Structure and dynamics of cyclopropane in solution by nuclear magnetic resonance coupled relaxation

5 AUTHORS, INCLUDING:

Mark S Brown
University of Colorado
58 PUBLICATIONS **993** CITATIONS

SEE PROFILE

Teh-Chang Chou
National Chung Cheng University
23 PUBLICATIONS **99** CITATIONS

SEE PROFILE

of negative spin densities. The qualitative correspondence between the signs of Δa^H and $\Delta \rho^\pi$ at deuterated para and ortho positions is complete. The italicized Δa^H in Table V are calculated from the observed deuterium hfs constants as follows:

$$\Delta a^H(\text{deuterium}) = (|a_{\text{TPM}}^H| - 6.514|a_{\text{DTPM}}^D|) \qquad (10)$$

The Q_{CD}^D values obtained from the ratios $(\Delta a^H/\Delta \rho^\pi)$ at these positions are, however, so large compared to any normal values of Q_{CH}^H that this qualitative agreement could, perhaps, be considered fortuitous. No such qualitative agreement is, again, found at the meta positions.

When the contribution of the calculated spin density changes are incorporated into the κ values and $(a_{\text{TPM}}^H/a_{\text{DTPM}}^H)$ ratios of Table II by

$$\kappa^{\text{cor}} = \kappa(\rho_{\text{DTPM}}^\pi/\rho_{\text{TPM}}^\pi) \qquad (11)$$

$$(a_{\text{TPM}}^H/a_{\text{DTPM}}^H)^{\text{cor}} = (a_{\text{TPM}}^H/a_{\text{DTPM}}^H)(\rho_{\text{DTPM}}^\pi/\rho_{\text{TPM}}^\pi) \qquad (12)$$

using ρ's from McLachlan's method with both Coulomb and resonance integral perturbations, we find the corrected values listed in Table II. The κ values change in the direction toward the κ values calculated from the vibrational model, but quantitatively the values of κ^{cor} are still far removed from the theoretical values.

As noted previously the effective total width of the spectrum decreases with increasing deuteration from 16.785 G for triphenylmethyl to 16.296 G for the completely deuterated radical. From the McLachlan spin density calculations with Coulomb and resonance integral perturbations the total spin density at the deuterium bonded ring positions changes from 0.6174 to 0.6149, which is a much smaller percentage change than in effective total width. When the effective total width for the completely deuterated radical is corrected by the ratio 0.6174/0.6149 we get 16.362. The ratio 16.785/16.362 = 1.026 could be interpreted as the effective overall isotope effect in triphenylmethyl upon

deuteration, and the positive deviation of this ratio from unity contrasts with the negative deviation expected from the vibrational model.

We have assumed in the above calculations that the structure of the triphenylmethyl radical does not change appreciably upon deuterium substitution, that is, that the angle of twist and the degree of planarity at the methyl carbon atom remains essentially the same as in the unsubstituted radical. The internal consistency of our results provides some evidence that this is a good assumption. For example, qualitatively, the κ values are the same in radicals IV and VI at the meta position even though radical IV has deuterium only at the meta position, whereas radical VI is completely substituted. One might expect that if deuterium substitution altered the structure of the radical appreciably this alteration would be most severe with substitution at the ortho position. Such does not seem to be the case.

Conclusions

The deuterium isotope effect on the ESR spectra of aromatic radicals has been examined in a series of deuterated triphenylmethyl radicals. The results indicate that the vibrational model of the effect, in which the only vibrations considered are the out-of-plane C–H or C–D vibrations of a $(C)_2C$–H or $(C)_2C$–D fragment, is not adequate to explain quantitatively the magnitude of the effect. This result has been observed previously[5,8,9] in even-alternant systems. Our results in the odd-alternant triphenylmethyl system indicate that the model may not even be qualitatively correct for this system.

We believe that a thorough analysis of the interaction between the electronic states and the vibrational modes of the molecule as a whole, rather than just fragments of the molecule, is required for an adequate understanding of the deuterium isotope effects which are observed.

Structure and Dynamics of Cyclopropane in Solution by Nuclear Magnetic Resonance Coupled Relaxation

Mark S. Brown, Charles L. Mayne, David M. Grant,* T. C. Chou, and Evan L. Allred

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received: June 7, 1983; In Final Form: November 7, 1983)

The spin–lattice relaxation of selectively labeled cyclopropane-*1-13C-2,2,3,3-d₄* (^{13}CH$_2$C$_2$D$_4$) dissolved in CD$_2$Cl$_2$ has been studied with carbon-13 NMR. Selective and nonselective π pulses were applied to the carbon and proton transitions of this AX$_2$ spin system and partially relaxed carbon-13 spectra were obtained for various evolution periods after the pulse. All experiments were performed at −81.5, −60, −20, and +20 °C. The data were analyzed in terms of a small-step rotational diffusion model for the rotational reorientation. The reorientation at −81.5 and −60 °C may be characterized by two diffusion coefficients. The unique axis lies parallel to the C_3 axis of cyclopropane. At −20 and +20 °C, only one diffusion parameter is obtained. Values obtained for the proton–proton distance at the lower temperatures agree reasonably well with values in the literature but become too large at the higher temperatures. Small but negative values for the carbon autocorrelation random field term j_C are observed at the lower temperatures. These results indicate that as temperature increases, the molecule enters a motional regime where the dipolar mechanisms become less efficient, spin rotation becomes more important, and greater uncertainty exists in the small-step motional model used to interpret the data.

Introduction

Nuclear magnetic resonance studies of intramolecular dipole-dipole interactions provide an effective and sensitive method for probing both the structure and the rotational diffusion of molecules in solution.[1,2] Experimental studies have been performed in both isotropic solution[3-10] and nematic phase.[11-18] Some of the most

revealing of these studies have utilized the ^{13}CH$_2$(AX$_2$) spin system. To date, methylene chloride[4,5] (^{13}CH$_2$Cl$_2$), methylene

(1) Werbelow, L. G.; Grant, D. M. *Adv. Magn. Reson.* **1977**, *9*, 189.
(2) Vold, R. L.; Vold, R. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *12*, 79.

