J. Phys. Chem. A **2001,** *105,* 7350−7355

Methyl Group Rotation and ^1H and ^2H Zeeman Relaxation in Organic Solids

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Received: March 26, 2001; In Final Form: June 1, 2001

We have measured the solid state ^{1}H and ^{2}H Zeeman relaxation rates R at room temperature in two methyl-deuterated samples of 1,9-dimethylphenanthrene. The ^{1}H dipolar rate R_d^9 (d for ^{1}H dipolar and 9 for 9-methyl group) and the ^{2}H quadrupolar rate R_q^1 (q for ^{2}H quadrupolar and 1 for 1-methyl group) were measured in 1-(trideuteriomethyl)-9-methylphenanthrene. The ^{1}H dipolar rate R_d^1 and the ^{2}H quadrupolar rate R_q^9 were measured in 1-methyl-9-(trideuteriomethyl)phenanthrene. Models are developed for both R_d^m and R_q^m ($m = 1$ or 9) due to methyl group rotation. In a large class of simple dynamical models for spin relaxation in the solid state, the ratios R_q^m/R_d^m are independent of the dynamics (except for the mass difference between the ^{1}H and ^{2}H nuclei). In the present case, these ratios are also independent of m. In addition, the ratios R_k^9/R_k^1 (k = d and q) are dependent only on the activation energy for methyl group rotation and another related dynamical parameter, but they are independent of the interaction being modulated. Because many parameters factor out, these ratios can be predicted with few or no adjustable parameters, depending on the sophistication of the theoretical model. The agreement between theory and experiment is good, even for the simplest theoretical models. These agreements give one a greater confidence in the models for quadrupolar and dipolar relaxation, but particularly the latter, which, because of spin diffusion, are more difficult to test.

Introduction

An excited nuclear spin system relaxes to its equilibrium state when an interaction between the nuclear spins and the environment changes with time. Simple, but quite successful models for the nuclear Zeeman relaxation rates R separate the time-independent parts (interaction constants, molecular and crystal structure, etc.) from the dynamical parts that modulate the interaction (rotation, translation, lattice vibrations, etc.).[1] Fitting experimentally determined rates R with even simple dynamical models provides information about intra- and intermolecular interactions that cannot be obtained from time-averaged solid state nuclear magnetic resonance (NMR) properties. The problem with dynamical models, though, is mainly one of uniqueness. Even if models fit the data very well, usually a quite different model may work just as well. At the very least, products or ratios of important parameters are often determined, but not the individual parameters themselves.

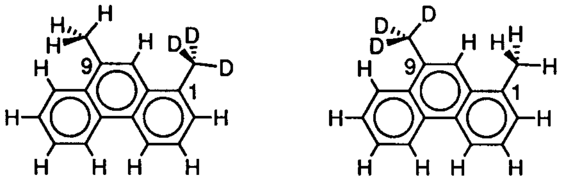

Figure 1. Schematic representations of the two molecules used in this study: 1-(trideuteriomethyl)-9-methylphenanthrene (1,9-DMP[1-d_3]) and 1-methyl-9-(trideuteriomethyl)phenanthrene (1,9-DMP[9-d_3]).

In this paper we report solid state ^{1}H (proton) and ^{2}H (deuteron) Zeeman spin relaxation rates R in the NMR rapid-motion limit in two polycrystalline samples of methyl-deuterated 1,9-dimethylphenanthrene (1,9-DMP), one with the 1-methyl group deuterated and the other with the 9-methyl group deuterated (Figure 1). We analyze the data with well-known simple models for the Zeeman relaxation rates R_k^m. The superscript m (=1 or 9) refers to the 1- or 9-methyl group in 1,9-dimethylphenanthrene. The subscript k = d refers to the dipolar relaxation rate for ^{1}H atoms in a C(^{1}H)$_3$ group and the subscript k = q refers to the quadrupolar relaxation rate for ^{2}H atoms in a C(^{2}H)$_3$ group. We also use ^{2}H NMR spectroscopy to measure the quadrupolar coupling constant that appears in the expressions for R_q^m. We compare the modeled and measured ratios R_q^m/R_d^m that factor out *most* of the dynamical parameters in the models. This is done for both methyl group

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10.1021/jp0111160 CCC: $20.00

sites in the molecule ($m = 1$ and 9). Finally, we compare the modeled and measured ratios R_k^1/R_k^9. This factors out *essentially all* the interaction parameters in the models and leaves only dynamical parameters that have been determined previously. This is done for both the dipolar (k = d) and quadrupolar (k = q) rates. There are no or few adjustable parameters in the theoretical ratios, and they are in reasonable agreement with the corresponding observed ratios. This procedure gives one confidence in using the separate models for the deuteron quadrupolar relaxation rates and for the proton dipolar relaxation rates but particularly for the latter where the nonlocal nature of the interactions make the models more difficult to generate and test.

