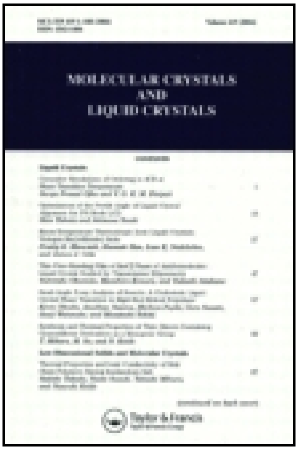

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: R. T. Thompson , D. W. Kydon & M. M. Pintar (1977): Spin Thermometric Analysis of Spin-Lattice Relaxation by the Order Director Fluctuation in Liquid Crystal MBBA, Molecular Crystals and Liquid Crystals, 39:1-2, 123-126

To link to this article: http://dx.doi.org/10.1080/15421407708083914

Mol. Cryst. Liq. Cryst., 1977, Vol. 39, pp. 123–126

Printed in Holland

Spin Thermometric Analysis of Spin–Lattice Relaxation by the Order Director Fluctuation in Liquid Crystal MBBA

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(*Received May 20, 1976; in final form August 13, 1976*)

The dominance of order director fluctuations or molecular diffusion as the nuclear spin relaxation mechanism in MBBA has recently been discussed again. By measuring T_1, $T_{1\rho}$, T_{1D} and applying spin thermometry the two mechanisms can be separated to give their respective contributions to the relaxation. It follows that diffusion is the dominant relaxation mode. Discussion of this and previous results are given.

Recently several research groups reported studies on the effectiveness of the order-director fluctuation (ODF) as a spin-lattice relaxation mechanism in the liquid crystal *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA). It was proposed that, if ODF is the predominant relaxation mechanism, both T_1 and $T_{1\rho}$ should display an angular dependence.[1,2]

With the order director $\vec{N_0}$ parallel to the magnetic field $\vec{H_0}$ the contribution of ODF to T_1^{-1} has been shown[2] to be $\sim 0.2\ \mathrm{sec}^{-1}$ at 291 K and 30 MHz. In this note we derive the ODF contribution by spin thermometric analysis of the experimental results in high and low fields.[3] The results of spin thermometric analysis support the published data.

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† This research supported by National Research Council of Canada.

The sample of MBBA was obtained commercially from Eastman Kodak Co. had a liquid crystal range between 10° and 45°C. The relaxation times T_1, $T_{1\rho}$ and T_{1D} were measured with the 90°– 90°, field locking and Jeener–Broekaert 90°– 45°– 45° pulse sequences, respectively. A Spin Lock Electronics CP2 coherent spectrometer was used for the measurements.

It has been shown that the relaxation in the rotating frame can be written[3] as a weighted average of T_{1X}^{-1} and T_{1D}^{-1}.

$$(H_1^2 + H_L'^2)T_{1\rho}^{-1} = H_1^2 T_{1X}^{-1} + H_L'^2 T_{1D}^{-1}$$

where H_1 is the strength of the rotating field and H_L' is the local field in the rotating frame. Introducing, $H_r = H_1/H_L'$, this equation can be written as:

$$(H_r^2 + 1)T_{1\rho}^{-1} = H_r^2 T_{1X}^{-1} + T_{1D}^{-1}$$

When we plot $(H_r^2 + 1)T_{1\rho}^{-1}$ against H_r^2 the slope of the resulting line is equal to T_{1X}^{-1} and the intercept, $T_{1\rho}^{-1}$ (0) should be equal to T_{1D}^{-1}. This is called a low field thermometric plot as the equation is only valid when $3H_L' \geq H_1 \geq H_L'$. At high fields, when the dipolar and Zeeman energies are decoupled, we have $T_{1\rho}^{-1} = T_{1X}^{-1}$.

At 295°K in MBBA the low field thermometric plot gives $T_{1\rho}^{-1}$ (0) $\sim T_{1D}^{-1}$ within experimental error, Figure 1. Also, the slope from this plot is equal to T_{1X}^{-1} obtained from the measurement of $T_{1\rho}$ at high H_1.

In the next step the following molecular motions were considered: One contribution to spin-lattice relaxation is by ODF. The ortho benzene protons are usually considered as the main source of the ODF relaxation but the CH_2 protons in the alkyl tail contribute as well. In fact the ODF relaxation of inter

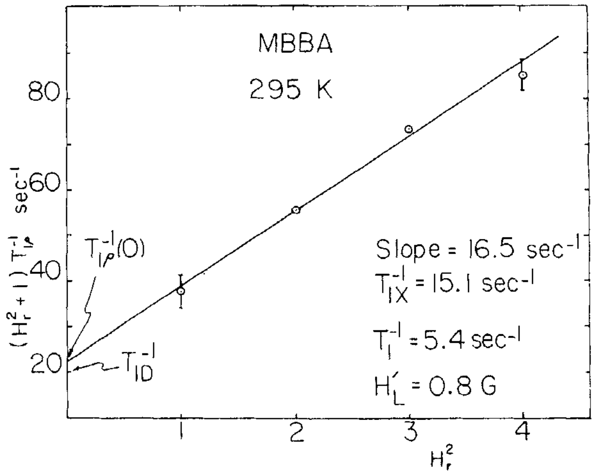

FIGURE 1 Low field spin thermometric plot for MBBA at 295°K.

CH_2 group proton pairs is comparable[4] in effectiveness to the relaxation by the ortho benzene protons. However, the "intra CH_2" relaxation by ODF, which is stronger than the ODF relaxation of the benzene protons, has to be considered separately as the p–p vector is not parallel to H_0.

