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

# Proton Dipolar Spin-lattice Relaxation in the Smectic Phases of TBBA

R. Y. Dong [a] , J. S. Lewis [b] , E. Tomchuk [b] , J. J. Visintainer [d] & E. Bock [c]

[a] Department of Physics, Astronomy, Brandon University, Brandon, Manitoba, Canada, R7A 6A9

[b] Department of Physics, University of Winnipeg, Winnipeg, Manitoba, Canada, R3B 2E9

[c] Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2

[d] The Goodyear Tire & Rubber Company, Research Division, 142 Goodyear Boulevard, Akron, OH, 44316

Version of record first published: 17 Oct 2011.

*Mol. Cryst. Liq. Cryst.*, 1983, Vol. 98, pp. 139–147
0026-8941/83/9804–0139/$18.50/0

Printed in the United States of America



# Proton Dipolar Spin-lattice Relaxation in the Smectic Phases of TBBA†

R. Y. DONG

*Department of Physics and Astronomy, Brandon University, Brandon, Manitoba, Canada R7A 6A9*

and

J. S. LEWIS and E. TOMCHUK

*Department of Physics, University of Winnipeg, Winnipeg, Manitoba, Canada R3B 2E9*

and

J. J. VISINTAINER‡ and E. BOCK

*Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

*(Received January 14, 1983)*

The proton dipolar spin-lattice relaxation time $T_{1D}$ was measured at several Larmor frequencies in the various smectic phases of the liquid crystal terephthal-bis-butylaniline (TBBA) as a function of temperature and orientation of the sample in an external magnetic field. The angular dependent $T_{1D}$ measurements are used to determine the importance of orientational order director fluctuations (ODF) in the dipolar field of the smectic phases of TBBA. In particular, the $T_{1D}^{-1}$ angular dependence in the $S_A$ phase is different from that in the $S_C$ and $S_G$ phases. This contrasts sharply with the $T_1^{-1}$ angular dependence in these phases which are all similar.

## INTRODUCTION

Proton dipolar spin-lattice relaxation time ($T_{1D}$) measurements have been used[1–4] to elucidate the abrupt change in molecular self-diffusion within the

†Work supported by the Natural Sciences and Engineering Research Council of Canada.
‡Present address: The Goodyear Tire & Rubber Company, Research Division, 142 Goodyear Boulevard, Akron, OH 44316.

layers of smectogens owing to the onset of two-dimensional order within each layer from hexagonal and/or herringbone packings.[5] Thus far only a few angular dependent studies of $T_{1D}$ [1,6,7] have been reported, and it is not clear to what extent orientational order director fluctuations[8] (ODF) relax the proton dipolar order in "true" liquid crystalline smectics such as smectic A ($S_A$) and C ($S_C$) phases. Recently one of us has shown[6] that the $T_{1D}$ angular dependence in the $S_A$ and chiral smectic C* phases of a ferroelectric liquid crystal (DOBAMBC) can be interpreted in terms of the angular dependent functions characteristic to ODF. We found that such an interpretation is possible for the $T_{1D}$ angular dependence in the $S_A$ and $S_C$ phases of terephthal-bis-butylaniline (TBBA). We report here the temperature dependence of $T_{1D}$ and its angular dependence in the $S_A$, $S_C$ and $S_G$ phases of TBBA at several Larmor frequencies.

## THEORY

In the weak collision limit, the dipolar spin-lattice relaxation time can be written[10] as

$$T_{1D}^{-1} = C_0 J_0(0) + C_1 J_1(\omega) + C_2 J_2(2\omega) \tag{1}$$

where the spectral densities $J_p(p\omega)$ involve correlation functions of the well known angular part of the magnetic dipole interaction between a spin ½ pair and the constants $C_0$, $C_1$ and $C_2$ are of the same order of magnitude. Modulations of the magnetic dipole interaction by ODF, the smectic order and a coupling between them produce a complicated expression[1] for $J_p(p\omega)$ in the $S_A$ phase. However, the expression simplifies under certain limit[1] to

$$J_p(p\omega) = f_p(\Delta) S^2 \frac{kT}{2\sqrt{2}\pi} \sum_{\alpha=1}^{2} \frac{1}{K_\alpha} \sqrt{\frac{\eta_\alpha}{K_3}} \frac{1}{\sqrt{p\omega}} \tag{2}$$

