

## Chapter IV

## DISCUSSION

IV.1 Dipolar Relaxation

The hamiltonian for dipole-dipole interaction between spin I and S can be written as

$$\hbar \mathcal{H} = \frac{\vec{\mu}_I \cdot \vec{\mu}_S}{r^3} - \frac{3(\vec{\mu}_I \cdot \vec{r})(\vec{\mu}_S \cdot \vec{r})}{r^5}, \quad (4.1)$$

where  $\mu$  = magnetic moment ,

$r$  = distance between the two spins ,

$$\text{or} \quad \hbar \mathcal{H} = \frac{\gamma_I \gamma_S \hbar^2}{r^3} [A + B + C + D + E + F], \quad (4.2)$$

where  $A = I_z S_z (1 - 3 \cos^2 \theta)$  ,

$$B = -\frac{1}{4} [I_+ S_- + I_- S_+] (1 - 3 \cos^2 \theta) ,$$

$$C = -\frac{3}{2} [I_+ S_z + I_z S_+] (\sin \theta \cos \theta e^{-i\phi}) ,$$

$$D = -\frac{3}{2} [I_- S_z + I_z S_-] (\sin \theta \cos \theta e^{i\phi}) ,$$

$$E = -\frac{3}{4} I_+ S_+ \sin^2 \theta e^{-i2\phi} ,$$

$$F = -\frac{3}{4} I_- S_- \sin^2 \theta e^{i2\phi} .$$

Eq. (4.2) can be written in the form

$$\mathcal{H} = \sum_{\mathbf{q}} F^{(\mathbf{q})} A^{(\mathbf{q})}, \quad (4.3)$$

where  $F^{(\mathbf{q})}$  = the random functions of the relative positions of two spins ,

$A^{(\mathbf{q})}$  = the operators acting on the spin variables ,

$$\text{and } F^{(1)} = \frac{\sin\theta \cos\theta e^{-i\phi}}{r^2}, \quad A^{(1)} = \alpha [I_Z S_+ + I_+ S_Z],$$

$$F^{(2)} = \frac{\sin^2\theta e^{-2i\phi}}{r^3}, \quad A^{(2)} = \frac{1}{2}\alpha I_+ S_+$$

$$F^{(0)} = \frac{1-3\cos^2\theta}{r^3}, \quad A^{(0)} = \alpha \left\{ -\frac{2}{3} I_Z I_Z + \frac{1}{6} (I_+ S_- + I_- S_+) \right\},$$

$$\text{where } \alpha = -\frac{3}{2} \gamma_I \gamma_S \hbar.$$

Assuming an isotropic random motion, then the autocorrelation function can be expressed as

$$F^{(q)}(t) F^{(q)*}(t+\tau) = \delta_{qq'} G^{(q)}(\tau), \quad (4.4)$$

$$J^{(q)}(\omega) = \int_{-\infty}^{\infty} G^{(q)}(\tau) e^{-i\omega\tau} d\tau. \quad (4.5)$$

The unperturbed hamiltonian is given by

$$\begin{aligned} \mathcal{H}_0 &= -\vec{\mu} \cdot \vec{H} \\ &= \omega_I I_I + \omega_S I_S. \end{aligned} \quad (4.6)$$

In the case of like spins, the equation of motion of the longitudinal magnetizations is

$$\frac{d}{dt} \langle I_{Z+I'_Z} \rangle = - (a_Z - a_0), \quad (4.7)$$

$$\begin{aligned} \text{where } a_Z &= \text{tr} \left\{ A_Z \rho^* \right\}, \\ a_0 &= \text{tr} \left\{ A_Z \rho_0 \right\}, \end{aligned}$$

$$A_Z = \frac{1}{2} \sum_{q,p} J_q(\omega_p^{(q)}) \left[ A_p^{(q)}, [A_p^{(-q)}, Q] \right],$$

$$Q = I_Z + I'_Z,$$

$$A_Z = \frac{2\alpha^2}{3} I(I+1) \langle I_{Z+I'_Z} \rangle \left\{ J^{(1)}(\omega_I) + J^{(2)}(2\omega_I) \right\}. \quad (4.8)$$

