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Relaxation in an A_2 coupled spin system dissolved in a perdeuterated liquid crystal: The intermolecular dipolar random field cross relaxation term

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A perdeuterated nematic liquid crystal N-(p-ethoxybenzylidene) -p-n-butylaniline (EBBA-d_{23}, 98% deuterium) was synthesized to study relaxation of small molecules dissolved in anisotropic solvents. Proton spin–lattice relaxation in the coupled A_2 spin system of methylene chloride (CH_2Cl_2) was studied using both perhydro and perdeutero EBBA as the solvent. The relaxation was modeled as intramolecular dipole–dipole interactions plus other mechanisms that were treated collectively as fluctuating external random magnetic fields. Comparison of relaxation in EBBA and EBBA-d_{23} allowed the first experimental measurement of the correlation coefficient between external random fields at the two protons due to dipolar interactions of the methylene protons with the protons or deuterons of the solvent (78% correlated). The selective nuclear Overhauser effect was also studied.

I. INTRODUCTION

In a previous study of spin–lattice relaxation in an A_2 coupled spin system dissolved in a nematic liquid crystal,[1] it has been shown that the incomplete averaging of the intramolecular dipolar spin–spin coupling[2] permits measurement of two relaxation observables. This enabled the partial separation of relaxation mechanisms in a way not possible in isotropic solvents. Unfortunately, it was not possible to calculate all the independent spectral densities and completely characterize the relaxation of the A_2 system. The relaxation was modeled as intramolecular dipole–dipole interactions plus other mechanisms that were treated collectively as external random magnetic fields. (It was assumed that there were no interference terms between the two different mechanisms.)

In the present paper, a 98% perdeutero nematic liquid crystal N-(p-ethoxybenzyledine)-p-n-butylaniline(EBBA-d_{23}) was synthesized as a means to compare the proton spin–lattice relaxation parameters of methylene chloride (CH_2Cl_2) dissolved in the perhydro and the perdeutero solvent. This comparison enabled the measurement of the dipolar power densities, including the cross correlated term, between the solute molecule and the solvent. This intermolecular dipolar mechanism was found to be strongly dominant in the protonated nematic liquid crystal.

II. THEORETICAL FORMULATIONS

If one is interested in studying only longitudinal relaxation, it has been derived from the Bloch–Redfield theory[3,4] that the time evolution of populations in an A_2 system can be expressed as a set of four coupled differential equations written in matrix form as

$$\frac{d}{dt}\mathbf{P}(t) = \mathbf{W}\left[\mathbf{P}(t) - \mathbf{P}^0\right] , \tag{1}$$

where the $P_i(t)$'s are eigenstate spin populations with P_i^0, the thermal equilibrium population, and the W_{ij} are the interlevel transition rates.

The theoretical values of W_{ij} as defined by Fig. 1 can be expressed in terms of three spectral densities as follows:

$$W_1 = J_1 + j_1 + k_1 ,$$
$$W_1' = j_1 - k_1 ,$$
$$W_0 = j_0 - k_0 ,$$
$$W_2 = 2J_2 . \tag{2}$$

The simplified notation is defined by

$$J_n \equiv J_{HH}^{(n)}(n\omega_H) \equiv \text{the intramolecular dipolar spectral densities,}$$

$$j_n \equiv j_H^{(n)}(n\omega_H) \equiv \text{the autocorrelated random field spectral densities,}$$
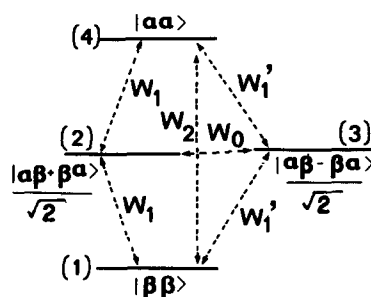

FIG. 1. Energy level diagram and interlevel transition rates for an isolated A_2 type system of two identical spins 1/2.

$k_n \equiv k_{HH}^{(n)}(n\omega_H) \equiv$ the cross correlated random field spectral densities.

The notation for spectral densities is taken from that of Werbelow and Grant.[4]

As the spin populations are not observable in an NMR experiment, it is appropriate to use a unitary linear transformation to obtain a new set of coupled differential equations[4] written in matrix form as

$$\frac{d}{dt}v(t) = \Gamma\left[v(t) - v^0\right] , \qquad (3)$$

where $\Gamma = QWQ^{-1}$ and $v(t) = QP(t)$.