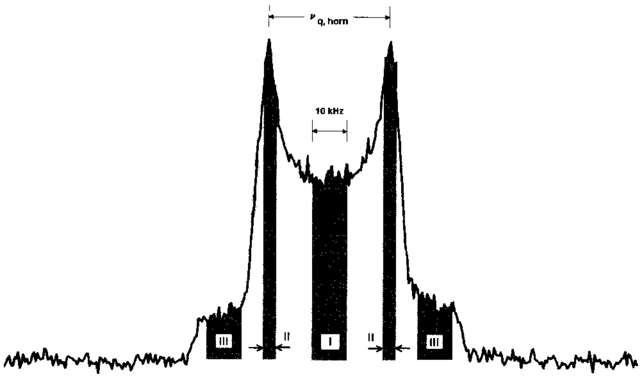

Figure 2. ^{2}H quadrupolar spectrum of 1-(trideuteriomethyl)-9-methylphenanthrene (1,9-DMP[1-d_3]). The spectrum of 1-methyl-9-trideuteriophenanthrene (1,9-DMP[9-d_3]) is indistinguishable from the spectrum shown. The horn splitting is $\nu_{q,horn} = 34 \pm 1$ kHz, as indicated, giving a "vibrationally-averaged quadrupolar coupling constant" of $\langle(eQ)(eq/h)\rangle = 157 \pm 4$ kHz, as discussed in the text. The line broadening used was 50 Hz, and the entire region shown is 180 kHz. The three shaded regions of the spectrum labeled I, II, and III correspond to three sets of molecules whose C(^{2}H)$_3$ rotation axes form an angle θ with the static magnetic field: (I) a 10 kHz wide region in the center of the spectrum corresponding to θ in the vicinity of $\cos^{-1}(1/\sqrt{3}) = 55°$ for all molecules, (II) a 3 kHz wide region corresponding to θ in the vicinity of 90° for about 80% of the molecules and in the vicinity of 35° for about 20% of the molecules, and (III) a 10 kHz wide region corresponding to θ in the vicinity of 0° for all molecules. The three regions are discussed in greater detail in the text.

Experiment

Two deuterated samples of 1,9-dimethylphenanthrene (1,9-DMP) were used (Figure 1), one with the 1-methyl group deuterated, and the other with the 9-methyl group deuterated. The preparation of 1-(trideuteriomethyl)-9-methylphenanthrene (1,9-DMP[1-d_3]) is reported elsewhere.[2]

The preparation of 1-methyl-9-(trideuteriomethyl)phenanthrene (1,9-DMP[9-d_3]) was accomplished in two steps, starting with a Wittig reaction of acetophenone-*methyl*-d_3 (Aldrich) with the ylide prepared from (*o*-methylbenzyl)triphenylphosphonium bromide using phenyllithium as the base. The product of this reaction was purified by chromatography on silicic acid using hexanes as the eluant to give a pale yellow oil. Analysis by combined gas chromatography and mass spectrometry indicated that this oil was a 2:1 mixture of the *Z* and *E* isomers of *o*-methyl-α′-(trideuteriomethyl)stilbene. This mixture of isomers was subjected to oxidative photocyclization[2,3] by ultraviolet irradiation in cyclohexane solution containing 10 mol % of iodine as the oxidant. Purification of the photocyclization product by recrystallization from methanol followed by sublimation at reduced pressure gave colorless crystals of 1-methyl-9-(trideuteriomethyl)phenanthrene: mp 86.0−87.5 °C (lit.[4] mp 87−88 °C for the all-protio 1,9-dimethylphenanthrene); ^{1}H NMR (270 MHz, CDCl$_3$ solution) δ 8.75 (m, 1H; H-5), 8.56 (d, J = 8.2 Hz, 1H; H-4), 8.07 (m, 1H; H-8), 7.79 (s, 1H; H-10), 7.68−7.62 (m, 2H; H-6, and H-3 or H-7), 7.49 (dd, J = 8.1, 7.2 Hz, 1H; H-7 or H-3), 7.42 (d, J = 7.0 Hz, 1H; H-2), 2.74 (s, 3H; 1-CH$_3$).

^{1}H and ^{2}H NMR spectra and relaxation rates R were measured at room temperature (293 ± 2 K) in polycrystalline 1,9-DMP-[1-d_3] and 1,9-DMP[9-d_3] using a fixed-field (7.05 T), variable-frequency Bruker MSL-300 solid state NMR spectrometer. The ^{1}H $\pi/2$ pulse width was typically 3 μs. The ^{1}H spectra at 300 MHz are featureless homogeneously broadened Gaussians (fwhm = 28 kHz) characteristic of organic solids composed of molecules having many closely spaced ^{1}H atoms.