Eq. (4.7) then becomes<sup>22</sup>

$$\frac{d}{dt} \langle I_z + I'_z \rangle = - \frac{1}{T_1} \left\{ \langle I_z + I'_z \rangle - \langle I_z + I'_z \rangle_0 \right\} \quad , \quad (4.9)$$

where

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) \left\{ J^{(1)}(\omega_I) + J^{(2)}(2\omega_I) \right\} \quad (4.10)$$

The time dependence of magnetization in the plane perpendicular to the magnetic field  $H_0$  is described by the equation

$$\frac{d}{dt} \langle I_x + I_x \rangle^{*23} = - \langle A_x \rangle^* \quad ,$$

$$\frac{d}{dt} \langle I_x + I'_x \rangle^* = - \frac{1}{T_2} \langle I_x + I'_x \rangle^* \quad ,$$

where

$$\frac{1}{T_2} = \gamma^4 \hbar^2 I(I+1) \left\{ \frac{3}{8} J^{(2)}(2\omega_I) + \frac{15}{4} J^{(1)}(\omega_I) + \frac{3}{8} J^{(0)}(0) \right\} \quad (4.11)$$

#### IV.2 Spin Lattice Relaxation in Liquid Crystals

Pincus<sup>11</sup> has proposed a model for NMR in liquid crystals, in which the elongated molecule has two identical nuclear spins located on the axis separated by a distance  $a$ . The mean intermolecular  $b$  is considered to be much larger than the nuclear separation  $a$ . Accordingly, the interaction between the spins on the neighboring

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<sup>22</sup> A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press London, 1961).

<sup>23</sup> indicates the interaction representation.

molecules can be neglected. In a smectic liquid crystal the molecular axes tend to be aligned parallel to one another along a direction labelled by the unit vector  $\vec{n}_0$ . However, there exist thermal fluctuations of the unit vector  $\vec{n}(r)$  about  $\vec{n}_0$ . These fluctuations may cause nuclear relaxation through the modulation of the dipole-dipole interaction of a pair of protons located on one molecule.

The principal mechanisms contributing to the nuclear relaxation are

1. the local fluctuation of the vector  $\vec{n}(r)$ ,
- and 2. the diffusive motion of the molecules.



By using Eq. (4.10) and assuming that the orientational fluctuations and diffusive motion are uncoupled, it follows that  $T_1$  due to a dipolar interaction between nuclei on the same molecule, for the case with an external magnetic field  $H$  parallel to the molecular axis  $n_0$ , is given by

$$\frac{1}{T_1} = \frac{\omega_D^2 k_B S T}{K [\omega(D + k/\eta)]^{1/2}}$$

- where
- $\eta$  = the nuclear resonance frequency,
  - $D$  = a constant depending upon the strength of the spin-spin interaction,
  - $k_B$  = the Boltzmann constant,
  - $K$  = the elastic deformation constant,
  - $D$  = the diffusion constant,
  - $\eta$  = the viscosity,
  - $S$  = the order parameter.

Lubensky<sup>24</sup> has calculated the longitudinal nuclear relaxation rate  $1/T_1$  by assuming the same model for liquid crystal as that of Pincus, and also by introducing the density correlation function. By using the Eq. (4.10), the longitudinal nuclear relaxation rate is given by

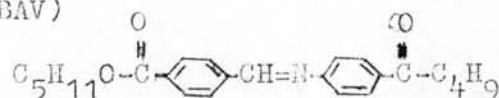
$$\frac{1}{T_1} = \frac{k_B T S^2}{K} \left[ \frac{1}{\omega(D + k/\eta)} \right]^{1/2} \quad (4.13)$$

The longitudinal nuclear relaxation rate obtained by Lubensky contains the factor  $S^2$  while that obtained by Pincus contains the factor  $S$ . Blinc et al.<sup>25</sup> has calculated the nuclear relaxation rate  $1/T_1$  and found that it is similar to that of Pincus.

The theoretical value for  $1/T_2$  has not been predicted yet.