(3) Mayne, C. L.; Alderman, D. W.; Grant, D. M. *J. Chem. Phys.* **1975**, *63*, 2514.
(4) Chenon, M. T.; Bernassau, J. M.; Mayne, C. L.; Grant, D. M. *J. Phys. Chem.* **1982**, *86*, 2733.
(5) Grant, D. M.; Chenon, M. T.; Mayne, C. L.; Werbelow, L. G. In "Proceedings of the 7th International Conference on Atomic Spectroscopy and the XX Collogue Spectroscopium Internationale", Praha: Czechoslovakia, 1977; Vol. 2, p 207.

iodide[6] ($^{13}CH_2I_2$), malonic acid[7] ($^{13}CH_2(COOH)_2$), and some labeled phospholipids[8,9] have been measured by using coupled relaxation techniques on the $^{13}CH_2$ moiety. The methylene halides[4-6] provided model systems to establish the validity of the method and to determine the degree of agreement between theory and experiment. These studies also clearly demonstrated the importance of cross-correlation effects in coupled spin systems. Selective pulse ("soft pulse") as well as nonselective pulse ("hard pulse") sequences were used to perturb the coupled system from equilibrium. From these studies the HCH bond angle and the elements of the rotational diffusion tensor have been determined. $^{13}CH_2I_2$ was found[6] to diffuse as an asymmetric top, while ^{13}C-H_2Cl_2 was found to diffuse as a "pseudosymmetric" top, where two of the diagonalized elements of the rotational diffusion tensor have values within experimental error of each other. The investigations of Fuson and Prestegard[7-9] on malonic acid and phospholipids used coupled relaxation to examine the motional behavior of the components of model membranes. Focusing primarily on the molecular motion rather than the method itself, they determined the spin system geometry via X-ray diffraction on a single crystal. Using X-ray results to fix the molecular geometry made it possible to study molecular reorientation by using only nonselective pulse perturbations. Malonic acid[7] followed the symmetric-top model of rotational diffusion. Several motional models were used to analyze the phospholipid results with proper allowances made for axial diffusion, rotational bond isomerization, and other effects.[8,9] In all the above systems, the HCH bond angle is at or near the tetrahedral value of 109°.

In this study an AX_2 spin system has been selected with different geometry and diffusion characteristics. The isotopically labeled cyclopropane, $^{13}CH_2C_2D_4$, was chosen because of its nontetrahedral HCH bond angle, previously measured via electron diffraction[19] (115.8° after vibrational correction[20]) and by proton NMR in a nematic solvent[21] (115.15° after vibrational correction[20]). The HCH cross-correlation power density, which affects the relaxation results, depends upon this angle. In addition, the molecule provides a good test of the method's ability to differentiate between spherical-top and symmetric-top rotational reorientation. Unlabeled cyclopropane is a symmetric-top molecule with moments of inertia $I_\perp = 4.2 \times 10^{-39}$ and $I_\| = 6.6 \times 10^{-39}$ g cm^2. The D_{3h} symmetry of cyclopropane leads to the expectation of symmetric-top diffusion. However, upon examination of a "space-filling" model of the compound, the almost spherical shape of the molecule becomes apparent. The diffusion tensor therefore provides a measure of the anisotropy of motion in this nearly spherical molecule. One must depend upon the statistics generated by the fitting programs to distinguish between the spherical-top and symmetric-top diffusion models.

Theoretical Considerations

The theoretical basis of this work depends upon the work of Bloch and Wangsness[22] and later Redfield.[23] The Redfield formalism is used to predict partially relaxed line intensities and these are fitted to the experimental results to give spin–lattice relaxation parameters. Information concerning the reorientation dynamics of the molecule can be extracted from the relaxation parameters associated with the intramolecular dipole–dipole interactions among the various nuclear spins in the molecule. All other significant relaxation mechanisms are described with a randomly fluctuating external magnetic field. The relaxation rates are linear combinations of spectral densities for the various interactions. For the dipole–dipole mechanism, the spectral densities are of the form

$$J_{ijkl}^{\mu\mu'}(\omega) = \xi_{ij}\xi_{kl}\int_0^\infty \langle Y_\mu^2[\phi_{ij}^{lab}(0)]Y_{\mu'}^2[\phi_{kl}^{lab}(\tau)]\rangle e^{-i\omega\tau}\,d\tau$$

where ij and kl represent pairs of interacting spins (internuclear vectors) and

$$\xi_{ij} = (6\pi/5)^{1/2}\gamma_i\gamma_j\hbar/r_{ij}^3 \qquad (1)$$

γ_i and γ_j are the gyromagnetic ratios of spins i and j, and r_{ij} is the i–j internuclear distance. The Y_μ^2 are the second-rank spherical harmonics with projection indices μ.[24] The dipolar spectral densities can be further expressed as a linear combination of Fourier transforms of ensemble averages of second-rank Wigner rotation matrices:

$$J_{ijkl}^{\mu\mu'}(\omega) = \sum_{mm'} K_{ijkl}^{mm'}\int_0^\infty \langle D_{m\mu}^2[\Omega(\tau)]D_{m'\mu'}^2[\Omega(0)]\rangle e^{-i\omega\tau}\,d\tau \quad (2)$$

Here $K_{ijkl}^{mm'}$ depends upon the molecular geometry[1] and all the molecular motion is contained in the rotation matrices. The ensemble average is calculated by using

$$\langle D_{m\mu}^2[\Omega(\tau)]D_{m'\mu'}^2[\Omega(0)]\rangle =$$
$$\int \int D_{m\mu}^2(\Omega) D_{m'\mu'}^2(\Omega') P(\Omega,\tau|\Omega') P(\Omega') \, d\Omega \, d\Omega' \quad (3)$$

in which $P(\Omega,\tau|\Omega')$ is a conditional probability which satisfies the diffusion equation of Favro[25]

$$-\frac{d}{dt}P(\Omega,\tau|\Omega') = \mathbf{M}\cdot\mathbf{D}\cdot\mathbf{M}P(\Omega,\tau|\Omega') \quad (4)$$