The ^{2}H $\pi/2$ pulse width was typically 3.5 μs. The ^{2}H spectra (Figure 2) at 46.1 MHz are Pake-like powder patterns characterized by a horn splitting of $\nu_{q,horn}^m = 34 \pm 1$ kHz (as indicated in Figure 2 without the superscript $m = 1$) and an asymmetry parameter of $\nu_{q,horn}^m = 0.05 \pm 0.02$. The spectra of the two compounds are indistinguishable, and the superscript m on $\nu_{q,horn}^m$ is kept only because in other studies, different sites may, in general, have different splittings. So long as η is small, the horn splitting $\nu_{q,horn}^m$ is related to the "observed quadrupolar coupling" $\nu_{q,obs}^m$ by[5]

$$\nu_{q,horn}^m = \frac{3}{4}\nu_{q,obs}^m(1 - \eta) \tag{1}$$

which gives $\nu_{q,obs}^m = 47.7 \pm 1.4$ kHz for both $m = 1$ and 9. For methyl groups, the "quadrupolar coupling" or the "vibrationally-averaged quadrupolar coupling constant" $\nu_q^m = \langle(eQ)(eq/h)\rangle^m$ (for ^{2}H quadrupole moment eQ and electric field gradient eq/h^1) is related to $\nu_{q,obs}^m$ by

$$\nu_{q,obs}^m = \nu_q^m\left[\frac{1}{2}(3\cos^2\beta - 1)\right] \tag{2}$$

where β is the angle the methyl group rotation axis makes with the C−^{2}H bond.

The ^{1}H and ^{2}H Zeeman relaxation rates R were measured with a $\pi - t - \pi/2(\text{add}) - t_R - \pi/2(\text{subtract}) - t_R -$pulse sequence with appropriate phase cycling. The repetition period t_R was greater than $8R^{-1}$. This sequence directly measures the parameter $\Delta M(t)$ in $\Delta M(t) = [M(\infty) - M(t)] = [M(\infty) - M(0)]$-$[\exp(-Rt)] = [\Delta M(0)][\exp(-Rt)]$ and does not require fitting to a value of $M(\infty)$. That is to say, the experiment alternates between measurements of $M(t)$ and $M(\infty)$ and performs the subtraction $[M(\infty) - M(t)]$. R was determined by a *Simplex* fit to the data for each run.

The ^{1}H rates R_d^m were determined by integrating over the entire spin-dipolar homogeneously broadened profile and were found to be $R_d^9 = 0.12 \pm 0.02$ s^{-1} for 1,9-DMP[1-d_3] (or, equivalently, 1,9-DMP[9-h_3]) and $R_d^1 = 0.061 \pm 0.009$ s^{-1} for 1,9-DMP[9-d_3] (or, equivalently, 1,9-DMP[1-h_3]). The quoted uncertainties reflect averaging over several experiments and are greater than those returned by the *Simplex* routine. They will include some measure of the many possible systematic errors that can occur when using a sophisticated NMR spectrometer such as the Bruker MSL-300.

The ^{2}H R_q^m values varied slightly across the inhomogeneous quadrupolar profile. The frequency position in the spectrum in Figure 2 can be related to the angle θ between the methyl group rotation axes and the applied magnetic field.[6] The spectrum involves two mirror-symmetric Pake-like patterns A and B, with

$\theta = 0$ (far left of the spectrum for A, far right of the spectrum for B in Figure 2) to $\theta = 90°$ (right-hand peak for A, left-hand peak for B), with the magic angle $\theta = \cos^{-1}(1/\sqrt{3}) = 54.7°$ for both in the center. Three R_q^m values were computed by integrating over the three shaded regions indicated in Figure 2. The first region (I) is 10 kHz wide in the center of the spectrum and corresponds to molecules that have the principal axis for the quadrupolar interaction (taken to be the methyl group reorientation axis) in the vicinity of the magic angle. The range integrated is from about 47° to about 63° for A (and from 63° to 47° for B). The second region (II) corresponds to a narrower 3 kHz region ($\Delta\theta \approx 5°$) in the vicinity of the peaks (horns). About 80% of the intensity corresponds to the vicinity of $\theta = 90°$ for A (B) and about 20% to the vicinity of $\theta = 35°$ for B (A). Finally, the third region integrated is the wings (edges) of the spectrum in the vicinity of $\theta = 0°$ only, for both A and B. The 10 kHz region integrated corresponds to θ from about $\theta = 0$ to about $\theta = 15°$. (This discussion assumes that the asymmetry parameter η can be taken to be zero.)

For regions II and III, the averages of the R_q^m for the two sides of the spectrum were computed. All the relaxation curves were found to be exponential within experimental uncertainty. In principle, the relaxation will not be exponential, in part because an integral over a finite region of inhomogeneously broadened regions characterized by slightly different rates is being computed, and, in part, because for regions I and II the ^{2}H line is formed from the superposition of two mirror-image powder patterns,[6] as discussed above, and for region II, no matter how narrow the region integrated, it will contain molecules whose methyl group rotation axes are oriented both near $\theta = 90°$ (about 80% of the sample) and near $\theta = 35°$ (about 20% of the sample). Nevertheless, the departures from exponentiality are too small to be observed. This is generally the case.[7]

The R_q^9 values in 1,9-DMP[9-d_3] are 7.0 ± 0.7, 6.2 ± 0.2, and 5.6 ± 0.1 s^{-1} for θ near 0, 55°, and 90°. The observed relaxation rates R_q^1 in 1,9-DMP[1-d_3] are 3.2 ± 0.3, 2.7 ± 0.1, and 2.42 ± 0.03 s^{-1} for θ near 0, 55°, and 90°. The signal is small in the wings of the spectrum (θ near 0), as can be seen from Figure 2, and this is reflected in the larger relative uncertainties in the associated R_q^m. As in the case of the R_d^m measurements, the quoted uncertainties in the R_q^m values are greater than those returned by the *Simplex* routine. In addition to having components arising from averaging over several measurements, they include the averaging over the left- and right-hand parts of the quadrupolar spectrum for regions II and III.