### IV.3 Chemical Nature of the Samples

#### IV.3.1 p-((p-Pentyloxycarbonyloxybenzylidene)amino)valerophenone (PCBAV)



The solid-smectic transition temperature is  $80^\circ\text{C}$  and the smectic-isotropic transition temperature is  $110^\circ\text{C}$ . The texture of

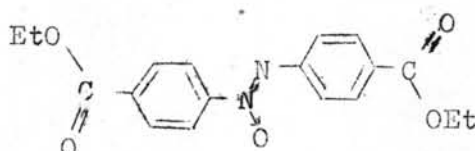
<sup>24</sup> T.C. Lubensky, "Molecular Description of Nematic Liquid Crystals," Physical Review A, 2(1970), 2497 .

<sup>25</sup> R. Blinc, D.L. Hogenboom, D.E. O'Reilly and E.M. Peterson, "Spin Relaxation and Self Diffusion in Liquid Crystals," Physical Review Letters, 23(1969), 969.

the smectic phase, as observed optically from a polarizing microscope is found to be fan-shaped. According to Sackmann and Demus<sup>26</sup>, this substance is classified as smectic A.

Excluding the CH group at the center of the molecule, this molecule consists of three different proton groups. They are the benzene protons and the proton groups at the alkyl end chains, viz., pentyl protons and butyl protons.

#### IV.3.2 Diethyl 4,4'-Azoxydibenzoate (DADB)



The solid-smectic transition temperature is 114°C. The smectic-isotropic transition temperature is 123°C. This substance shows the fan-shaped **texture** first when it is heated from the solid state and shows the polygon texture at the temperature near the smectic-isotropic transition. It is classified as smectic A.

The molecule consists of two different proton groups, benzene protons and the ethyl protons at the two end chains. The end chain protons are of the same kind.

A theoretical model<sup>27</sup> for the smectic A phase, based on an

<sup>26</sup> H. Sackmann and D. Demus, Liquid Crystals, edited by Glenn H. Brown, G. J. Dienes and H. M. Laube (Gordon and Breach, Science Publishers, New York, London, Paris, 1967), pp. 341.

<sup>27</sup> W. L. McMillan, "Simple Molecular Model for the Smectic A Phase of Liquid Crystals" Physical Review A, 4(1971), 1233.

extension of the Maier-Saupe model<sup>28</sup>, has been proposed by McMillan. This simple model exhibits three phases, viz., an isotropic liquid, a nematic, and a smectic A phase. This theoretical model leads to a satisfactory agreement with the existing experimental results. The calculated order parameter for the model which exhibits both the smectic A and the nematic phases shows no discontinuity at the smectic-nematic transition. This point is particularly interesting in connection with the present investigation.

#### IV.4 Concluding Remarks

The essential features of the curves of  $T_1$  plotted versus temperature of PCBAV (Fig. 3.3) and of DADB (Fig. 3.7) are similar. These curves do not simultaneously increase or decrease as the temperature increases. However, the slope changes its sign at the solid-smectic and smectic-isotropic transitions. On the other hand, the magnitudes of  $T_1$  of PCBAV and of DADB are slightly different. This is not surprising in view of the fact that the formula structures of the molecules of both organic compounds, although not exactly identical, are indeed very similar. The proton groups are located at the central rigid part of the molecule, at the benzene rings, and at the alkyl end chains which are presumably flexible<sup>27</sup>. It should also be noted that the pentyl and butyl chains of PCBAV are longer, and hence have more protons, than the ethyl chains

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<sup>28</sup> G. Maier and A. Saupe, in Liquid Crystals, edited by Glenn H. Brown, G. J. Dienes, and H. N. Lubes (Gordon and Breach, Science Publishers, New York, London, Paris, 1967), pp. 195.



of DADB. The difference between PCBAV and DADB is that the molecule of PCBAV is asymmetric while that of DADB is symmetric .

#### Smectic phase

Starting with the theoretical value of  $T_1$

$$\frac{1}{T_1} = \frac{\omega_D^2 k_B T S^2}{K [\omega(D + K/\eta)]^{1/2}} \quad , \quad (4.13)$$

The viscosity  $\eta$  in this phase has been found to be related to the molecular order and to increase with decreasing temperature<sup>29</sup> .