The Q matrix was chosen such that the $v_i(t)$'s include the maximum number of relaxation observables, and such that it possesses the spin inversion symmetry which renders the Γ matrix partially diagonal, thus simplifying the data reduction.[4,5] Here the $v_i(t)$'s are referred to as "magnetization modes." Using the matrix Q defined previously, one obtains the magnetization modes as

$$v_1(t) = \tfrac{1}{2}(P_1 + P_2 + P_3 + P_4)$$

= total spin population, invariant in a closed system;

$$v_2(t) = \frac{1}{\sqrt{2}}(P_1 - P_4)$$

= total z magnetization, sum of the two A_2 transitions, always observable;

$$v_3(t) = \frac{1}{\sqrt{6}}(P_1 - 2P_2 + P_4) \qquad (4)$$

= difference between the two A_2 transitions, belongs to the symmetric manifold, observable only in anisotropic solvents;

$$v_4(t) = \frac{1}{2\sqrt{3}}(P_1 + P_2 - 3P_3 + P_4)$$

= difference between the total spin population of the triplet and the singlet manifolds, not observable.
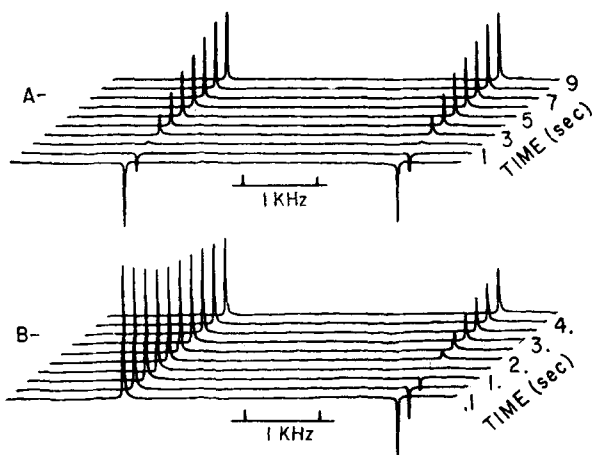

FIG. 2. PMR spectra of CH_2Cl_2 dissolved in EBBA-d_{23} at various time t after (a) application of a 180° hard pulse to invert both the A_2 transitions, and (b) after application of a 180° selective soft pulse to invert the high field transition.
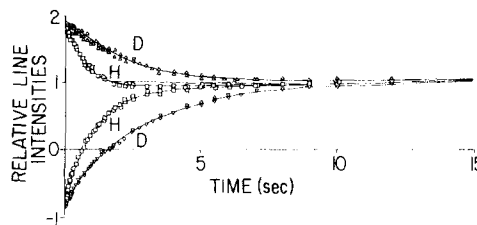

FIG. 3. Plots of the normalized transition intensities of CH_2Cl_2 dissolved in the deuterated (D) and the protonated (H) nematic solvent following a 180° selective soft pulse on the proton high field transition. Note the strong double exponential behavior of line intensities in the protonated EBBA.

With these normal modes, Γ is defined by the following linear combinations of spectral densities:

$$\Gamma_{22} = -(J_1 + 4J_2 + 2j_1) ,$$

$$\Gamma_{33} = -[3J_1 + \tfrac{1}{3}(10j_1 + 8k_1) + \tfrac{2}{3}(j_0 - k_0)] ,$$

$$\Gamma_{34} = \Gamma_{43} = \frac{2\sqrt{2}}{3}[(j_0 - k_0) - (j_1 - k_1)] ,$$

$$\Gamma_{44} = -\tfrac{4}{3}[(j_0 - k_0) + 2(j_1 - k_1)] .$$

All the other Γ_{ij}'s are identically zero.

The total magnetization v_2 decouples from the other modes because of their different spin inversion symmetry and thus evolves independently with a single time constant, while theoretically v_3 and v_4 are coupled and must evolve as double exponentials.

It is the purpose of this paper to measure the elements of Γ in a perdeutero and in a perhydro nematic phase. One can then expect to obtain a detailed measurement of the intermolecular dipolar interaction.