Theory

The nuclear Zeeman relaxation rate R_k^m resulting from ^{1}H dipolar (k = d) or ^{2}H quadrupolar (k = q) interactions in the mth methyl group being modulated by methyl group rotation is given by Abragam[8] and Slichter[1] in terms of the spectral densities that characterize the motion. We assume that the expressions for the relaxation rate can be separated into products of two factors, one that characterizes the magnitude of the interaction and another that characterizes the motion. Further, we assume that the relaxation is exponential and that a powder average is appropriate.[9] R_k^m is given by

$$R_k^m = A_k^m[j_{(k)}^m(\omega) + 4j_{(k)}^m(2\omega)] \tag{3}$$

where $j_{(k)}^m(\omega)$ is the reduced spectral density and the A_k^m characterize either the dipolar (k = d) or the quadrupolar (k = q) interaction, as discussed below. The reduced spectral density $j_{(k)}^m(\omega)$ does not have any dependence on the interaction per se. However, the subscript k must be kept because dipolar relaxation rates R_d^m are determined by the rotation of three ^{1}H nuclei, the quadrupolar relaxation rates R_q^m are determined by the rotation of three ^{2}H nuclei, and the motion will depend on the ^{1}H−^{2}H mass difference as shown below. The subscript k is in parentheses as a reminder that the parameter's dependence on the interaction is on the moment of inertia of the methyl group only, and this is not a dynamical parameter.

For ^{1}H relaxation, where spin−spin interactions are modulated by the motion, and where a common spin temperature is maintained among all ^{1}H nuclei (i.e., rapid spin diffusion), A_d^m (i.e., k = d) is conveniently expressed as

$$A_d^m = c^m \frac{n}{N}\frac{9}{40}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6} \tag{4}$$

for ^{1}H magnetogyric ratio $\gamma = 2.675 \times 10^8$ kg^{-1} s A, $\mu_0/4\pi = 10^{-7}$ m s^{-2} kg A^{-2}, and r the ^{1}H−^{1}H separation in a methyl group. A value for r is discussed in the next section. The factor $^9/_{40}$ can be conveniently, although somewhat artificially, factored into the products $2(^3/_4)(^3/_{20})$. The factor $[(^3/_{20})(\mu_0/4\pi)^2(\gamma^4\hbar^2/r^6)]$ is a convenient starting point and comes from the basic relaxation theory for a pair of spin $^1/_2$ particles undergoing isotropic reorientation [ref 8, page 300, eq 105 (with $(\mu_0/4\pi)^2$ inserted to give SI units)]. The factor $^3/_4$ can be thought of as a correction for the fact that the motion of any given ^{1}H−^{1}H vector is not isotropic but confined to a plane.[9] The factor 2 comes from the fact that each ^{1}H spin in the methyl group is involved in two spin−spin interactions. The factor n/N is the ratio of the number n of ^{1}H nuclei whose dipole−dipole interactions are being modulated to the total number N of ^{1}H nuclei in the molecule. For 1,9-DMP[1-d_3] and 1,9-DMP[9-d_3] $n/N = 3/11$. The parameter $c^m \geq 1$ allows for the consideration of models that take into account the modulation of ^{1}H−^{1}H spin−spin interactions in addition to the six intramethyl interactions. If only intramethyl ^{1}H−^{1}H interactions are considered, $c^m = 1$. Indeed, we shall use $c^m = 1$ for both $m = 1$ and 9 (as determined in ref 2), but this may not be the case in other studies. When intramethyl−extramethyl spin−spin interactions are taken into account, c is greater than unity but usually only by a few percent.[10] This is discussed further in the next section. The numerical value of A_d^m for 1,9-DMP[1-d_3] and 1,9-DMP[9-d_3] is presented in the next section. We note here that there is no m dependence to A_d^m in the present case.

For ^{2}H relaxation, Torchia and Szabo[7] develop both a three-site jump model and a diffusion model for methyl group rotation, both of which account for the variation of R_q^m across the spectrum in Figure 2. Edholm and Blomberg[11] develop a hybrid model where the group diffuses in a 3-fold potential. A_q^m in eq 3 is given by

$$A_q^m = \frac{3\pi^2}{20}(\nu_q^m)^2\left\{1 + \frac{1}{2}f(1 + 3\cos^2\theta)\right\} \tag{5}$$

where θ is the angle between the methyl group rotation axis (the time-averaged principal axis of the quadrupolar interaction) and the applied magnetic field. The parameter $f = 0$ for the free-diffusion model (in which case there is no θ dependence) and $f = 1$ for the three-site jump model.[7] For a 3-fold barrier of 13 kJ mol^{-1}, characteristic of methyl reorientation in peri methyl groups in many methyl-substituted planar aromatic compounds (including methylphenanthrenes[2,12]), Edholm and Blomberg[11] find that $f = 0.76$. *Again, there is no m dependence to* A^m_q *in the present case.*