where $S$ is the nematic order parameter; $K_1$, $K_2$ and $K_3$ are the splay, twist and bend elastic constants (with $K_2 = \bar{K}_2$ and $K_3 = \bar{K}_3$ in $S_A$ phase), respectively; $\eta_\alpha$ are the corresponding viscosities; $f_p(\Delta)$, the angular dependent functions are given by

$$\begin{aligned} f_0(\Delta) &= 18(\cos^2 \Delta - \cos^4 \Delta) \\ f_1(\Delta) &= \frac{1}{2}(1 - 3\cos^2 \Delta + 4\cos^4 \Delta) \\ f_2(\Delta) &= 2(1 - \cos^4 \Delta) \end{aligned} \tag{3}$$

and $\Delta$ is the angle between the director and the external field. Blinc *et al.*,[1] reported that in the fast motion limit and with two spin approximation, the

dipolar spin-lattice relaxation rate due to ODF has the following angular dependence:

$$T_{1D}^{-1} \propto J_1(\omega) \propto f_1(\Delta) \tag{4}$$

in the smectic A phase of TBBA. This corresponds to setting $C_0 = C_2 = 0$ in Eq. 1, but fails to explain the $T_{1D}$ angular dependence in the $S_C$ phase[11] of TBBA and the $S_C^*$ phase[6] of DOBAMBC. This is because the $T_{1D}$ angular dependence in the $S_A$ phase is different from that in the $S_C$ and $S_G$ phases. Now $C_2$ appears to be zero in Eq. 1 because of the dissimilarity between the $T_1$ and $T_{1D}$ angular dependencies in these smectic phases. In the $S_A$ phase, the $T_1$ angular dependence[1] is given by

$$T_1^{-1} = Ag(\Delta) + B \tag{5}$$

where the isotropic $B$ term is added to account for relaxation mechanisms other than ODF and $g(\Delta) = f_1(\Delta) + 1/\sqrt{2} f_2(\Delta)$, while the $T_{1D}$ angular dependence is written[6] as

$$T_{1D}^{-1} = ah'(\Delta) + b \tag{6}$$

where $h'(\Delta) = 1/8 f_0(\Delta) + f_1(\Delta)$ and the isotropic $b$ term is again added to account for relaxation mechanisms other than ODF (*e.g.*, molecular self-diffusion and reorientations about the long molecular axis). A similar expression[6] for $T_{1D}$ in the $S_C$ phase is

$$T_{1D}^{-1} = ah(\Delta) + b \tag{7}$$

where $h(\Delta) = 1/9 f_0(\Delta) + f_1(\Delta)$. The ratios $C_0/C_1$ for Eqs. 6 and 7 are those found to work in the $S_A$ and $S_C^*$ phases of DOBAMBC.

## EXPERIMENTAL

The proton $T_1$ and $T_{1D}$ measurements were made with a Bruker SXP4-100 MHz pulsed spectrometer. $T_1$ was measured by the standard 180°-$\tau$-90° pulse sequence, while $T_{1D}$ was determined by the well-known Jeener-Broekaert technique, using 90° ($x$)-45° ($y$)-45° ($y$) pulse sequence. All measurements were made by cooling the sample from the nematic phase and had an experimental error of ±5% for $T_1$ and ±10% for $T_{1D}$. The angular dependent studies were done by rotating the sample in the external magnetic field with an accuracy of ±2°. In the $S_C$ phase, care was taken to measure $T_{1D}$ before molecules had a chance to follow[12] the field. At 90 MHz, sample was reheated to nematic for alignment after each rotation in the $S_C$ phase. There was difficulty in measuring $T_{1D}$ at $\Delta$ near 90° in the $S_C$ phase at this high field.

The liquid crystal TBBA was obtained commercially. All samples were sealed in a vacuum without further purification by the freeze-pump-thaw method. The temperatures of the sample were maintained by an air flow and measured with a copper-constantan thermocouple.

## RESULTS AND DISCUSSIONS

Figure 1 shows a plot of proton $T_{1D}$ versus the temperature at $\omega/2\pi$ = 90, 60, 28, 15 and 12 MHz. Proton $T_{1D}$ appears to exhibit a maximum (at ~190°C) within the $S_A$ phase at the Larmor frequencies studied except at 90 MHz, the maximum shifts towards the $N$-$S_A$ phase transition. Our $T_1$ data (not shown) at several frequencies all show a maximum at the $N$-$S_A$ phase transition in agreement with Blinc *et al.*[1] As expected, $T_{1D}$ undergoes an abrupt drop[1] at the $S_C$ to $S_G$ (tilted $B$) phase transition. This is due to pseudo-hexagonal packing of molecules within the layer. It is also observed that $T_{1D}$ is frequency independent in the $S_G$, $S_C$ and partly in the $S_A$ phase (below 190°C). There is, however, a definite $T_{1D}$ field dependence in the nematic phase of TBBA. This was used to argue that ODF is a relaxation mechanism for the dipolar spin system of nematogens.[9] For direct comparison with the $T_{1D}$ data, we present in Figure 2 the $T_1$ angular dependent