The viscosity is highly anisotropic<sup>30</sup> , being low in the direction parallel to the layers. The elastic constant is known to depend upon the degree of molecular order . This dependence has been measured and found to vary as  $S^2$  . Thus the temperature and the frequency dependence of  $T_1$  is of the form

$$\frac{[ ( S^2/\eta + D ) ]^{1/2}}{T}$$

The variation of  $S$  with temperature is found to be small<sup>27</sup> in the smectic phase . Consequently , for the case where the diffusion effects are small or when  $D \ll K/\eta$  ,

<sup>29</sup> C.G. Kartha and A.R.K.L. Padmini , " Ultrasonic and Viscous Behaviour of Polymesomorphic Liquid Crystals , " Journal of the Physical Society of Japan, 31(1971),904

<sup>30</sup> S.V. Letcher and A.J. Barlow, " Dynamic Shear Properties of Some Smectic Liquid Crystals , " Physical Review Letters , 26(1971),172 .

<sup>31</sup> A. Saupe , Z. Naturforsch. , 15a(1960),815 .



$T_1$  is proportional to

$$(\eta\omega)^{1/2}/T.$$

The intermolecular dipole-dipole interaction may reasonably be neglected since it is expected to be much reduced by the random thermal motion of the molecules<sup>32</sup>. The main significant contributions are therefore the intramolecular dipole-dipole interactions. The characters of the temperature dependence of  $T_1$  for PCBAV and for DADB are similar to that of the nematic liquid crystal PAA<sup>17,25</sup>. The principal difference is that the measured value of  $T_1$  of PAA is longer than those of PCBAV and of DADB. Thus, if in this phase the molecular relaxation is dominated at all frequencies by the elastic fluctuations of the local anisotropy<sup>33</sup>, then the temperature and the frequency dependence of  $T_1$  should be the same as that discussed above.

#### Temperature dependence of $T_1$

The temperature dependence of  $T_1$  does not strictly follow the theoretical prediction. It appears that simple theoretical ideas cannot satisfactorily account for the temperature dependence of  $T_1$ . It is thus necessary to consider the positions of the proton groups in the molecule, viz., the benzene protons and the ethyl, pentyl or butyl protons. From the previous study<sup>14</sup>, it has been shown

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<sup>32</sup> Glenn H. Brown, J.W. Doane and Vernon D. Neff, CRC: A Review of Other Structure and Principal Properties of Liquid Crystals (Butterworths London, 1971), pp.50.

<sup>33</sup> B. Cabane, Nuclear Relaxation in Liquid Crystals (8<sup>th</sup> Colloquium on NMR Spectroscopy, 1971).

that the end chain groups correspond to the temperature more than the benzene protons . Thus the temperature dependence of  $T_1$  might have an important contribution from short-range phenomena involved in the motions of ethyl protons in DADB or pentyl and butyl protons in PCBAV . Since ethyl ,pentyl and butyl protons are in a situation incompatible with the assumption used in deriving the expression for  $T_1$  , they must be considered separately and the foregoing theoretical results should apply to benzene protons only. But the motion of the alkyl groups at the end chain of each molecule might be too fast to cause the nuclear relaxation in the smectic phase. These motions dominate in the solid phase as Dong et al.<sup>13</sup> has suggested for PAA . If we consider these motions in view of the collective motion of each cluster of molecules , the motions will be slow enough to contribute to the nuclear relaxation .

As the behavior of  $T_1$  with varying temperature in the region of the top of the peak (Fig. 5.3 ) changes rather markedly , the reasonable interpretation is that the mechanisms contributing to  $T_1$  are of several different kinds and it does not take a long time to change from one mechanism to another as the temperature increases. However , this does not necessarily mean that the different mechanisms always come from the different groups of protons .

#### Frequency dependence of $T_1$

The theoretical idea proposed by Pincus<sup>11</sup> , that the long-range order fluctuations cause the nuclear relaxation through the modulation of the dipole-dipole interaction , as has been discussed

previously, predicts the square root frequency  $\omega^{1/2}$  dependence for  $T_1$ . The experimental results measured at 7.85, 10.25 and 11.65 MHz support this prediction. We have obtained a straight line on plotting  $T_1$  versus  $\omega^{1/2}$  (Fig. 3.8).