In the fast-motion limit, $\omega\tau^m_{(k)} \ll 1$, for correlation time $\tau^m_{(k)}$ where the subscript (k) reminds us that the only dependence on the type of interaction is going to be the moment of inertia of the $C(^1H)_3$ group for k = d and the moment of inertia of the $C(^2H)_3$ group for k = q. We note that the correlation time is uniquely defined as the area of the reduced correlation function which, in turn, is uniquely defined as the Fourier transform of the reduced spectral density $j^m_{(k)}(\omega)$.[13]

The relaxation rate is

$$R^m_k = 10\epsilon^m\tau^m_{(k)}A^m_k \tag{6}$$

This expression is familiar except perhaps for the factor $\epsilon^m \le 1$, which is a parameter that appears in dynamical models where an exponential correlation function ($\epsilon^m = 1$) does not fit the data but instead a distribution of exponential correlation times is required.[13] As discussed in the next section, the factor ϵ^m is about 0.8 for both the $m = 1$ and the $m = 9$ methyl groups.[2] The results of this paper are in no way affected by the inclusion of ϵ^m because it cancels in all the ratios that will be computed below.

We assume $\tau^m_{(k)}$ can be modeled by an Arrhenius relationship

$$\tau^m_{(k)} = \tau^m_{(k)\infty}\exp\left(\frac{E^m}{k_BT}\right) \tag{7}$$

where $k_B = 1.38 \times 10^{-23}$ J K^{-1} = 8.31 J K^{-1} mol^{-1} is Boltzmann's constant. For a barrier $E^m \gg k_BT$ [12 kJ mol^{-1} = $k_B(1.4 \times 10^3$ K)], the methyl group spends most of its time at the bottom of the barrier and $(\tau^m_{(k)\infty})^{-1}$ can be thought of as the attempt frequency for crossing the barrier (i.e., the methyl group rotates clockwise or counterclockwise by $2\pi/3$). In the harmonic approximation,[12,14]

$$\tau^m_{(k)\infty} = \frac{2\pi}{3}\sqrt{\frac{2I_{(k)}}{E^m}} \tag{8}$$

The only k dependence in $\tau^m_{(k)}$ and, indeed, *the only k dependence in any aspect of the motion, is in the moment of inertia* $I_{(k)}$. The only m dependence is the energy barrier E^m for methyl group rotation and the parameter ϵ^m, in eq 6, that accounts for a distribution or correlation times. In the next section we discuss the possibility that E^m for a $C(^1H)_3$ group may be different from E^m for a $C(^2H)_3$ group. The relaxation rate can now be expressed as

$$R^m_k = 10[\sqrt{I_{(k)}}A^m_k]\left[\frac{2\pi}{3}\epsilon^m\frac{\sqrt{2}}{\sqrt{E^m}}\exp\left(\frac{E^m}{k_BT}\right)\right] \tag{9}$$

Two sets of ratios are of interest. First, the ratio of the ^{2}H quadrupolar relaxation rate to the ^{1}H dipolar relaxation rate for the mth methyl group is

$$\frac{R^m_q}{R^m_d} = \frac{\sqrt{I_{(q)}}}{\sqrt{I_{(d)}}}\frac{A^m_q}{A^m_d} = \sqrt{2}\frac{A_q}{A_d} \tag{10}$$

where the ratio of the moments of inertia $I_q/I_d = 2$ has been used and where we note that there is no m dependence to this ratio in the present case. *This is an extraordinarily simple relationship!*

The second set of ratios of interest consists of the ratio of the ^{2}H quadrupolar relaxation rate for the 9-$C(^2H)_3$ group to that of the 1-$C(^2H)_3$ group and the ratio of the ^{1}H dipolar relaxation rate for the 9-$C(^1H)_3$ group to that of the 1-$C(^1H)_3$ group. The former ratio is obtained by dividing eq 9 with k = q and $m = 9$ by eq 9 with k = q and $m = 1$. The latter ratio is obtained by dividing eq 9 with k = d and $m = 9$ by eq 9 with k = d and $m = 1$. *Because the* A^k_m *are independent of m, these ratios are identical in the present case since the interaction dependence (k = d or q) factors out.* This single ratio is

$$\frac{R^9_k}{R^1_k} = \frac{j^9_{(k)}(0)}{j^1_{(k)}(0)} \tag{11}$$

$$= \frac{\epsilon^9\tau^9_{(k)}}{\epsilon^1\tau^1_{(k)}} \tag{12}$$

$$= \left(\frac{\epsilon^9}{\epsilon^1}\right)\sqrt{\frac{E^1}{E^9}}\exp\left(\frac{E^9 - E^1}{k_BT}\right) \tag{13}$$

Again, *this is an extraordinarily simple relationship*, involving only the activation energies for methyl group rotation and the ratio ϵ^9/ϵ^1, which is about one.[2]

Data Analysis and Discussion

We have measured ^{1}H Zeeman relaxation rates R_d due to the modulation of $^1H-^1H$ spin−spin interactions by methyl group rotation. We have also measured ^{2}H Zeeman relaxation rates R_q due to the modulation, by methyl group rotation, of the interaction between the quadrupole moment of the ^{2}H nucleus and the electric field gradient at the site of the nucleus, predominantly due to the distribution of electrons in the adjacent $^2H-^{12}C$ bond. The intermolecular van der Waals interactions that determine the crystal structures are independent of whether one or the other methyl group in 1,9-dimethylphenanthrene (1,9-DMP) is deuterated. The crystal structures of the two solids are the same. As discussed below, the electrostatic interactions that determine the methyl barrier are also independent of whether the methyl group is deuterated. The mass difference between a $C(^1H)_3$ group and a $C(^2H)_3$ group has been taken into account.