$\mathbf{M}$ is the angular momentum operator and $\mathbf{D}$ is the rotational diffusion tensor. In this "small-step" diffusion model, the above equation is solved by developing the time-dependent probability as an expansion in rotation matrices. In the case of $^{13}CH_2$, the four dipolar spectral densities are J_{CH}, J_{HH}, J_{HCH}, and J_{CHH} in the notation of Chenon et al.[4]

The lattice components of the random field are defined as

$$B_0^1(i,t) = B_z(i,t) - B_0(i)$$

$$B_{\pm1}^1(i,t) = \mp(1/2^{1/2})[B_x(i,t) \pm B_y(i,t)]$$

and the random field spectral densities are of the form

$$j_{ij} = (1/2)\gamma_i\gamma_j\int_0^\infty (-1)^q\langle B_q^1(i,\tau) B_q^1(j,\tau)\rangle e^{-i\omega\tau}\,d\tau \quad (5)$$

$B_q^1(i,t)$ is the qth component (in the spherical basis) of the field at nucleus i. As with the dipolar spectral densities, it is possible to distinguish between autocorrelated and cross-correlated spectral densities, depending on whether one or two nuclei appear in the expression for j_{ij}, respectively. In this analysis j_{CH} is assumed to be negligible since random field interaction which would affect both proton and carbon frequencies is unlikely. Thus, three random field terms are used in this work: j_C, the carbon autocorrelation random field; j_H, the proton autocorrelation random field; and j_{HH}, the proton–proton cross-correlation term. These random field terms primarily account for paramagnetic impurities

(6) Mayne, C. L.; Grant, D. M.; Alderman, D. W. *J. Chem. Phys.* **1976**, *65*, 1684.

(7) Fuson, M. M.; Prestegard, J. H. *J. Chem. Phys.* **1982**, *76*, 1539.

(8) Fuson, M. M.; Prestegard, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 168.

(9) Fuson, M. M.; Prestegard, J. H. *Biochemistry* **1983**, *22*, 1311.

(10) Bovee, W. M. M. *J. Mol. Phys.* **1975**, *29*, 1673.

(11) Bodenhausen, G.; Szeverenyi, N. M.; Vold, R. L.; Vold, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6265.

(12) Vold, R. R.; Vold, R. L. *J. Chem. Phys.* **1979**, *71*, 1508.

(13) Courtieu, J. M.; Fagerness, P. E.; Grant, D. M. *J. Chem. Phys.* **1977**, *65*, 1202.

(14) Courtieu, J. M.; Mayne, C. L.; Grant, D. M. *J. Chem. Phys.* **1977**, *66*, 2669.

(15) Courtieu, J. M.; Jullien, J.; Lai, N. T.; Guillois, A.; Gonord, P.; Kan, S. K.; Mayne, C. L. *J. Chem. Phys.* **1980**, *72*, 953.

(16) Bernassau, J. M.; Black, E. P.; Grant, D. M. *J. Chem. Phys.* **1982**, *76*, 253.

(17) Courtieu, J.; Lai, N. T.; Mayne, C. L.; Bernassau, J. M.; Grant, D. M. *J. Chem. Phys.* **1982**, *76*, 257.

(18) Black, E. P.; Bernassau, J. M.; Mayne, C. L.; Grant, D. M. *J. Chem. Phys.* **1982**, *76*, 265.

(19) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, 538.

(20) Lucas, N. J. D. *Mol. Phys.* **1971**, *22*, 233.

(21) Snyder, L. C.; Meibloom, S. *J. Chem. Phys.* **1967**, *47*, 1480.

(22) Wangsness, R. K.; Bloch, F. *Phys. Rev.* **1953**, *89*, 728. Bloch, F. *Ibid.* **1956**, *102*, 104; **1957**, *105*, 1206.

(23) Redfield, A. G. *IBM J. Res. Dev.* **1957**, *1*, 19; *Adv. Mag. Reson.* **1965**, *1*, 1.

(24) Rose, M. E. "Elementary Theory of Angular Momentum"; Wiley: New York, 1957.

(25) Favro, L. D. *Phys. Rev.* **1960**, *119*, 53.

and the spin-rotation mechanism. Intermolecular dipolar interactions, to the extent that they contribute, could invalidate our three-spin model and could affect our calculated values for both the dipolar terms and the random field terms. In dilute solutions where interaction between $^{13}CH_2$ groups on different molecules is minimal, the main contribution to the random field term appears to be spin rotation. At lower temperatures, the spin-rotation mechanism is "frozen-out" and accordingly the random field terms are expected to be small but positive. Previous experimental studies have exhibited a very high degree of agreement between theory and experiment. In the work on $^{13}CH_2Cl_2$,[4] however, it was found at the lower temperatures that the value for j_C became small but negative. This problem may be circumvented by locking j_C to zero during the fit, since the quality of the fit and the values of the other parameters are insensitive to this decrease in the number of degrees of freedom of the fit. At higher temperatures, the term is positive and has a magnitude sufficient to reflect the importance of the spin-rotation contribution. The behavior of the random field terms in the case of cyclopropane is interesting because previous carbon T_1 studies have shown that the contribution from spin rotation at room temperature is quite large[26] ($T_{1SR} = 74.6$ s vs. $T_{1D} = 72.2$ s). In this work the behavior of the random field has been studied from conditions where the spin-rotation contribution varies from small (−81.5 °C) to large (+20 °C).