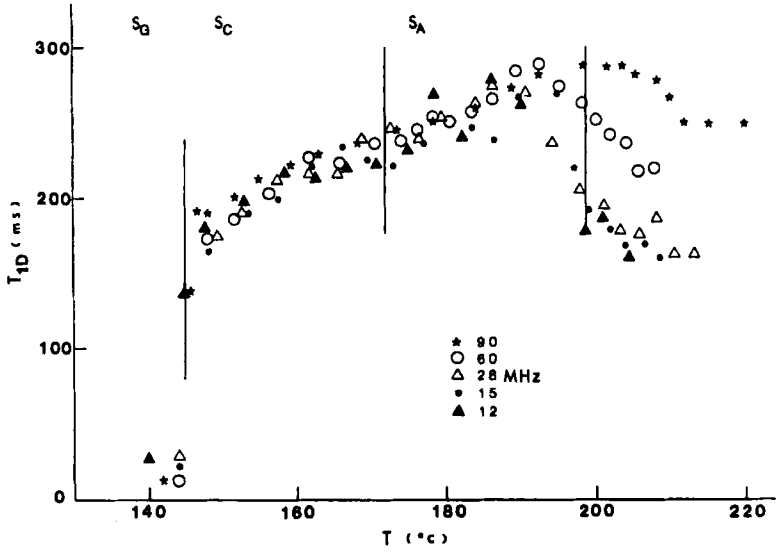


FIGURE 1 Plot of proton dipolar spin-lattice relaxation time $T_{1D}$ versus temperature in TBBA at $\omega/2\pi$ = 90, 60, 28, 15 and 12 MHz.

data at 60 and 15 MHz in the $S_A$ phase (at 189°C). The solid curves are a least-squares fit to Eq. 5 with $A = 0.14\ s^{-1}$ and $B = 0.28\ s^{-1}$ at 60 MHz, and $A = 0.23\ s^{-1}$ and $B = 0.28\ s^{-1}$ at 15 MHz. The $T_1$ angular dependences of the $S_C$ and $S_G$ phases of TBBA[1b] are similar. Figures 3 and