Mallory et al.[2] measured the ^{1}H dipolar rate R^9_d in 1,9-DMP-[1-d_3] between 83 and 230 K at 8.50 and 53.0 MHz. The R^9_d maximum resulting from $\omega\tau^9_{(d)} \approx 1$ for the 9-methyl group is observed, as are the fast ($\omega\tau^9_{(d)} \ll 1$) and slow ($\omega\tau^9_{(d)} \gg 1$) motion limits at both frequencies. R^9_d is independent of ω for $\omega\tau^9_{(d)} \ll 1$ (above 170 K), as expected. From a complete fit of these data, R^9_d at 293 K is predicted to be 0.13 s^{-1}, in good agreement with the observed value $R^9_d = 0.12 \pm 0.02$ s^{-1} at 300 MHz reported here. This comparison is important. Large systematic errors can be made in the measurement of such small relaxation rates. The two measurements were made at vastly different frequencies (300 MHz here and 8.50 and 53.0 MHz in ref 2). The spectrometer and probe assemblies are very different, as are the measurement techniques and data analysis. The measurement at 293 K reported here is at a temperature significantly higher than 230 K, the highest temperature employed in the low-frequency study. Last, but not least, the sample sat on the shelf for 10 years between studies. This agreement gives one confidence in both measurements.

Mallory et al. did not have 1,9-DMP[9-d_3], but they did measure the ^{1}H dipolar rate $R^{1\&9}_d$ in fully protonated 1,9-DMP between 80 and 250 K at 8.50 and 53.0 MHz. The two maxima

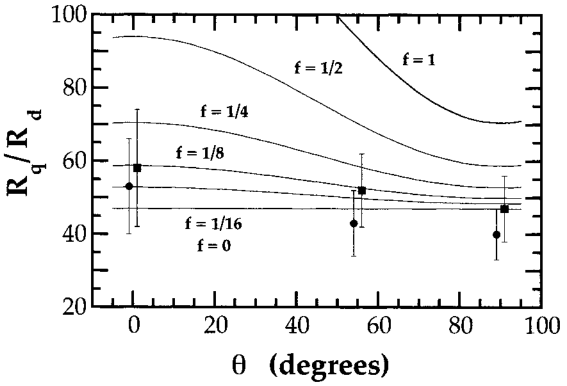

Figure 3. R_q^1/R_d^1 (closed circles) and R_q^9/R_d^9 (closed squares) vs θ, the angle the C(^{2}H)$_3$ rotation axes makes with the static magnetic field. The theoretical curves, as discussed in the text, are given by $R_q/R_d = (47)[1 + (f/2)(1 + 3\cos^2\theta)]$ with f as indicated.

in $R_d^{1\&9}$ resulting from the conditions $\omega\tau_{(d)}^9 \approx 1$ and $\omega\tau_{(d)}^1 \approx 1$ were observed and $R_d^{1\&9}$ is independent of ω for $\omega\tau_{(d)}^1$, $\omega\tau_{(d)}^9 \ll 1$ (above 170 K) as expected. A complete fit of these data and those for R_d^9 in 1,9-DMP[1-d_3] can be used to predict R_d^1 at 293 K. The predicted value of 0.052 s^{-1} will have a large uncertainty (about 25%), but it can be compared with the value of 0.061 ± 0.009 s^{-1} observed here. Again, this agreement is reassuring.

The ratios of the (three) observed ^{2}H rates R_q^1 in 1,9-DMP-[1-d_3] to the (single) ^{1}H rate R_d^1 in 1,9-DMP[9-d_3] (i.e., DMP-[1-h_3]) are 53 ± 13, 43 ± 9, and 40 ± 7 for θ in the vicinity of 0, $\cos^{-1}(1/\sqrt{3})$, and 90°. Similarly, the ratios of the (three) ^{2}H rates R_q^9 in 1,9-DMP[9-d_3] to the (single) ^{1}H rate R_d^9 in 1,9-DMP[1-d_3] (i.e., DMP[9-h_3]) are 58 ± 16, 52 ± 10, and 47 ± 9 for θ in the vicinity of 0, $\cos^{-1}(1/\sqrt{3})$, and 90°. These ratios are shown in Figure 3. The uncertainties are extremal values using $(R_q + \Delta R_q)/(R_d - \Delta R_d)$ and $(R_q - \Delta R_q)/(R_d + \Delta R_d)$ values, which probably overestimates the uncertainties in the ratios. For example, the uncertainties for the three sets of ratios for the three values of θ are coupled because they all have the same denominator. Thus, even though a θ independence is apparently consistent with the three sets of values if the uncertainties are assumed to be uncorrelated (see Figure 3), this is not that case. The ordering $R_q^m(0°) > R_q^m(55°) > R_q^m(90°)$ is clear. The theoretical values of this ratio are given by eq 10 as $\sqrt{2}A_q/A_d$. A_d is given by eq 4 and A_d is given by eq 5.