Experimental Section

Preparation of Cyclopropane-1-^{13}C-2,2,3,3-d_4. Under a nitrogen atmosphere, a solution of 2.0 g (12.4 mmol) of diethyl malonate-2-^{13}C (Prochem B.O.C. Ltd.) in 10 mL of anhydrous ether was added dropwise during 1 h to a stirred mixture of 1.0 g (23.8 mmol) of lithium aluminum deuteride (Stohler Isotope Chemicals) in 10 mL of anhydrous ether. Following this, the reaction was refluxed for 10 h and then treated successively with 2 mL of water and 1.8 mL of 10% sodium hydroxide. After standing overnight, the resulting mixture was extracted in a Soxhlet extractor with ether. Evaporation of the ether gave 0.7 g (70%) of *propane-2-^{13}C-1,1,3,3-d_4-1,3-diol.*

A mixture of 0.7 g (8.6 mmol) of the labeled diol, 5 mL of 48% hydrobromic acid, and 1 mL of concentrated sulfuric acid was refluxed for 12 h. During this time an additional 2 mL of concentrated sulfuric acid was added. After this, 10 mL of 48% hydrobromic acid was added and the mixture was distilled until appearance of insoluble organic product ceased. The organic layer was separated and then was washed with 3 mL of water, 3 mL of cold 50% sulfuric acid (twice), 3 mL of water (twice), 3 mL of saturated sodium bicarbonate, and 3 mL of water. The product in ether was dried with sodium sulfate and the solvent was removed by evaporation to give 1.2 g (67%) of *1,3-dibromopropane-2-^{13}C-1,1,3,3-d_4.*

A slurry of 722 mg (11 mg-atom) of activated zinc,[27] 522 mg (4.9 mmol) of sodium bicarbonate, 136 mg (0.9 mmol) of sodium iodide, and 10 mL of 75% aqueous ethanol was stirred and gently refluxed as 1.02 g (4.9 mmol) of the labeled dibromide was added over 30 min. The mixture was then stirred and refluxed for an additional 7 h. During this time a slow stream of nitrogen was passed through the system into a liquid-nitrogen-cooled trap. A 195-mg (85%) sample of *cyclopropane-1-^{13}C-2,2,3,3-d_4* was distilled from the trap into a cold 12-mm NMR tube containing 3 mL (3.205 g) of CD_2Cl_2, and the tube was degassed by the freeze–pump–thaw method and sealed under vacuum to give a composition of 12.1 mol % cyclopropane. Carbon-13 NMR spectra showed only the 1:2:1 triplet of the AX_2 spin system, plus the CD_2Cl_2 signal further downfield. The proton spectrum reveals the expected ^{13}C proton scalar coupled doublet, plus the singlet due to molecules containing ^{12}C at the center of the doublet. The ratio of integrated proton intensities is 1:2.7:1, indicating a ^{13}C enrichment of 43%.

Relaxation Studies. The relaxation experiments were performed on a modified Varian XL-100-15 spectrometer equipped with a 16K Varian 620L-100 computer and a homemade pulsed spin decoupler based on a Hewlett-Packard Model 5105A frequency synthesizer. This system and the method of data collection have been previously described elsewhere.[3] The system has since been modified so that the spectrometer's 620L computer is interfaced via a serial communications link to a PDP 11/34 computer, equipped with a Computer Labs/Pertec disk system. The communications network utilizes hardware and software previously described.[28] Data are acquired in the following fashion: First, all the different parameter sets are created on the 620L computer and stored on the PDP 11/34 disk. The 620L computer then solicits a parameter file from the PDP 11/34 and collects one transient using those parameters, after which it returns the parameters and FID to the PDP 11/34 for storage on the disk. This process is repeated for each parameter set having a different τ value (the time between the perturbing and observe pulses). After a transient has been collected for each parameter set, the first data file (parameters and fid) is again sent to the 620L and another transient is collected and added to the fid. The entire cycle is repeated until all the fid's have accumulated the desired signal to noise. In addition, the sequence of τ values was scrambled, so that data points at the same section of the curve are collected at different times in the cycle. As previously discussed,[3] these procedures have been found necessary to average out spectrometer drift and variations in sensitivity over all data points. This was particularly important in the longer runs (up to several days) in this study.

Three different preparations of the spin system were used: coupled inversion recovery (CIR), where a carbon π pulse inverts the three lines; proton hard pulses (HP), inverting both proton lines; and a soft proton pulse (SP), inverting one line of the proton doublet. Following the spin system preparation, the system is allowed to evolve for a time τ, followed by a $\pi/2$ observe pulse in the carbon-13 domain. The resulting free induction decays are collected, Fourier transformed, and the partially relaxed line intensities measured.[4]

Relevant spectrometer parameters were as follows: spectral width 512 Hz; acquisition time 8 s; exponential time constant −0.2 s for sensitivity enhancement; recycle delay, from 82 s at −81.5 °C up to 500 s at +20 °C, adjusted at each temperature to be at least 10 times the longest nominal T_1 of carbon and protons. The value of the coupling constant, J_{CH}, is 160 Hz.

Parameters relevant to the inversion recovery experiment were π (180°) pulse 106 μs, and 90° pulse 50 μs. For the hard-pulse experiment, 10 W of decoupler power was used, with a proton π pulse width of 180 μs. In the soft-pulse experiment, it was found that a simple low-power proton pulse did not provide sufficient perturbation, so an intermediate soft pulse ("medium soft pulse") as described by Bovee[10] was used. The proton rf field is set so that the π-pulse time $\tau_{180} = 3^{1/2}/(2J_{CH})$; thus, when a π pulse is applied on resonance to one line, the other line of the doublet nutates through 2π about its effective field in the rotating frame and is effectively unperturbed. The amplitude used was 2.6 V ±10% peak to peak, with a pulse width of 5.6 ms. The experimental criteria for adjusting the perturbing pulse have been previously described.[6] For each of the three different experiments, 23–31 different data points were collected. A few points in each run, usually eight, were duplicated with the same τ value, to ensure reproducibility. All three experiments were performed at four different temperatures (−81.5, −60.0, −20.0, and +20.0 °C). Temperatures are estimated to be accurate within ±1 °C.