III. ANALYSIS OF RELAXATION IN AN A_2 COUPLED SPIN SYSTEM CH_2Cl_2

Two experiments, soft and hard pulse, were performed on each of the two samples of methylene chloride, one dissolved in EBBA-d_{23} and the other in EBBA. The concentration in each sample (~ 10 mol%) was adjusted such that the dipolar splitting was the same in both samples at 33 °C in order to guarantee equality of ordering in the two samples. This splitting was made equal to $\tfrac{3}{2}D_{HH} = 3638 \pm 1$ Hz, where D_{HH} is the partially averaged through space dipolar spin–spin coupling.[2]

In the following, boundary conditions and relaxation variables are defined in terms of parameters that will be used for the nonlinear least squares fitting procedure used for each experiment.[6]

A. Soft pulse experiment

Here one inverts selectively via the decoupler channel [Fig. 2(b)] the upfield transition by means of a 20 ms 180° soft pulse. When such a perturbation is applied, the populations of the irradiated levels are inverted and v_3 is strongly perturbed. The intensity of both lines at various times t after the preparing pulse is measured; and the time evolution of the intensity of each line for each sample was plotted as shown in Fig. 3. Note that
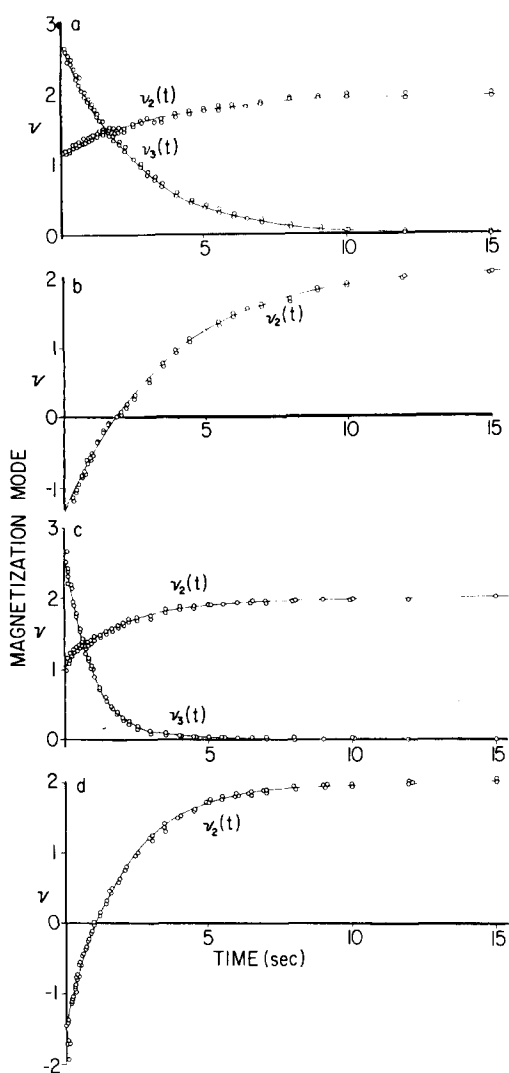
FIG. 4. Results of the nonlinear least squares fit to experimental measurements of the return to equilibrium of the magnetization modes of CH_2Cl_2 for various perturbations and solvents: (a) soft pulse on the high field transition, EBBA-d_{23}; (b) proton hard pulse, EBBA-d_{23}: (c) soft pulse on the high field transition, EBBA; (d) proton hard pulse, EBBA. The circles are data points. The lines are the calculated best fits.

the relaxation in the deuterated solvent is much longer than that in the hydrogenated one, indicating the importance of the intermolecular dipolar relaxation processes. Note also the nonexponential behavior of the downfield transition in the perhydro-EBBA solvent. This line is taller than its equilibrium value just after the preparing pulse, but decreases very rapidly to become less than the equilibrium value and then increases again to equilibrium. This phenomenon can be easily predicted by theory. Using a unitary transformation on the relaxation matrix leading to the time evolution of each transition $(P_1 - P_2)$ and $(P_2 - P_4)$, these observables are found to be strongly coupled to each other.

From these data, the magnetization mode variables $\nu_2(t)$ and $\nu_3(t)$ are calculated by taking sums and differences of line intensities at each time. The results are plotted as illustrated by Fig. 4.

The boundary conditions can be expressed as

$$\nu^{(1)}(0) = K_1 \begin{bmatrix} 2 - \alpha_1 \\ 3\alpha_1 \\ 0 \end{bmatrix}, \quad \nu^{(1)}(\infty) = K_1 \begin{bmatrix} 2 \\ 0 \\ 0 \end{bmatrix}, \tag{6}$$

where K_1 is a proportionality factor taking account of the spectrometer response and α_1 is included to account for the preparing pulse efficiency.