The only as yet unspecified parameter in A_d in eq 4 is r, the ^{1}H−^{1}H separation in a C(^{1}H$_3$) group. The only as yet unspecified parameter in A_q in eq 5 is β in eq 2, the angle the C(^{2}H$_3$) rotation angle makes with the C−^{2}H bond. George et al.[15] have carried out RHF/6-31G* calculations of the HCH and HCC bond angles involving the methyl group in toluene in a conformation analogous to those shown in Figure 1. On the basis of the averages of their results (HCH 107.4°, 107.8°, 107.8°, and HCC 111.2°, 111.2°, and 111.3°), we have assumed that our phenanthrene derivatives have ^{1}H−C−^{1}H and ^{2}H−C−^{2}H angles of 107.7° and have ^{1}H−C−C and ^{2}H−C−C angles of 111.2°. For methyl groups with this assumed H−C−H angle of 107.7° and an assumed C−H bond distance of 1.10 Å,[16] the ^{1}H−^{1}H distance of separation in a C(^{1}H$_3$) group would be $r = 1.78 \times 10^{-10}$ m which gives, via eq 4, $A_d^m = c^m(1.10 \times 10^9\ \mathrm{s}^{-2})$. *Given that* $c^m = 1$ *for both* $m = 1$ *and* $m = 9$, *there is no m dependence to* A_m^d *in the present case.* For completeness, we note that the value of r used here is to be compared with $r = 1.797 \times 10^{-10}$ m for an idealized tetrahedral structure. The parameter r enters A_d as r^{-6}, so this 1% difference in r results in a 6% difference in A_d. With an assumed ^{2}H−C−C angle of 111.2°, the angle between the C(^{2}H$_3$) rotation axis and the C−^{2}H bond axis would be $\beta = 68.8°$. This is to be compared with $\beta = \cos^{-1}(^1/_3) = 70.53°$ for the idealized tetrahedral structure. The factor $(^1/_2)(3\cos^2\beta - 1) = -0.304$ for $\beta = 68.8°$ compared with -0.333 for $\beta = 70.53°$, a difference of 10%. Thus, from eq 2, $\nu_q = \nu_{q,obs}/(-0.304) = -157 \pm 4$ kHz for $\nu_q = 47.7 \pm 1.4$ kHz as presented in the Experiment section. (This is to be compared with a value of $\nu_q = -143 \pm 4$ kHz that would result from the idealized tetrahedral structure.) We take ν_q as positive since the sign refers only to the orientation of the principal axis of the quadrupolar tensor. This 10% difference is squared in eq 5 and so leads to a 20% effect in A_q. Using $\beta = 68.8°$, the value of $(3\pi^2/20)(\nu_q^m)^2$ in eq 5 is $(3\pi^2/20)(\nu_q^m)^2 = (3.65 \pm 0.19) \times 10^{10}$ s^{-2}. *Given that there is no m dependence to* ν_q^m, *there is no m dependence to* A_q^m *in the present case.*

If A_q is given by eq 5 with $f = 0$, there are no adjustable parameters and the ratio $R_q^m/R_d^m = \sqrt{2}A_q/A_d = 47 \pm 3$, as shown by the $f = 0$ horizontal line in Figure 3. *The agreement between the calculated and observed ratios (Figure 3), using this simple free-diffusion model for methyl group rotation is remarkably good.* Of course, no θ dependence is predicted. If A_q is given by eq 5, the theoretical ratio, then, is $(47)[1 + (f/2)(1 + 3\cos^2\theta)]$, where θ is determined by the position in the quadrupolar spectrum and f is determined by the model. Predictions are shown in Figure 3 as different solid lines for different values of f and can be compared with the experimental values.

The uncertainties in the ratios of the experimental relaxation rates are large, but two general conclusions can be drawn. First, small f values ($f \leq 0.3$) fit the data better than larger f values. In particular, the value of $f = 0.76$ found by Edholm and Blomberg[11] seems high. In terms of the model,[7,11] this implies that a methyl group "diffusing through" a 3-fold barrier is a better picture than a methyl group instantaneously hopping among its possible orientations. Second, the two methyl groups are different. The 1-methyl group data correspond to a smaller f value than the 9-methyl group data. In principle at least, this has nothing to do with the barrier, which is smaller for the 1-methyl group than it is for the 9-methyl group, as discussed in the next paragraph. However, it is reasonable that the parameter f and the barrier are correlated in some manner. *This model for methyl group rotation leads to good agreement between the calculated and the experimental ratios of relaxation rates.*

