary to experimental observation. We therefore conclude that the variation in a_N cannot be explained by variations of relative proportions of two magnetically different populations of DTBN. That there may be a small admixture of one DTBN spectrum into the "main" DTBN spectrum cannot be entirely ruled out. This possibility could affect the absolute magnitude of τ_c but not the temperature variation. The same temperature profile is observed in various samples and this tends to indicate that admixtures of other spectra is not important because one would expect different proportions of the two sites in various samples.

The magnitude of a_N for DTBN in adamantane is very curious, being larger than a_N for DTBN in a crystal of tetramethyl-1,3-cyclobutanedione[11] (15.2 G) or in a non-polar solvent, e.g. n-pentane (15.4 G).[22] Departures of the line separation from the isotropic hyperfine coupling may occur if the motion of the nitroxide is anisotropic as shown by Williams et. al.[23] Unfortunately these authors did not give quantitative details but direct measurement of the line separations in the simulated spectra given in Figure 11 of reference (23) shows that the "apparent" coupling constant *decreases* as τ_c decreases if the nitroxide undergoes y axis anisotropic motion. Figures 4 and 5 show that the change in τ_c and a_N with temperature bear the same relationship with one another. We conclude that the curious variation of a_N with the temperature may be due to anisotropic motion. Unfortunately, this interpretation must remain tentative until further evidence is found, because only "x-axis anisotropy" can be identified unequivo-

cally.[23] The temperature dependence is not likely to be due to intramolecular changes in the DTBN molecule because no such variation has been observed in other systems. An alternative explanation is that the environment presented by the plastic crystal perturbs the unpaired spin distribution. Below the phase transition, the coupling constant behaves quite normally. We note that care must be exercised when interpreting temperature variations of coupling constants of radicals isolated in this matrix: for example, the temperature dependence of the coupling constants for radiation produced fragments.[24]

The fact that the intensity of the sharp lines which are due to isolated DTBN molecules decrease and the intensity of the broad underlying lines due to clustered DTBN molecules increase when the sample is stored at 77°K indicates that some *translational* motion takes place also. Thus, we show that translational diffusion occurs at low temperatures as well as at higher temperatures.[5]

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