Fitting Procedures. Three different fitting routines were available in the laboratory for analysis of the data. These have all been previously described[4,6,7] in the literature. Two of these routines use the magnetization mode approach, in which normal modes of magnetization, constructed from symmetry-adapted basis

(26) Berger, S.; Kreissl, F. R.; Roberts, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 4348.

(27) Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 2879.

(28) Alderman, D. W.; Hamill, W. D., Jr.; Mayne, C. L.; Grant, D. M. In "Computer Networks in the Analytical Chemistry Laboratory"; Levy, G. C., Terpstra, D., Eds.; Wiley-Interscience, New York, 1981.

TABLE I: Diffusion Coefficients, Proton–Proton Distance, Spectral Densities, Pulse Efficiencies, and Scaling Factors for Cyclopropane at −81.5, −60, −20, and +20 °C[a]

T, °C	−81.5	−60	−20	+20
$10^{-10}D_\perp$, s^{-1}	4.91 ± 0.05	10.4 ± 0.1	23.0 ± 0.2	34.2 ± 0.2
$10^{-10}D_\parallel$, s^{-1}	10.4 ± 0.5	17.3 ± 1.1		
r_{HH}, Å	1.844 ± 0.005	1.847 ± 0.006	1.865 ± 0.009	1.865 ± 0.009
j_C, s^{-1}	0 (locked)	0 (locked)	0 (locked)	0.00148 ± 0.00015
$j_H = j_{HH}$, s^{-1}	0.01203 ± 0.00035	0.00592 ± 0.00019	0.00276 ± 0.00012	0.00192 ± 0.00013
J_{CH}, s^{-1}	0.02062	0.01022	0.00499	0.00335
J_{HCH}, s^{-1}	−0.00270	−0.00155	−0.00069	−0.00046
J_{CHH}, s^{-1}	0.01113	0.00528	0.00240	0.00161
J_{HH}, s^{-1}	0.01505	0.00706	0.00301	0.00202
α_{SP}	0.917 ± 0.009	0.946 ± 0.009	0.971 ± 0.010	0.980 ± 0.017
α_{HP}	0.919 ± 0.011	0.937 ± 0.013	0.893 ± 0.015	0.832 ± 0.018
α_{CIR}	0.974 ± 0.003	0.983 ± 0.003	0.975 ± 0.005	0.998 ± 0.006
κ_{SP}, mm	458 ± 4	483 ± 4	507 ± 5	476 ± 7
κ_{HP}, mm	1271 ± 7	1111 ± 6	1267 ± 7	1239 ± 11
κ_{CIR}, mm	2033 ± 8	2033 ± 7	1538 ± 10	2160 ± 14
Δ	1960.238	1879.717	2559.915	8559.640

[a] Fits at −81.5, −60, and −20 °C are with j_C locked to zero. Fits at −81.5 and −60 °C use the symmetric-top model (two diffusion coefficients), and fits at −20 and +20 °C use the spherical-top model (one diffusion coefficient). SP = soft pulse, HP = hard pulse, CIR = coupled inversion recovery.

operators, are fitted to the data. One of these programs, written by Mayne et al.[6] and referred to as the magnetization mode fit (MMF) in Chenon et al.,[4] utilizes the method of steepest descents to fit spectral densities to the data and then inverts the equations via a Newton–Raphson procedure to determine the structural and diffusional parameters. A second magnetization mode fitting routine,[7] written by Fuson, will fit either structural and dynamical parameters or spectral densities by using a direct search algorithm. The third approach, which was used for all the fits reported here, is known as the line intensity fit (LIF),[4] in which dynamical and structural parameters are fitted directly to the relative partially relaxed line intensities and the sum of squares is minimized with a quasi-Newton algorithm.[29] Errors are computed and reported as in Chenon et al.[4] Although the most complete set of fits was done with LIF, the other routines were used to verify the results. In spite of the differing details of each fitting routine, agreement between the results given by each program is within the statistical limits of error. For uniformity and simplicity, therefore, only the results from the LIF are reported here.

The coordinate system is chosen so that the protons of the $^{13}CH_2$ system are in the X–Y plane, with positive X axis bisecting the HCH angle. The positive Y axis is perpendicular to the plane of the carbon ring, and the Z axis is perpendicular to the plane of the $^{13}CH_2$ moiety. In all fits, the value 1.08 Å was used for the r_{C-H} distance, a value obtained from vibrational corrections[20] to the electron diffraction[19] value. A further assumption is made that the random fields are completely correlated at H and H′ (j_{HH} is locked to j_H).

The parameters in the LIF routine were as follows: the three diffusion coefficients, D_{XX}, D_{YY}, and D_{ZZ}; the proton–proton distance, r_{H-H}; the carbon autocorrelation random field spectral density, j_C; the proton autocorrelation random field spectral density, j_H; the proton–proton cross-correlation spectral density, j_{HH} (locked to j_H); the carbon–proton cross-correlated random field spectral density, j_{CH} (locked to zero); a pulse efficiency parameter for each experiment, α; and a scaling factor, κ, for each experiment. The α's and κ's do not provide structural or dynamical information but are necessary to describe pulse imperfections and spectrometer response for each experiment.[4]

The values of the fitted parameters, with the estimated errors, are listed in Table I. The fits in Table I have the j_C terms locked to zero at −81.5, −60.0, and −20.0 °C. The dipolar spectral densities listed are computed from the fitted parameters and do not have error estimates, since errors are not conveniently propagated through the calculations. The data extracted from the spectra and the least-squares fit are represented by the results for

$T = -81.5$ °C, shown in Figure 1.

The data were fitted by using spherical-top and symmetric-top models for the diffusion. All symmetric-top fits were done with $D_\perp = D_{XX} = D_{ZZ}$ and D_{YY} (corresponding to diffusion about the C_3 axis of cyclopropane) was taken as the unique tensor element $D_\parallel$.