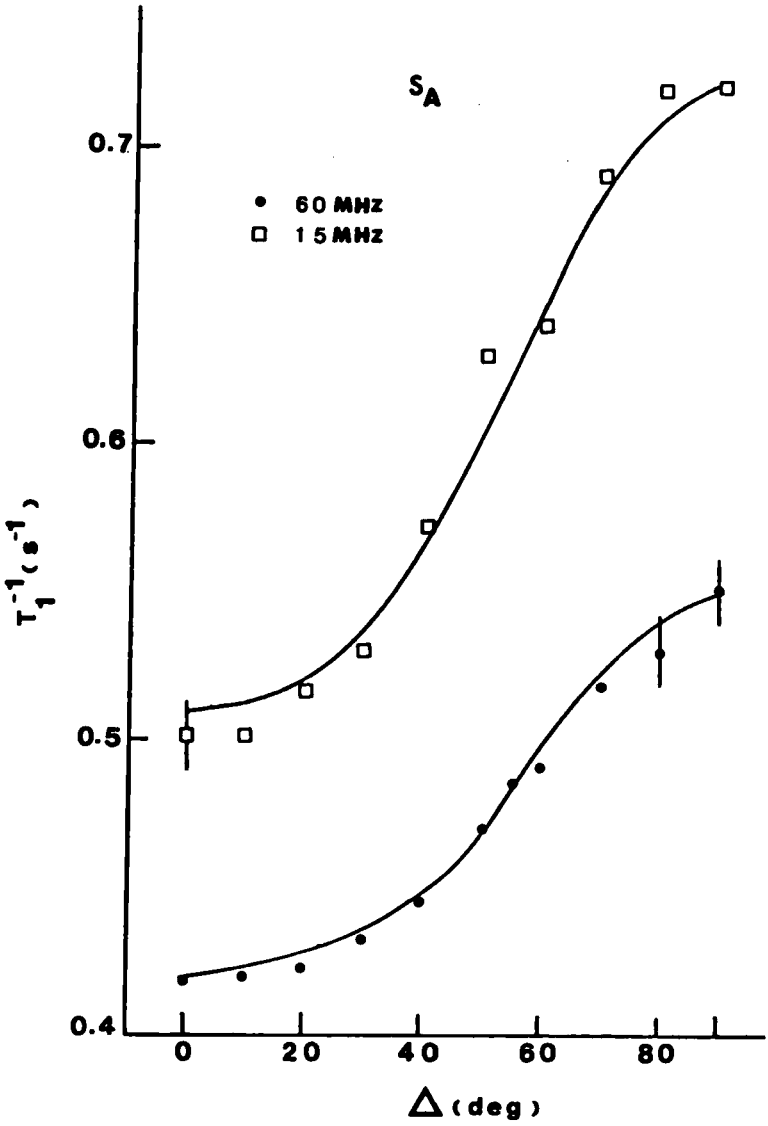


FIGURE 2 Plot of proton Zeeman spin-lattice relaxation rate versus the angle Δ in the $S_A$ phase at 189°C. Solid curves are theoretical fit.

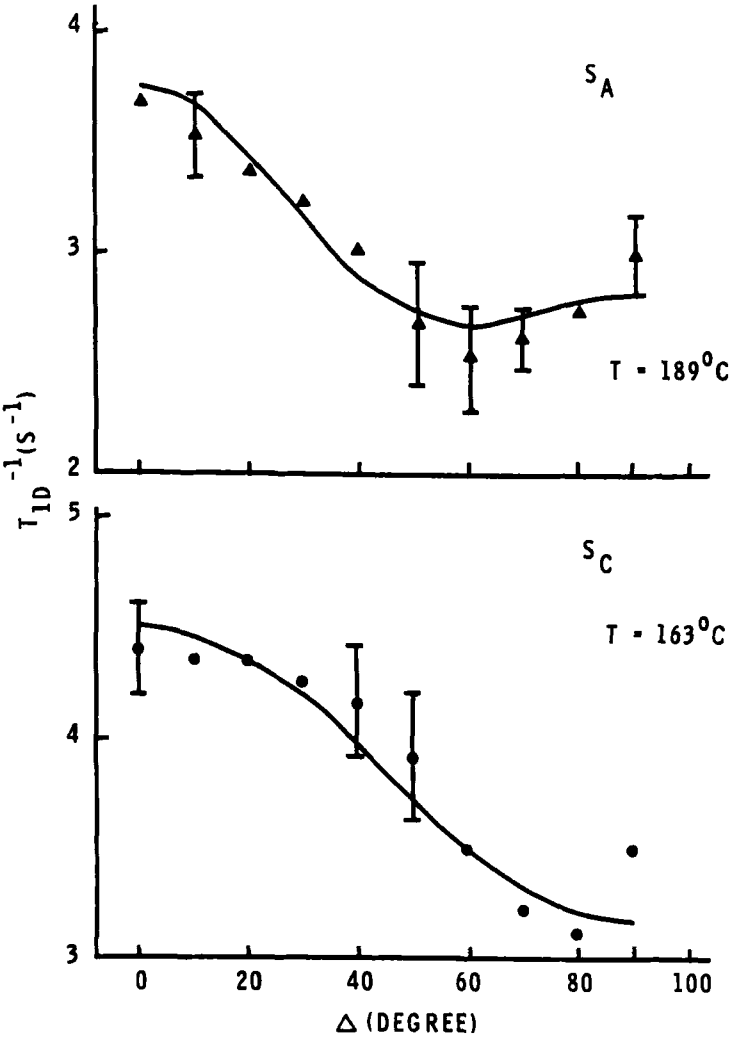


FIGURE 3 Plot of proton dipolar spin-lattice relaxation rate versus the angle Δ in the $S_A$ and $S_C$ phases at $\omega/2\pi$ = 90 MHz. Solid curves are theoretical fit.