Instead of looking at the ratios R_q^m/R_d^m of the relaxation rates for the two different interactions for a specific methyl group position m, we look at the ratios R_k^9/R_k^1 of the relaxation rates for the interaction k = q and k = d of the two methyl group positions given by eq 13. We assume that the rotation barriers for the C(^{2}H)$_3$ groups in the two phenanthrene derivatives are the same as those determined experimentally (see the following) for the corresponding C(^{1}H)$_3$ groups. It is well established that C(^{2}H)$_3$ groups are slightly smaller than C(^{1}H)$_3$ groups, with bond distances[17] about 0.005 Å shorter for C−^{2}H than for C−^{1}H, and van der Waals radii[18] about 0.003 Å shorter for ^{2}H than for ^{1}H. In principle, then, the steric components of the rotation barriers should be slightly smaller in magnitude for the C(^{2}H)$_3$ groups than for the C(^{1}H)$_3$ groups. But the reported magnitudes of this type of steric effect typically are in the range of only 0.04−0.10 kJ mol^{-1} for various other compounds in which the intramolecular steric crowding is similar to that in our compounds.[19]

So, the ratio R_k^9/R_k^1 is, in practice, independent of the interaction k and depends only on the activation energy for methyl group rotation E^m, and the parameter $\epsilon^m \leq 1$,[13] which is of order unity.[2] The barrier $E^9 = 12.1 \pm 0.5$ kJ mol^{-1} for the 9-C(^{1}H$_3$) group has been determined from R_d^9 vs temperature measurements at two Larmor frequencies (as discussed above[2]) in 1,9-DMP[1-d_3]. E^1 for the 1-C(^{1}H$_3$) group has not been measured directly but has been determined, albeit with less accuracy, to be $E^1 = 8 \pm 1$ kJ mol^{-1}, using a subtraction procedure involving the measurement of $R_d^{1\&9}$ vs temperature at two Larmor frequencies in 1,9-DMP (where both methyl groups contribute to the observed rate) and R_d^9 in 1,9-DMP[1-d_3] (where only the 9-methyl group contributes).[2] This same study determined $\epsilon^1 = 0.8 \pm 0.1$ and $\epsilon^9 = 0.76 \pm 0.03$.

Thus, from eq 13, we compute $R^9/R^1 = 4.4 \pm 2.1$ for *both* the dipolar *and* the quadrupolar rates. Unfortunately, the uncertainty in this "theoretical" ratio is large. The uncertainty in E^1, which appears in an exponent, dominates. This ratio is to be compared with the experimental ratio $R_q^9/R_q^1 = 2.0 \pm 0.6$ for the dipolar ^{1}H relaxation rates and the ratios $R_q^9/R_q^1 = 2.2 \pm 0.5$, 2.3 ± 0.2, and 2.31 ± 0.07 for the quadrupolar relaxation ^{2}H rates for $\theta = 0$, 55°, and 90°.

We make three significant points. First, the observed ratios R^9/R^1 are the same for both interactions, as predicted by the theory. Second, the observed ratio R_q^9/R_q^1 for the quadrupolar interaction is independent of θ, the angle the C(^{2}H)$_3$ rotation axis makes with the magnetic field, and the observed ratio R_d^9/R_d^1 for the dipolar interaction is independent of the ^{1}H$-$^{1}H separation in the C(^{1}H$_3$) group. Indeed, these ratios are independent of the geometry. Although this observation is contained in the first comment, we emphasize that this is in agreement with the prediction that this ratio is a measure of the methyl group dynamics only and *is independent of the NMR measurement!* Third, the predicted ratio is in reasonable agreement with the measurements, which are more accurate. This gives one confidence in the values of the activation energies for methyl group rotation, which came from a different study.

Summary

This paper is part of a larger, long-term study of methyl group rotation. The goal is to find accurate models for NMR relaxation rates resulting from methyl group rotation in the high-temperature, thermally activated regime. The goal is also to relate the various parameters in the dynamical models to structure, as determined by X-ray analysis, NMR spectroscopy, calorimetry, and other techniques.[20] By analysis of ratios of various relaxation rates, this current study aids in the determination of the meaningfulness of theoretical expressions for the Zeeman relaxation rates for ^{1}H dipolar and ^{2}H quadrupolar relaxation and the parameters they contain.

The expression being tested is eq 6, with parameters given by eqs 7 and 8 for both dipolar and quadrupolar relaxation and an additional parameter given by eq 4 for dipolar relaxation and by eq 5 for quadrupolar relaxation. Examining the ratio of the quadrupolar to the dipolar relaxation rates for a particular site in the molecule 1,9-dimethylphenanthrene, allows a test of those aspects of the model (i.e., the parameters) that do not explicitly depend on the methyl group dynamics but depend only on the strengths of the interactions being modulated. Examining the ratio of the relaxation rate at one site in the molecule to that of another site for both dipolar and quadrupolar relaxation rates, we have been able to test those aspects of the model that do not explicitly depend on the strengths of the interactions being modulated, but rather depend only on the methyl group dynamics. Theoretical and experimental values for the ratios of relaxation rates are in good agreement and gives one reason to have more faith in the models.

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