B. Coupled inversion recovery

In this experiment, one inverts both the proton transitions by a 180° hard pulse [Fig. 3(a)]. Such a symmetric perturbation does not affect the $\nu_3(t)$ mode, which always remains equal to zero. So this experiment can give information only about Γ_{22}. The boundary conditions can be defined from a pulse efficiency α_2 and a spectrometer response K_2 as

$$\nu^{(2)}(0) = K_2(-\alpha_2), \quad \nu^{(2)}(\infty) = K_2. \tag{7}$$

IV. NONLINEAR LEAST SQUARES FIT AND RESULTS

Similar data were taken on both perhydro- and perdeutero-EBBA samples as follows: For the soft pulse experiment, the two line intensities were measured 64 times for various values of t. For the hard pulse experiment, the intensities were measured 128 times for various values of t. As the relative intensities of the two A_2 transitions were very dependent on field homogeneity, they were generally not directly comparable. So when these intensities were added or subtracted, they first were normalized to their individual thermal equilibrium values.

Note that in all these experiments a 6° observing pulse was used as it is known that, in a strongly coupled homonuclear spin system, relative intensities are dependent on the observing flip angle[1,7] and are proportional to population differences only in the limit of small flip angle.

The data analysis was performed with a nonlinear least squares fitting program based on the same principles as that described by Mayne and co-workers[6] and implemented on a Texas Instruments 980A computer. The data were treated collectively to fit both the dynamical and the spectrometer response parameters as defined by Eqs. (6) and (7). These parameters define a B^T vector to be fitted as in Ref. 6:

$$B^T = (\Gamma_{22}, \Gamma_{33}, \Gamma_{34}, K_1, \alpha_1, K_2, \alpha_2). \tag{8}$$

The results of the fit are listed in Table I for both samples. Subscripts H and D refer respectively to the protonated and deuterated solvents, respectively. The quality of the fit is illustrated by the values of the marginal standard deviations of the parameters listed in Table I as well as the plots in Fig. 4.

Furthermore, as shown by Eq. (5), in general there will be a finite coupling term between ν_3 and ν_4 depending only on the random field spectral densities. ν_3 can, for all our experiments, be fit with a single exponential with no more than 1% deviation of the data from the best fit and with no detectable trends in these deviations (Fig. 4). One can then conclude that the coupling term

TABLE I.   Relaxation of CH_2Cl_2 in EBBA.

Parameter	Value	Marginal standard deviation	Parameter	Value	Marginal standard deviation
Γ_{22}^{D}	-0.276 s^{-1}	0.002	Γ_{22}^{H}	-0.524 s^{-1}	0.004
Γ_{33}^{D}	-0.377 s^{-1}	0.001	Γ_{33}^{H}	-1.065 s^{-1}	0.008
B_{1}^{D}	2.001	0.004	B_{1}^{H}	1.964	0.005
B_{2}^{D}	-0.841	0.006	B_{2}^{H}	-0.897	0.008
B_{3}^{D}	-0.001	0.005	B_{3}^{H}	0.001	0.005
B_{4}^{D}	2.705	0.008	B_{4}^{H}	2.657	0.011
B_{5}^{D}	1.028	0.003	B_{5}^{H}	0.982	0.003
B_{6}^{D}	-1.702	0.005	B_{6}^{H}	-1.725	0.006

$\Gamma_{34} = \Gamma_{43}$ is equal to zero within experimental error. This fact is quite important as it allows one to predict that the ν_4 mode will never be perturbed from equilibrium as there is no way to put magnetization into it.