4 present the $T_{1D}$ angular dependent data at 90 and 28 MHz, respectively, in the $S_A$ and $S_C$ phases of TBBA. Similar data was also obtained at 60 MHz in these smectic phases. One can conclude that the angular behavior of $T_{1D}$ is independent of the Larmor frequency as expected, but is in sharp contrast with the angular behavior of $T_1$ (Figure 2). In the $S_A$ phase (at 189°C), the $T_{1D}$ angular dependent data is fitted by a least-squares regression program

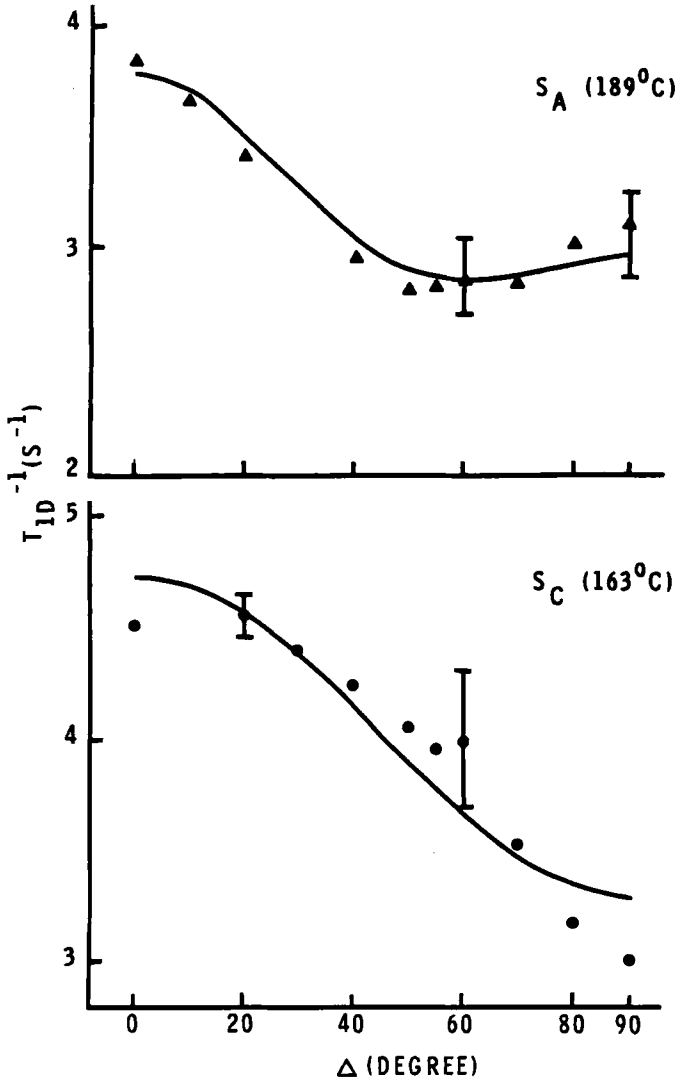


FIGURE 4 Same as Figure 3 at $\omega/2\pi = 28$ MHz.

to Eq. 6 as given by the solid curve with $a = 1.93\ s^{-1}$ and $b = 1.82\ s^{-1}$ at 90 MHz (Figure 3), and $a = 1.62\ s^{-1}$ and $b = 2.16\ s^{-1}$ at 28 MHz (Figure 4). In the $S_C$ phase (at 163°C), the $T_{1D}$ angular dependent data is fitted in the same manner to Eq. 7 as given by the solid curve with $a = 2.64\ s^{-1}$ and $b = 1.86\ s^{-1}$ at 90 MHz (Figure 3) and $a = 2.88\ s^{-1}$

and $b = 1.86\ s^{-1}$ at 28 MHz (Figure 4). As can be seen from these figures, the fits are quite satisfactory, thereby supporting the ratio $C_0/C_1$ being 1/18 and 1/9 in the smectic A and C phases of TBBA, respectively. Furthermore, ODF contribute significantly to the relaxation rate of dipolar spin system in the $S_A$ and $S_C$ phases, being maximum (about 60% of the dipolar spin-lattice relaxation rate) at $\Delta = 0$. In the $S_G$ phase of TBBA, the $T_{1D}^{-1}$ is independent of the angle $\Delta$ as shown in Figure 5 for several frequencies. This is consistent with the fact that molecular self-diffusion[4,7] becomes the dominant relaxation mechanism for the dipolar order in the low symmetry smectic phases such as $S_G$ and $S_B$. Moreover, the diffusive jumps are in the 'slow' motion regime in which Eq. 1 is not applicable. For the correlation