### Isotropic

The interpretation of the results of the NMR measurements on protons in the isotropic liquid is not quite straightforward, since there are possibly many different contributions to the relaxation rate  $1/T_1$ , there are many inequivalent protons in molecule, viz., the benzene protons and the protons of two end chains of the molecule. Also it is not clear whether the motion of these molecules can reasonably be described by a model in which they are considered to be "rigid bodies".

The modulation through self diffusion of the intermolecular nuclear interactions is expected to give rise to a frequency independent contribution to  $1/T_1$ . Furthermore, the experimental results show that in the region of the smectic-isotropic transition,  $T_1$  does not depend linearly on the temperature. Presumably, this demonstrates the presence of the smectic short range order clusters. At high temperature the diffusion process is expected to provide the relaxation mechanism as in ordinary liquids.

### Final conclusion

In view of the lack of experimental data on the diffusion constant  $D$  and viscosity  $\eta$ , it is not possible to state at the moment whether the theory and experiment agree quantitatively.

On the assumptions that the effect of diffusion is small and that the behaviors of the viscosity  $\eta$  is similar to those observed by Kartha and Padmini<sup>28</sup> as discussed above, we cannot conclude that, in the smectic phase, the thermal fluctuation of the smectic order is the only mechanism contributing to  $T_1$ . A correct prediction of the temperature dependence alone cannot totally account for the experimental results. Also it is known that the rate of the slow mode for orientation fluctuation is about  $10^3 \text{ sec}^{-1}$ <sup>34</sup>, the reciprocal of which is longer than the magnitude of the period of the resonance rf field. On the other hand, we cannot conclude that the orientational fluctuations are not contributing to  $1/T_1$  at all, because the frequency dependence prediction fits the experimental results. Thus it is clear that these orientational fluctuations provide relaxation mechanisms contributing to  $1/T_1$ . Since the magnitude of  $T_1$  decreases as the temperature increases in the region before the smectic-isotropic transition occurs, we can conclude that in that region the orientational fluctuations are dominated.

The molecules of liquid crystals are comparatively long<sup>27</sup>. The molecule can have complicated internal degrees of freedom such as twisting of the plate about a given direction, stretching and bending. From Raman spectral evidence, there is present the acoustic longitudinal mode:

<sup>34</sup> Group d'Etude des Cristaux Liquides (Orsay), "Dynamics of Fluctuations in Nematic Liquid Crystals," The Journal of Chemical Physics, 51(1969), 816.

accordianlike longitudinal mode of molecules in the liquid crystals<sup>35</sup>. In the NMR study, the collective molecular motions, can be considered in addition to the individual molecular motions, viz., a slow cooperative mode which has been proposed by Dong et al<sup>13</sup>. There is also the mode involving the displacements of the smectic layers<sup>4,36</sup>, in particular the local displacement of the neighboring layers without an angular rotation of the  $\bar{z}$ -direction. Thus, in the region that the theory cannot at present fully account for, there are many other possible mechanisms different from the orientational fluctuations which can contribute significantly to the relaxation.

The most probable modes are the modes that have the time orders of magnitude which are close to the period of the resonance frequency, viz., the orientational fluctuations, the translation diffusion and the slow cooperative mode which includes the displacements of the layers.

We would like to comment in this regard that the viscosity that appears in the expression for  $1/T_1$  is in fact not the total viscosity but only that related to the liquid crystal order. Hence, its temperature dependence will be more pronounced than

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<sup>35</sup> Joel M. Schnur, "Raman Spectral Evidence for Conformational Changes in the Liquid-Crystal Homologous Series of the Alkoxyazoxybenzenes," Physical Review Letters, 29(1972), 1141.

<sup>36</sup> Noel A. Clark and P.S. Pershan, "Light Scattering by Deformation of the Plane Texture of Smectic and Cholesteric Liquid Crystals," Ibid., 30(1973), 3.

that of the total viscosity.

In the isotropic region the translational diffusion causes the relaxation except in the vicinity of the smectic-isotropic transition. The results of  $T_2$  in a smectic phase are of the order of 10 micro-seconds and show a clear break at the smectic-isotropic transition.