V. DISCUSSION

From comparison of the dynamical parameters in both solvents, it is clear that relaxation in the deuterated solvent is much slower than in the hydrogenated one. However, among the various expected relaxation mechanisms, only one can be affected by this change, viz., the intermolecular dipolar relaxation. So one can conclude that proton relaxation of small molecules dissolved in a nematic phase is very sensitive to this mechanism.[8,9] Furthermore, quantitative data on this mechanism can be extracted from the relaxation data as follows:

First assume that the rf terms can be separated into intermolecular dipolar contributions $j_{1,DD}$ and $k_{1,DD}$, and other contributions $j_{1,0}$ and $k_{1,0}$ so that

$$j_1 = j_{1,DD} + j_{1,0} ,$$
$$k_1 = k_{1,DD} + k_{1,0} . \tag{9}$$

If one also assumes that the reorientation of the CH_2Cl_2 is not affected by substituting deuterium for hydrogen in the EBBA, then all mechanisms for relaxation except the intermolecular dipolar interactions between the EBBA and CH_2Cl_2 must be unaltered. Now, if one uses the third of equations (5) to eliminate the quantity $(j_0 - k_0)$ from the second, then Eq. (9) allows one to write a set of two equations for each solvent where the sets differ only in the intermolecular dipolar terms:

$$J_1 + 4J_2 + 2j_{1,DD}^{H} + 2j_{1,0} = -\Gamma_{22}^{H} ,$$

$$J_1 + 4J_2 + 2j_{1,DD}^{D} + 2j_{1,0} = -\Gamma_{22}^{D} ,$$

$$3J_1 + 4j_{1,DD}^{H} + 4j_{1,0} + 2k_{1,DD}^{H} + 2k_{1,0} = -\left(\Gamma_{33}^{H} + \frac{1}{\sqrt{2}}\,\Gamma_{34}^{H}\right),$$

$$3J_1 + 4j_{1,DD}^{D} + 4j_{1,0} + 2k_{1,DD}^{D} + 2k_{1,0} = -\left(\Gamma_{33}^{D} + \frac{1}{\sqrt{2}}\Gamma_{34}^{D}\right), \tag{10}$$

Taking differences between similar equations in different solvents then yields

$$j_{1,DD}^{H} - j_{1,DD}^{D} = -\tfrac{1}{2}(\Gamma_{22}^{H} - \Gamma_{22}^{D}) ,$$

$$2j_{1,DD}^{H} - 2j_{1,DD}^{D} + k_{1,DD}^{H} - k_{1,DD}^{D}$$
$$= -\frac{1}{2}\left[\Gamma_{33}^{H} - \Gamma_{33}^{D} + \frac{1}{\sqrt{2}}\,(\Gamma_{34}^{H} - \Gamma_{34}^{D})\right] . \tag{11}$$

Recall that the concentrations of the samples were carefully adjusted to produce equal dipolar splitting, which means that the ordering parameters are the same in both samples. Since these ordering parameters are themselves directly related to molecular reorientation,[2] Eq. (11) should be valid. Furthermore, these assumptions do not depend on assumptions of extreme narrowing or equality of various projections of the dipolar spectral densities.

A further simplification can now be effected by noting that the change in the strength of the dipole–dipole interaction upon substituting deuterium for hydrogen is governed solely by the ratio of the gyromagnetic ratios and by the total spin angular momentum[10(a)] so that

$$j_{1,DD}^{D} = K_{HD}\, j_{1,DD}^{H} ,$$
$$k_{1,DD}^{D} = K_{HD}\, k_{1,DD}^{H} , \tag{12}$$

where

$$K_{HD} = [R\alpha + (1-\alpha)]$$

and

$$R = \frac{\gamma_D^2 I_D(I_D + 1)}{\gamma_H^2 I_H(I_H + 1)} = 0.06284 .$$

Using Eqs. (11) and (12) and the values of the Γ_{ij} given in Table I, it is possible to calculate the intermolecular dipolar spectral densities given in Table II.

The fact that $\Gamma_{34} = 0$ within experimental error at first seems rather surprising, since the most plausible ex-

TABLE II.   Intermolecular dipolar spectral densities for CH_2Cl_2.

Spectral density	Value (s^{-1})
$J_{1,DD}^{H}$	0.135
$J_{1,DD}^{D}$	0.0109
$J_{1,DD}^{H}$	0.105
$k_{1,DD}^{D}$	0.0085

planations for this result are either the random fields are fully correlated ($j_0 = k_0$, $j_1 = k_1$) or the various projections of a spectral density term are equal ($j_0 = j_1$, $k_0 = k_1$). However, the values in Table I indicate that, at least for the intermolecular dipolar mechanism, full correlation is not consistent with the experimental findings. In addition, it has been found[11] that assumptions of equality of different projections are not in general justified in anisotropic solvents. However, only the less restrictive condition $j_0 - k_0 = j_1 - k_1$ needs to be satisfied in order for Γ_{34} to equal zero. So one must conclude that at least this less stringent condition is satisfied to within experimental error.