At −81.5 °C, the spherical-top model yielded a fit with a reasonable variance, Δ, and only a small relative error in the single diffusion coefficient D, indicating that the molecular reorientation is well approximated by a spherical-top diffuser. When a symmetric-top model is used, however, Δ decreases significantly, but the relative errors of $D_\parallel$ and $D_\perp$ remain about the same as for the spherical-top D. The anisotropy in diffusion as measured by the ratio $D_\parallel/D_\perp$ is 2.12. To check the symmetric-top assumption the data were also fitted by using a general asymmetric-top model. The resulting fit had a large relative error (22%) in the diffusion component about the 3-fold axis (D_{YY}). Also, the values for D_{XX} and D_{ZZ} were similar, and the errors were highly correlated. As the relaxation experiments were able to distinguish two distinct motions, the symmetric-top model provides the best fit, as one might have expected from the molecular symmetry. Similar results were found for fits at −60 °C and $D_\parallel/D_\perp$ equals 1.66.

At −20 °C, there is no longer any statistical basis for proposing anisotropic motion. The symmetric-top model converges to values that are within error of each other and $D_\parallel/D_\perp = 1.06$. A spherical-top fit yields a value for the single diffusion constant D that is within one standard deviation of $D_\perp$ in the symmetric-top fit, and the value of Δ does not increase significantly when fewer diffusion parameters are used. Thus, the fits at −20 °C suggest a spherical-top model for the diffusion. A similar situation is encountered at +20 °C. The symmetric-top fit yields $D_\parallel/D_\perp = 0.91$, but the relative error on $D_\parallel$ is now quite large (21%) and the spherical-top D again has the same value as $D_\perp$, so a spherical-top model may be used to fit the data. It should be noted that as the temperature increases relaxation rates decrease and the experimental runs become longer. This increases the scatter in the data making the results less reliable.

The role of the carbon autocorrelation random field term j_C was investigated in the fitting process. When j_C is unlocked at −81.5 °C in the symmetric-top fit, a small but nonzero value of -8.57×10^{-3} s^{-1} was obtained. Although this value had a large relative error of ±18%, zero is not included within the error limits. The negative value obtained for j_C is not physically achievable and indicates that this parameter may be compensating for a breakdown in the simple model. In previous investigations, j_C has been locked to zero to avoid the physically untenable negative values, and fortunately locking j_C to zero in the present case does not significantly alter the error estimates of the other fitted parameters. Thus, the fit with j_C locked to zero is reported in Table
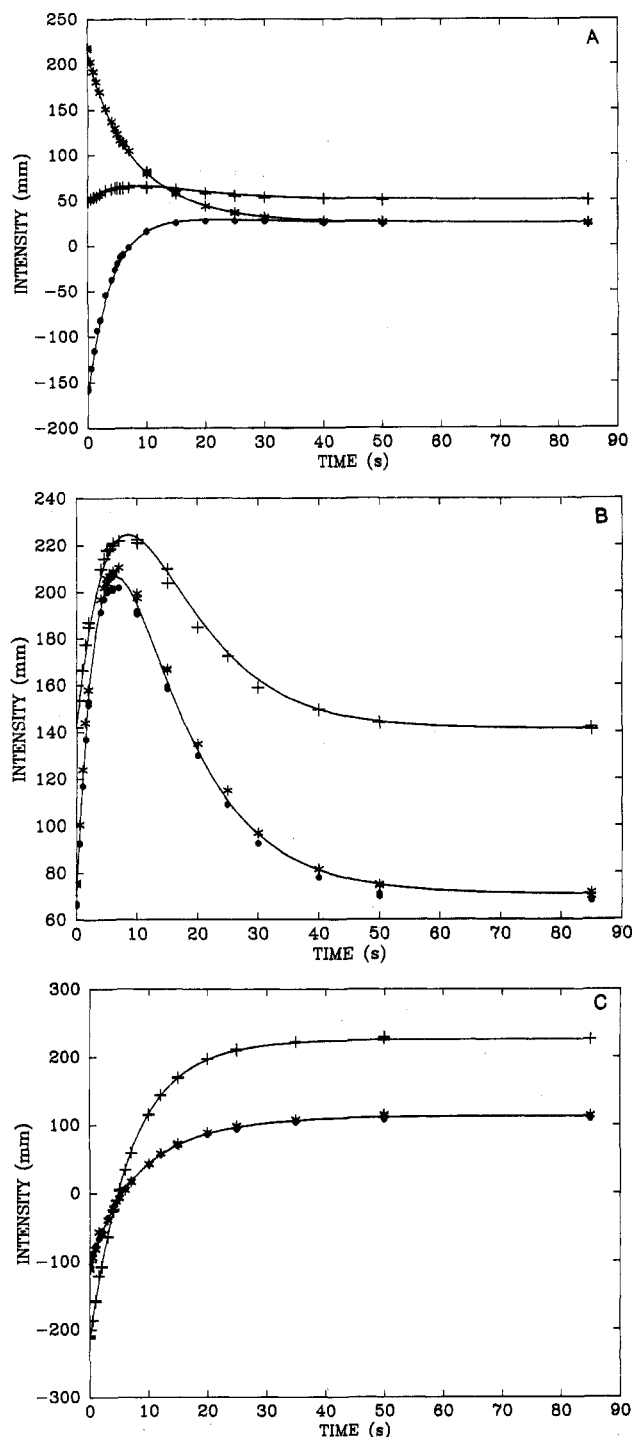
(29) International Mathematical and Statistical Library, Houston, TX.

Brown et al.

Figure 1. Results of nonlinear least-squares fit with j_C locked to zero of relaxation data for labeled cyclopropane in CD_2Cl_2 at 81.5 °C: (A) soft pulse; (B) hard pulse; (C) coupled inversion recovery.

I. The data analysis is similar at −60 and −20 °C where the absolute values of the j_C are even smaller, but still negative. Thus, fits are reported in Table I for j_C locked to zero. At +20 °C the j_C term has the anticipated positive value due to the appearance of a significant spin-rotation contribution.