APPENDIX





## APPENDIX 1

 $T_1$  (PCBAV) DATA

$T_1$  = Spin lattice relaxation time

$$T_1 = 1.063 \bar{\tau} \text{ null} / \ln 2$$

where 1.063 is the time scale correction<sup>17</sup>

At the proton resonance frequency 7.85 MHz. .

January 18, 1973

T( °C)	$\bar{\tau}$ null(m sec)	$T_1$ (m sec)
109.5	250	384
107.5	230	353
106	235	361
104.5	240	368
96	220	338
93.5	200	308
92	190	292
88	150	230
85	145	223
82	130	199
80	100	153
81	120	184

January 20, 1973

T(°C)	$\bar{\tau}$ null(m sec)	$T_1$ (m sec)
110	190	282
109	200	307
107	215	330
103	220	338
102	225	345
100	230	355
98.5	240	368
97.5	230	353
95	205	315
90.5	185	284
88	170	261
85	150	230
81.5	130	199
80	120	184
79	150	230
78	160	246

January 19, 1973

T(°)	$\bar{\tau}$ null(m sec)	$T_1$ (m sec)
110	190	282
107.5	210	322
105	220	338
102	230	353
100	240	368
99	245	376
97.5	230	353
92	200	307
88	185	284
85.5	160	246
83.5	140	215
80	120	184
78	155	238

January 21, 1973

T(°)	$\bar{\tau}$ null(m sec)	$T_1$ (m sec)
110	192	295
106.5	210	322
104.5	220	338
102	230	353
100	240	368
99	245	376
98	220	338
95.5	200	307
92.5	190	292
89.5	180	276
84	140	215
81.25	120	184
80	110	168

January 24, 1973

T	$\tau$ null(m sec)	$T_1$ (m sec)
109	198	302
105	210	338
102.5	225	345
101	235	361
99.9	245	376
98	220	338
96.5	210	322
94	200	307
90.5	170	261
86	150	230
83	145	219
82	140	215
80	120	184
70	190	292

January 28, 1973

T( $^{\circ}$ C)	$\tau$ null(m sec)	$T_1$ (m sec)
110	195	299
107	215	330
103	225	345
101.5	230	353
100.5	240	368
99	243	373
98	235	360
96	210	322
92	200	307
87	190	292
84.5	160	246
81.75	136	200
80	110	169
79	130	199
77	140	215

January 26, 1973

T( $^{\circ}$ C)	$\tau$ null(m sec)	$T_1$ (m sec)
110	192	295
109	205	314
106	210	322
104	220	338
101.5	230	353
100	235	361
99	205	376
98.5	240	368
96.5	215	330
93	200	307
89	185	284
89	200	307
83	135	207
81.5	125	192
80	115	176
78.25	150	230
77	170	261



## APPENDIX 2

 $T_1$  (PCBAV) DATA

$T_1$  = spin lattice relaxation time

$$T_1 = 1.063 \tau_{\text{null}} / \ln 2$$

where 1.063 is the time scale correction<sup>17</sup>

At the proton resonance frequency 10.25 MHz.

June 30, 1972

T(°C)	$\tau_{\text{null}}$ (m sec)	$T_1$ (m sec)
113.5	185	284
110	175	268
106	180	276
105	210	322
104	244	374
99	265	406
89	265	406
85	255	391

July 5, 1972

T(°C)	$\tau_{\text{null}}$ (m sec)	$T_1$ (m sec)
130	290	445
125	288	442
122	270	414
118	265	391
116.5	230	353
115.5	210	322
114	210	322
112	202	313
105	178	275
103	180	276

July 2, 1972

T(°C)	$\tau_{\text{null}}$ (m sec)	$T_1$ (m sec)
121	270	414
118	265	406
116	250	384
110	195	298
102	200	307
96	225	345
91.5	238	365
90	230	353
87	222	338
80	193	305

July 7, 1972

T(°C)	$\tau_{\text{null}}$ (m sec)	$T_1$ (m sec)
124.6	290	445
120	178	426
114.5	250	384
112	230	353
109.5	198	320
106	200	322
104	170	261