It is interesting to note that the intermolecular dipolar mechanism contributes more than one half of the total relaxation for the protonated nematic solvent ($2 j_{1,DD}^H = 0.270$ s^{-1}, $\Gamma_{22} = 0.524$ s^{-1}). Also, these results show that the intermolecular dipolar interaction is 78% correlated. This means that $W_i' = (j_1 - k_1)$ will probably not be zero (since the other rf mechanisms are unlikely to exactly compensate the intermolecular dipolar mechanism so as to make W_1' equal zero), and the isolated state 3 in Fig. 1 cannot be neglected when studying A_2 coupled relaxation.

VI. SELECTIVE NUCLEAR OVERHAUSER EFFECT

It is evident that when saturating selectively one of the A_2 transitions with an rf field, a population redistribution will occur and the system reaches a new equilibrium state where the intensity of the other transition is modified. For example, suppose that we irradiate the $2 \to 4$ transition shown in Fig. 1; then the selective Overhauser enhancement will be defined as

$$\eta_{12(24)} = \frac{(P_1 - P_2)}{(P_1^0 - P_2^0)} - 1 .$$

Equation (3) could be considered suitable to calculate η, but this is actually not the case as the matrix transformation used to obtain Eq. (5) does not yield an equation to which appropriate steady state solutions can easily be had when the irradiating field is on.[10(b)] So to perform the calculation of η, we must start from Eq. (1). Even when saturating the $2 \to 4$ transition, one can write

$$dP_1/dt = - (W_1 + W_1' + W_2)(P_1 - P_1^0) + W_1(P_2 - P_2^0)$$
$$+ W_1'(P_3 - P_3^0) + W_2(P_4 - P_4^0) \qquad (13)$$

and

$$dP_3/dt = + W_1'(P_1 - P_1^0) + W_0(P_2 - P_2^0)$$
$$- (2W_1' + W_0)(P_3 - P_3^0) + W_1'(P_4 - P_4^0) .$$

When the irradiation is on, the system reaches a new equilibrium state where $dP_1/dt = dP_3/dt = 0$ and $P_2 = P_4$. Then, using Eqs. (14) and the relations $(P_1^0 - P_2^0)$ $= (P_2^0 - P_4^0) = \frac{1}{2}(P_1^0 - P_4^0)$ derived from the high temperature approximation to the Boltzmann thermal equilibrium populations, one has

$$\eta_{12(24)} = \frac{2W_1'W_2 + W_0W_2 + W_1'^2}{2W_1W_1' + W_0W_1 + W_0'W_1' + 2W_1'W_2 + W_0W_2 + W_1'^2} .$$
$$(14)$$

η can be expressed in terms of the Γ's using Eqs. (2) and (5):

TABLE III. Selective nuclear Overhauser effect for CH_2Cl_2 in EBBA.

	Directly measured	Calculated from Table I, Γ_{22} and Γ_{33} values
$\eta_{12(24)}^D$	0.36 ± 0.03	0.37
$\eta_{12(24)}^H$	0.17 ± 0.03	0.19

$$\eta_{12(24)} = \frac{\Gamma_{44}(3\Gamma_{22} - \Gamma_{33}) + \Gamma_{34}^2}{\Gamma_{44}(3\Gamma_{22} + \Gamma_{33}) - \Gamma_{34}^2} . \qquad (15)$$

This equation can give another experimental verification of the result $\Gamma_{34} = 0$, since, in this case, η should be independent of Γ_{44}:

$$\eta_{12(24)} \approx \frac{3\Gamma_{22} - \Gamma_{33}}{3\Gamma_{22} + \Gamma_{33}} . \qquad (16)$$

This value can be calculated for both solvents from the results in Table I. On the other hand, the experimental value of η can be easily measured by turning on the decoupler long enough to saturate the $2 \to 4$ transition and thus to reach a new steady state and then off during the observing pulse and the data acquisition to prevent any spin tickling effect. Such experiments were performed on both samples. In Table III, the results are tabulated and compared with values calculated according to Eq. (16) using the values of Γ_{ij} in Table I.

The excellent agreement between these results gives credence to the approximation $\Gamma_{34} = 0$ used in going from Eq. (15) to (16). However, it is also evident that η provides no new information that might be used in further unraveling the relaxation mechanisms.