In the situation where there is no molecular motion the p–p vector for the intra CH_2 would be perpendicular to H_0. Since we have molecular motion this is not true. It has been obtained experimentally that $R_{\mathrm{ODF}}(\text{intra CH}_2) \simeq 3R^b_{\mathrm{ODF}}$, where R^b_{ODF} is the rate due to the ortho benzene protons. If the molecules were rigid the factor would be 6 instead of 3.[5] It has been recognized that the molecular diffusion contributes a dominant relaxation rate (R_z). In addition, there is also a slow molecular motion which adds to T_{1X}^{-1} and T_{1D}^{-1} but does not contribute to T_1^{-1} (i.e., $\omega_0\tau_s \gg 1$, but $\omega_1\tau_s \lesssim 1$). Such contribution by a slow molecular mode has to be invoked to give the relaxation equations real solutions. It remains unproven at the present time whether the slow mode is a cooperative angular displacement of molecular groups or a zone boundary drift in the liquid crystal. With this in mind the following spin thermometric equations can be written:

$$\begin{aligned} T_1^{-1} &= \tfrac{8}{21} R^b_{\mathrm{ODF}} + \tfrac{4}{21} R_{\mathrm{ODF}}(\text{inter CH}_2) \\ &\quad + \tfrac{6}{21} R_{\mathrm{ODF}}(\text{intra CH}_2) + R_z \\ &= T_1^{-1}(\mathrm{ODF}) + Rz \end{aligned} \tag{3}$$

$$T_{1X}^{-1} = 2.5T_1^{-1}(\mathrm{ODF}) + R_z + R_s \tag{4}$$

$$\begin{aligned} T_{1D}^{-1} &= \frac{3}{M_2(\mathrm{MBBA})}\frac{8}{21} M_2(\text{Benzene})R^b_{\mathrm{ODF}} + \frac{4}{21} M_2(\text{CH}_2\text{ inter}) \\ &\quad \times R_{\mathrm{ODF}}(\text{CH}_2\text{ inter}) + \tfrac{6}{21} M_2(\text{CH}_2\text{ intra})\, R_{\mathrm{ODF}}(\text{intra CH}_2) \\ &\quad + R_z + wR_s \end{aligned} \tag{5}$$

where the factor "w" in T_{1D}^{-1} can be between 1 and 2. When $\omega_0\tau \ll 1$, we can write $T_1^{-1} = T_{1X}^{-1} = \frac{1}{2}T_{1D}^{-1}$. When $\omega_0\tau \simeq 1$, we have $T_{1X}^{-1} < T_{1D}^{-1} < 2T_{1X}^{-1}$. In the temperature region where $\omega_0\tau \gg 1$ and $\omega_1\tau \ll 1$, $T_{1X}^{-1} = T_{1D}^{-1}$. Note that the weights for intra CH_2 and inter CH_2 are different because two of the protons have a negligible inter contribution.

In our system of equations we have one more unknown than equations therefore we must make an estimate as to the size of "w." The value "w" $= 1$ is used and can be justified by comparison with the p-pentylbenzoic acid (PPeBa).[4] If the slow mode is thermally activated then it should be much slower in MBBA than in PPeBA since there is about 100°C difference in the temperature of their nematic phases. Therefore $w(\mathrm{MBBA}) < w(\mathrm{PPeBa}) \sim 1.5$.

Experimentally we found that $M_2(\text{MBBA}) = 2.4 \pm 0.2G^2$. The value for the other second moments have been estimated in a study of the alkoxybenzoic acid homologous series[4] and these values will be used here: $M_2(\text{CH}_2 \text{ inter}) \sim 1.6 \pm 0.4G^2$, $M_2(\text{Benzene}) \sim 1.6 \pm 0.2G^2$ and $M_2(\text{CH}_2 \text{ intra}) \approx 1.8 \pm 0.4G^2$. With these values, and considering $R^b_{\text{ODF}} = R_{\text{ODF}}(\text{inter CH}_2) = \frac{1}{3}R_{\text{ODF}}(\text{intra CH}_2)$ the equations become:

$$T_1^{-1} = 1.4R^b_{\text{ODF}} + R_z$$
$$T_{1X}^{-1} = 3.5R^b_{\text{ODF}} + R_z + R_s$$
$$T_{1D}^{-1} = 3.0R^b_{\text{ODF}} + 2R_z + wR_s$$

As mentioned, we set $w = 1$ and obtain at 22°C:

$$R^b_{\text{ODF}} = 0.3 \pm 0.2 \text{ sec}^{-1}$$
$$R_z = 5.0 \pm 1.0 \text{ sec}^{-1}$$
$$R_s = 9.1 \pm 2.0 \text{ sec}^{-1}$$

The value of 0.3 sec^{-1} for $T_1^{-1}(\text{ODF})$ is within experimental accuracy $(\pm 0.2 \text{ sec}^{-1})$ equal to the value obtained by the angular dependence.[2] It should be noted that if no slow mode were considered the value of the ODF contribution would be an order of magnitude too high. This further substantiates the existence of the slow mode. As can be seen the ODF contributes more to T_{1X}^{-1} than it does to T_1^{-1} but in T_{1X}^{-1} there is also the contribution of R_s which is much larger than R^b_{ODF}. On the other hand the diffusion contribution is almost by an order of magnitude larger than ODF rate. Thus, the frequency dependence of T_1^{-1} gives information on the dispersion of R_z rather than R_{ODF}. Of course, the above equations only hold for N_0 parallel to H_0. If the angular dependence is considered the corresponding modifications of Eqs. 3 to 5 have to be made.

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