January 14, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
109.5	230	352
108	240	368
106	258	396
104.5	300	460
102	260	445
101	280	430
100	270	414
95	260	399
94	220	338
92	210	322
90	200	307
88	180	276
85	160	245
82	145	222
80	140	214

January 14, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
80	170	261
81.5	180	276
84	190	292
88	200	307
89	220	338
90	240	368

January 15, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
108	210	322
106.5	230	253
104	235	361
102	240	368
96	220	338
92.5	200	307
90	190	292
89	180	276
88	160	246

January 15, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
109	210	321
107	215	330
104	220	338
101	240	369
99.5	250	384
98.5	230	353
96.5	210	321
94.5	200	307
93	190	292
90	180	276
88.5	170	261
87	160	246
82	140	215
80	140	215
78	160	256
76.5	210	321

January 16, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
110	210	307
107	215	330
104	220	338
101	240	369
99	250	384
97.5	230	353
96.5	210	321
94.5	200	307
93	190	292
90	180	272
88.5	170	261
87	160	246
82	140	215
80	140	215
78	160	256
76.5	200	307

January 17, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
108	210	321
104.5	230	351
103	235	361
101	250	384
98.5	260	399
96	240	368
93	220	338
90	200	307
87.5	190	292
84	180	276
80	170	261
79	180	276

March 25, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
120	320	
119	295	452
118.25	285	437
117	275	422
116	265	406
115.5	250	384
113.75	235	361
112.25	225	345
111	218	334
110	210	321

March 18, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
114	240	368
113	225	345
111	220	338
110	210	322
108	220	338
106.5	240	368
103	250	384
99	260	399
80	120	184

March 25, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
116.5	260	399
115.75	250	384
114	235	361
113.5	230	353
111.5	225	345
110.5	215	330

## APPENDIX 3

 $T_1$  (PCBAV) DATA

$T_1$  = Spin lattice relaxation time

$$T_1 = 1.063 \tau \text{ null} / \ln 2$$

where 1.063 is the time scale correlation <sup>17</sup>

At the proton resonance frequency 11.65 MHz.

January 31, 1973

February 10, 1973

$T(^{\circ}\text{C})$	$\tau \text{ null (m sec)}$	$T_1 \text{ (m sec)}$	$T(^{\circ}\text{C})$	$\tau \text{ null (m sec)}$	$T_1 \text{ (m sec)}$
110	245	376	110	225	345
108.25	250	384	107.5	235	360
104.8	260	399	103.5	250	383
103.8	265	406	102.5	255	391
101.8	275	422	100	270	414
99	290	445	99	285	436
98	285	437	97.75	250	384
95.5	260	399	96	240	363
92	240	368	94.5	225	345
87.5	210	322	92	200	307
84.5	180	276	89	180	276
82	160	246	82.25	150	230
80.5	145	222	81.20	140	215
80	138	212	80	135	207
			78.5	140	214

February 9, 1973

February 11, 1973

$T(^{\circ}\text{C})$	$\tau \text{ null (m sec)}$	$T_1 \text{ (m sec)}$	$T(^{\circ}\text{C})$	$\tau \text{ null (m sec)}$	$T_1 \text{ (m sec)}$
110	230	353	110	218	334
108.5	245	376	107.5	230	353
105.8	250	384	103.5	255	361
102.2	270	414	102	265	406
101.2	280	414	100.25	275	421
100.5	285	436	99	285	437
99	292	448	97.75	270	430
97.8	285	436	95.2	250	384
94.2	255	391	92.6	230	353
91.75	245	376	87	205	314
90.2	235	360	82.75	160	245
87.75	210	322	80	140	215
83.5	190	292	79.2	160	245
82	160	246			
80	135	207			

February 12, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
110	225	345
107	230	353
105	245	351
103.5	225	391
102	260	399
100	275	421
99	283	434
98	278	426
96.75	265	406
95.5	255	391
92	230	353
88	195	299
85.75	175	268
81	145	222
80	138	212
79	155	238
77.5	180	276
75.5	200	307