Discussion

Temperature-dependent results show both the validity of the relaxation model and some of its limitations. At the lower temperatures (−81.5 and −60 °C), where the fit is better statistically, the molecule is in a motional regime where the relaxation occurs mainly via the dipolar mechanism. For higher temperatures, the dipolar mechanisms become less efficient as other interactions become important, and the information obtained from the fitting
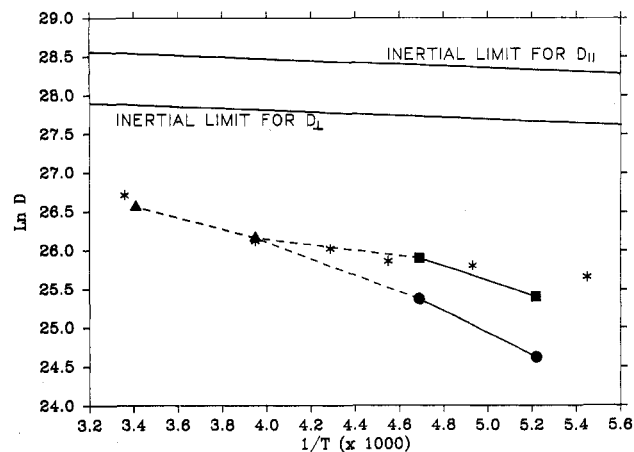

Figure 2. Plot $\ln D$ vs. $1/T$: (●) $D_\perp$, (■) $D_\parallel$, and (▲) spherical-top D, (*) values of $D_\perp$ as determined by Besnard et al.[30] The inertial limits for the two motions are shown at the top of the figure. See text for explanation and discussion.

procedure becomes less definitive and greater uncertainty exists in the motional model.

At −81.5 and −60 °C, cyclopropane reorients as a symmetric top (see Table I). Rotational diffusion about the unique y axis, parallel to the C_3 axis of cyclopropane, is $D_\parallel = D_{YY} = 1.04 \times 10^{11}$ s^{-1} about twice the value of $D_\perp = D_{XX} = D_{ZZ} = 4.9 \times 10^{10}$ s^{-1}. At −60 °C, $D_\parallel = 1.73 \times 10^{11}$ s^{-1} and $D_\perp = 1.04 \times 10^{11}$ s^{-1}. At higher temperatures the molecule is in the regime where spin rotation is an important relaxation mechanism, and the NMR relaxation data become less sensitive to the dipolar relaxation mechanisms limiting ones ability to measure any anisotropy, if important, in the reorientational motions. Consequently, at −20 and +20 °C, the elements of the diffusion tensor all come out within error of each other. Thus, a spherical-top diffusion model may be used to fit the data, and only one diffusion parameter is required to characterize the motion. At −20 °C, $D = 2.30 \times 10^{11}$ s^{-1} and at +20 °C, $D = 3.42 \times 10^{11}$ s^{-1}.

In Figure 2, an Arrhenius plot of $\ln D$ vs. $1/T$ helps to illustrate these results. The slopes of the solid lines give activation energies for the reorientational motions. The lower straight line connects the values of $D_\perp$ at −81.5 and −60 °C represented by the solid circles and yields an activation energy $E_\perp = 2.8$ kcal/mol. The upper line connects the $D_\parallel$ at these temperatures (shown as solid squares) and the activation energy $E_\parallel = 1.9$ kcal/mol. These values must be taken as estimates since they are derived from lines with only two data points. As the temperature increases, the nonlinearity of $\ln D$ vs. $1/T$ for both motions becomes apparent, as represented by the dashed lines asymptotically approaching each other. This indicates that the molecule is moving into a motional regime where spin rotation is important and where enough large reorientation displacements are occurring that the simple "small-step" model is likely to be inadequate. The rotational diffusion model is only valid if the motion of the molecule is below the inertial limit given by the condition[30]

$$D_\perp{}^* = D_\perp(I_\perp/kT)^{1/2} < 1/6^{1/2}$$

$$D_\parallel{}^* = D_\parallel(I_\parallel/kT)^{1/2} < 1$$

The inertial limits for the two motions are shown at the top of Figure 2. At −81.5 °C, the Ds are about 5% of these respective inertial limits. At +20 °C, however, D is 27% of the limit for the perpendicular motion and nearly 14% of the parallel limit straining the limits of the diffusional model. This may explain the deviation from straight-line behavior in Figure 2 at the two higher temperatures.

These diffusion parameters are compared to the results of a previous study by Besnard et al.[30] in which the diffusion coefficients of neat liquid cyclopropane at 7 atm were determined by using

(30) Besnard, M.; Lascombe, J.; Nery, H. *J. Phys. (Orsay, Fr.)* **1980**, *41*, 723.

depolarized Raman techniques. The values of $D_\perp$ obtained in that study are shown in Figure 2 as asterisks. Figure 2 shows reasonable agreement in the values of $D_\perp$ between the two studies especially at higher temperatures. At -20 °C, for example, the values of their symmetric-top $D_\perp$ and our spherical-top D are within error of each other. The Raman study, however, proposes an anisotropy $D_\parallel/D_\perp$ of about 10 at the temperatures studied. They also pointed out that their results were consistent with C^{13} NMR T_1s determined from decoupled inversion recovery and NOE experiments in which cross-correlation is ignored. This conclusion is consistent with our data providing the relaxation is relatively insensitive to the $D_\parallel$ parameter. To check this point, fits were done with the $D_\parallel$ parameter locked to a value about 10 times the value of $D_\perp$ with $D_\perp$ free to vary. The resulting fits of our data were quite poor at all temperatures and thus it is concluded that the assumption in the previous study concerning $D_\parallel$ is inconsistent with the present study. In the Raman study, values for $D_\parallel$ are all near or at the inertial limit, and thus the diffusion assumption used to obtain the values is violated. The authors conclude that the anisotropy could be as small as 5 or as large as 12 and thus acknowledge difficulty in determining $D_\parallel$. Due to this uncertainty, the values of $D_\parallel$ obtained in the Raman study are not included in Figure 2.