VII. SUMMARY

The comparison of relaxation parameters of methylene chloride dissolved both in EBBA and perdeutero-EBBA nematic liquid crystals reveals that the most important mechanism using the EBBA solvent is intermolecular dipolar interactions between the protons of CH_2Cl_2 and those of the nematic crystalline phase. The fluctuating fields at the two protons of CH_2Cl_2 due to this mechanism are found to be 78% correlated. It was also found that the transition probability connecting the isolated singlet state to the triplet manifold of the A_2 system is probably not negligible. Thus, the singlet state affects the relaxation of the A_2 system in spite of the fact that it does not participate in any transition in the A_2 spectrum. The selective nuclear overhauser effect was investigated and found not to yield any information not available from the relaxation measurements.

A study similar to the one reported herein of an A_3 spin system is currently underway, and it is hoped that, since this system presents more measureable dynamic quantities to the experimenter, some of the questions left unanswered by this study will be answered.

VIII. EXPERIMENTAL

A. Instrumentation

These data were obtained on a Bruker WP-60 FT spectrometer equipped with a NTC-120 data K7 system.

The sample was inserted in the probe without rotation. The field was locked on an external D_2O sample without autoshim. The temperature was maintained constant at 306 K (33 °C) with the Bruker B-ST 100/700 system.
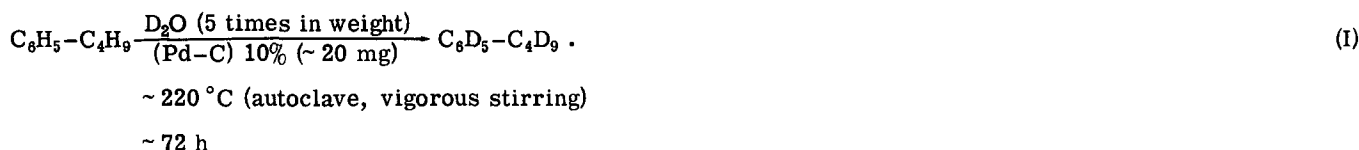
B. Preparation of the perdeuterated EBBA nematic phase

The total synthesis was performed from low cost deuterated materials: D_2O, C_6D_6, C_2D_5OD, and D_2SO_4. It

was carried out in several steps following known synthetic procedures for hydrogenated homologs, but modified in order to reduce deuterium–hydrogen exchange between reagents and solvents by use of materials having no labile hydrogen.

The percentage of deuterium was monitored by mass spectrometry (Varian Atlas CH4) at each step: (1) preparation of perdeuterated *para-n*-butylaniline:
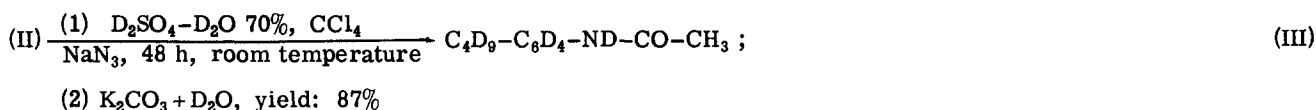
(a)

$$C_6H_5-C_4H_9 \xrightarrow[\text{(Pd-C) 10\% (~ 20 mg)}]{\text{D_2O (5 times in weight)}} C_6D_5-C_4D_9 \ . \tag{I}$$

$\sim 220\,°C$ (autoclave, vigorous stirring)

$\sim 72\ h$

The exchange is repeated five times with fresh D_2O and renewed Pd–C each time:

(b) (see Ref. 12)

$$(I) \xrightarrow[\text{CCl}_4,\ \text{room temperature}]{(1)\ \text{AlCl}_3 + CH_3COCl} C_4D_9-C_6D_4-CO-CH_3 \ ; \tag{II}$$

(2) $DCl + D_2O$, yield: 90%

(c)

$$(II) \xrightarrow[\text{NaN}_3,\ 48\ h,\ \text{room temperature}]{(1)\ D_2SO_4-D_2O\ 70\%,\ CCl_4} C_4D_9-C_6D_4-ND-CO-CH_3 \ ; \tag{III}$$

(2) $K_2CO_3 + D_2O$, yield: 87%

(d)

$$(III) \xrightarrow[\substack{190\,°C\ \text{and vigorous stirring,} \\ 48\ h,\ \text{yield:}\ 40\%}]{(1)\ \text{NaOD}-D_2O\ 50\%} C_4D_9-C_6D_4-ND_2 \ . \tag{IV}$$