February 13, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
110	225	345
108.5	230	353
106.2	245	376
104	255	391
101	265	406
100	275	421
99	280	430
98	270	415
96	260	399
92.5	240	368
91	220	338
86.75	195	299
83	163	253
80.75	145	222
80	132	202
79	150	230
77	165	253
75.5	175	278

February 14, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
109.5	220	337
108.25	225	345
104.8	245	376
101	265	406
100	270	414
99	282	433
98	250	384
97.25	245	376
91.75	210	322
88.5	190	291
86	175	268
83.5	155	233
82	150	230

February 14, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
110	225	345
108	230	353
105	240	368
103	250	384
101.5	258	396
100.25	275	421
99	282	433
98.25	270	414
97	250	384
93	230	353
89.75	200	307
87	185	284
86	175	268
83.5	155	238
81.5	145	222
80	130	199
79	150	230
77.75	158	242
76	165	253
75	170	261



## APPENDIX 4

 $T_1$  (DADB) DATA

$T_1$  = Spin lattice relaxation time

$$T_1 = 1.063 \tau \text{ null} / \ln 2$$

where 1.063 is the time scale correction.<sup>17</sup>

At the proton resonance frequency 10.25 MHz.

September 1, 1972

T(°C)	$\tau$ null(m sec)	$T_1$ (m sec)
120	190	292
119	215	330
118	200	307
114	150	230
112	170	261

January 7, 1973

T(°C)	$\tau$ null(m sec)	$T_1$ (m sec)
120	160	246
118	170	261
116	140	215
114	120	184
112	140	215

October 6, 1972

T(°C)	$\tau$ null(m sec)	$T_1$ (m sec)
120	200	307
119	220	338
117	240	368
116	210	311
114	190	292

January 17, 1973

T(°C)	$\tau$ null(m sec)	$T_1$ (m sec)
118	110	169
116	90	138
115.5	85	130.5
114	80	123
113	95	146

January 7, 1973

T(°C)	$\tau$ null(m sec)	$T_1$ (m sec)
120	125	192
118	190	292
115.5	150	230
114.5	130	199
114	120	184
112	130	199
108	195	299

January 17, 1973

T(°C)	$\tau$ null(m sec)	$T_1$ (m sec)
119	200	307
117	190	292
116	160	246
114	120	184
113	150	230

February 27, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
120	190	291
119	210	322
118	200	307
116.5	180	276
114	140	214
113	155	238

March 16, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
126	220	338
125	210	322
124	190	291
123	160	246
121	180	276
119	200	307

February 28, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
120	195	299
119	215	330
117.5	195	299
116.5	175	268
114	130	199
113	150	230
111.5	165	253

March 17, 1973

T(°C)	$\tau$ null(m sec)	T <sub>1</sub> (m sec)
131	350	537
130	335	511
129	310	475
128	280	430
127	250	384
126.5	240	368
125	230	353
123.5	170	261
123	150	230
121	180	276
120	195	299
119	200	307
116.5	180	276
115.5	165	253
114	145	222
112.25	200	307

March 3, 1973

T(°C)	$\tau$ null(msec)	T <sub>1</sub> (m sec)
124.5	200	307
123	180	276
121.5	155	238
120	138	212
119	158	242
117.5	148	227
115	120	184
114	110	169

## APPENDIX 5

 $T_1$ (DADE) DATA

$T_1$  = Spin lattice relaxation time

$$T_1 = 1.063 \tau \text{ null} / \ln 2$$

where 1.063 is the time scale correction.<sup>17</sup>

At the proton resonance frequency 11.65 MHz.

February 16, 1973

February 17, 1973

$T(^{\circ}\text{C})$	$\tau$ null(m sec)	$T_1$ (m sec)	$T(^{\circ}\text{C})$	$\tau$ null(m sec)	$T_1$ (m sec)
120	210	322	120	210	322
119	220	338	119	225	345
118	200	307	117.5	200	307
117.5	188	288	116.5	180	276
115.25	165	253	115.25	175	269
			114.5	168	258
120	190	292	114	160	246
119	200	307			
118	190	292			
116.5	180	276			
115	165	253			
120	200	307			
119	222	325			
118	200	307			
117.25	190	292			
115.5	170	261			