The values for the methylene proton–proton distance are 1.844 Å at -81.5 °C and 1.847 Å at -60 °C, giving bond angles of 117.2° and 117.5°, respectively. These values are within ±2% of the electron diffraction value[19] of 115.8°, corrected for vibration,[20] and of the nematic solvent proton NMR value[21] of 115.15° (also corrected for vibration).[20] It is important to realize that our experiments actually measure an inverse sixth-power quantity, and so the values of r_{HH} reported in Table I are vibrationally averaged. The closer the protons approach one another in the vibrations, the greater they are weighted statistically. Corrections for vibrational averaging are expected to be smaller than our other errors and therefore the results were not subjected to standard adjustments for vibrational motion.[20] At -20 °C, r_{HH} = 1.865 Å and at $+20$ °C, r_{HH} = 1.865 Å. These values fail to agree with the literature and probably indicate that the diffusion model is breaking down. This r_{HH} parameter is quite sensitive in the LIF and would be affected adversely as the diffusion model becomes less appropriate. This trend of larger bond angles at higher temperatures was also seen in the results on $^{13}CH_2Cl_2$.[4]

The values of the spectral densities are quite illuminating. At the higher temperatures, the faster motion results in decreased efficiency of the dipolar relaxation mechanisms giving dipolar spectral densities which become nearly 1 order of magnitude less at $+20$ °C than at -81.5 °C. It is also evident from the data in Table I that either proton or carbon random field terms are significant at all temperatures. At -81.5 °C the proton random field spectral densities $j_H = j_{HH}$ = 0.0120 s^{-1} are comparable with the dipolar spectral densities. At -60 °C, $j_H = j_{HH}$ = 0.00592 s^{-1}, about half the value at -81.5 °C, but still significant, especially since the dipolar spectral densities are also smaller in magnitude. At -20 °C $j_H = j_{HH}$ = 0.00276 s^{-1} and at $+20$ °C $j_H = j_{HH}$ = 0.00192 s^{-1}. The increase of j_H and j_{HH} at lower temperature is ascribed to residual intermolecular dipole–dipole interactions, which are more efficient at lower temperatures. Since the sample is relatively concentrated (12.1 mol %), some contribution from intermolecular interactions can be expected. At higher temperatures, the spin-rotation mechanism becomes more important, and the intermolecular dipole–dipole interaction becomes less efficient. Thus, the decrease in the proton random fields with increasing temperature is less dramatic between -20 and $+20$ °C.

The values obtained for the carbon autocorrelation random field spectral density, j_C, illustrate limitations in the model used to interpret the data. At the lower temperatures, where the dipolar mechanisms dominate the relaxation, this term is expected to be either within error of being zero or positive. At -81.5, -60, and

-20 °C when j_C is unlocked, it assumes a negative value. While the relative errors in j_C are much larger than any of the other errors in the fit (about 18–21%), they are never large enough to include the value zero. This feature was noticed before in the CH_2Cl_2 study.[4] At $+20$ °C, j_C becomes significantly positive, although with a large relative error (10%), indicating that spin-rotation mechanism has become more important for carbon. The contribution of residual intermolecular interaction on the j_C is expected to be minimal, since the carbon is not located at the periphery of the molecule and is less able to interact with spins in neighboring molecules. The smaller carbon-13 magnetic moment further reduces such effects when compared with intermolecular proton–proton terms. The tendency of this term to be small but negative at lower temperature and the high relative errors at all temperatures indicate that the value of j_C is not well determined. Only the intramolecular dipole–dipole mechanism, which contributes significantly to the relaxation at lower temperature, appears to be well characterized. As j_C is not precisely determined experimentally and as the rotational reorientation no longer occurs in small steps once the molecule enters the motional regime where spin rotation is important, use of the general random field formalism is felt to be sufficient for these data. A more explicit treatment of the contribution of spin rotation using the full spin-rotation Hamiltonian would introduce additional parameters in the fit. This was felt to be unsatisfactory since even the limited number of parameters used here for spin rotation are not well determined. As the random field formalism has the same functional form as the spin-rotation interaction (first-rank tensors), the numbers obtained from the fits for the random field terms will be good estimates of the spin-rotation contribution only when this mechanism dominates other first-rank relaxation mechanisms.

An interesting value for J_{HCH} has been observed in this study. This cross-correlated spectral density was found at all temperatures to be negative. This is a direct consequence of the larger HCH angle found for the methylene in cyclopropane as compared with previous methylenes. The absolute magnitude decreases as the temperature is elevated, as do all dipolar spectral densities. There is, however, very little change in the value between -20 and $+20$ °C, where a small value is observed (-6.9×10^{-4} s^{-1} at -20 °C and -4.6×10^{-4} s^{-1} at $+20$ °C). It is believed that this is the first time a negative dipolar spectral density has been observed, although this has been anticipated theoretically.[1]

Summary

This study experimentally shows that, within the limits of error, the reorientational motion of labeled cyclopropane dissolved in CD_2Cl_2 at -81.5 and -60 °C may be characterized by two diffusion coefficients. The unique axis lies parallel to the C_3 axis of cyclopropane. At higher temperatures, the molecule enters the motional regime where the dipolar mechanisms becomes less efficient, spin rotation becomes more important, and greater uncertainty exists in the small-step motional model used to interpret the data. Consequently, only one diffusion parameter is obtained at -20 and $+20$ °C. Values obtained for the proton–proton distance at the lower temperatures agree reasonably well with electron diffraction and nematic solvent NMR data on cyclopropane. The results demonstrate the importance of cross-correlation in coupled spin systems, and the large HCH bond angle in cyclopropane resulted in observation of a negative value for the dipolar spectral density J_{HCH}, in agreement with theory.