(2) C_6D_6
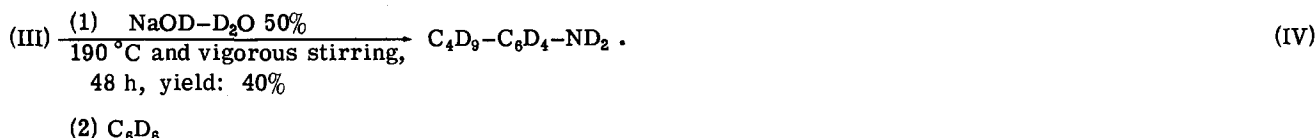
(2) For the preparation of perdeuterated *p*-ethoxybenzaldehyde, we have

(a)

$$C_6D_6 + Br_2 \xrightarrow[\text{room temperature, yield: 75\%}]{CCl_4} C_6D_5Br \ ; \tag{V}$$

(b) (see Ref. 13)

$$(V) \xrightarrow[\text{(a) Mg, ether, room temperature}]{} C_6D_5OD \tag{}$$

(b) O_2, room temperature

(c) $D_2SO_4-D_2O$ 50%, O °C
    yield: 28%

(c) (see Ref. 14)

$$(VI) \xrightarrow[\substack{\text{Dicyclohexyl carbodi-imide} \\ \text{sealed tube, 120\,°C,} \\ \text{yield: 50\%}}]{+C_2D_5OD} C_6D_5-O-C_2D_5 \tag{VII}$$

(d) (see Ref. 15)

$$(VII) \xrightarrow[\substack{\text{(a) Zn(CN)}_2,\ \text{AlCl}_3,\ \text{dry DCl} \\ \text{in } C_6D_6,\ 50\,°C,\ \text{vigorous} \\ \text{stirring for 5 h, yields: 30\%}}]{} C_6D_5-O-C_6D_4-CDO \tag{VIII}$$

(b) D_2O, O °C (Gatterman reaction)
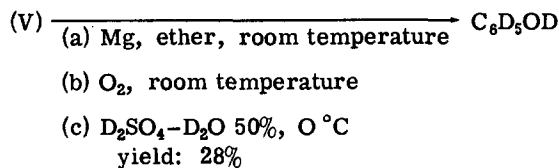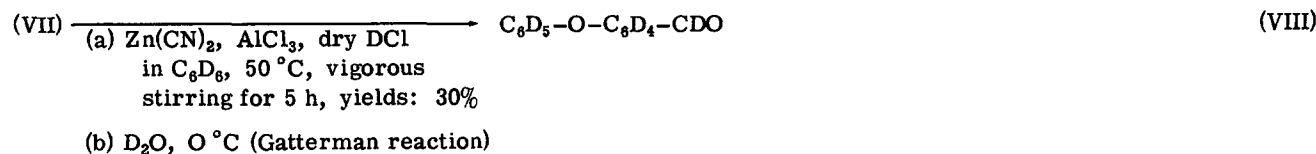
(3) For the preparation of perdeuterated EBBA, we have

$$(IV) + (VIII) \xrightarrow[\text{apparatus, 6 h, yield: 90\%}]{C_6D_6, \text{ Dean–Stark}} C_4D_9-C_6D_4-N=CD-C_6D_4-O-C_2D_5 .$$
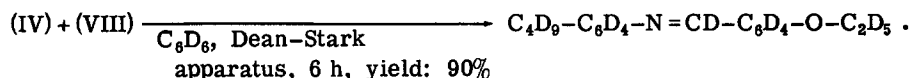
The crude EBBA 98% deuterium enriched was purified by distillation under vacuum and used for NMR experiments without further purification.

C. Sample preparation·n

Two samples were prepared; each was approximately 10 mole% in CH_2Cl_2. One sample used commercial EBBA as the solvent; the other used the EBBA-d_{23} prepared above. The concentration of CH_2Cl_2 was adjusted slightly so that each sample exhibited a dipolar splitting of the proton resonance of 3638 ± 1 Hz at 33 °C. Each sample was then subjected to two freeze–pump–thaw cycles and sealed in a 5 mm o.d. NMR tube under vacuum.

ACKNOWLEDGMENTS

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