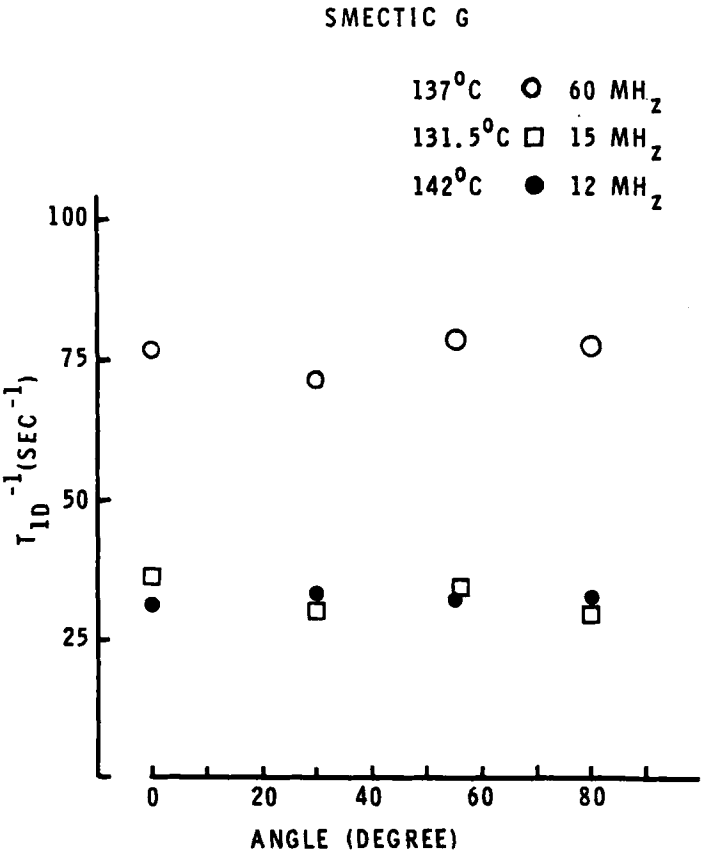


FIGURE 5 Plot of proton dipolar spin-lattice relaxation rate versus the angle $\Delta$ in the $S_G$ phase at $\omega/2\pi$ = 60, 15 and 12 MHz.

time $\tau_c$ between two successive molecular jumps much longer than the spin-spin relaxation time $T_2$, one can use

$$T_{1D}^{-1} = \frac{2(1-p)}{\tau_c} \tag{8}$$

as given by Slichter and Ailion[13] where $p$ is a geometrical factor. This enables one to estimate the self-diffusion constant in the $S_G$ phase[1a] ($D \leq 10^{-10}$ cm$^2$/s) of TBBA.

## SUMMARY

In both the $S_A$ and $S_C$ phases of TBBA, an angular dependence characteristic to ODF is observed for $T_{1D}^{-1}$. In both phases, ODF and diffusion each contribute approximately 50% to $T_{1D}^{-1}$. No angular dependence is observed for $T_{1D}^{-1}$ in the $S_G$ phase because the relaxation mechanism is mainly molecular self diffusion.

### Acknowledgments

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We also thank Messrs. E. Samulaitis and K. Krebs for their technical assistance.

### References

1. (a) R. Blinc, M. Luzar, M. Vilfan and M. Burgar, *J. Chem. Phys.*, **63**, 3445 (1975); (b) R. Blinc, M. Luzar, M. Mali, R. Osredkar, J. Seliger and M. Vilfan, *J. Phys. (Paris), Colloq.*, **37**, C3–73 (1976).
2. J. R. Owers-Bradley, I. E. Calder, J. B. Ketterson and W. P. Halperin, *Mol. Cryst. Liq. Cryst.*, **76**, 175 (1981).
3. R. Y. Dong, *J. Mag. Reson.*, **48**, 280 (1982).
4. G. J. Krüger, H. Spiesecke, R. Van Steenwinkel and F. Noack, *Mol. Cryst. Liq. Cryst.*, **40**, 103 (1977).
5. J. Doucet, in "The Molecular Physics of Liquid Crystals," edited by G. R. Luckhurst and G. W. Gray (Academic Press, London, 1979), chap. 14.
6. R. Y. Dong and J. Sandeman, *J. Chem. Phys.*, **78**, 4649 (1983).
7. G. J. Krüger, H. Spiesecke and R. Van Steenwinkel, *J. Phys. (Paris), Colloq.*, **37**, C2–123 (1976).
8. P. Pincus, *Solid State Commun.*, **7**, 415 (1969).
9. R. Y. Dong, M. Wiszniewska, E. Tomchuk and E. Bock, *Mol. Cryst. Liq. Cryst.*, **27**, 259 (1974).
10. R. Van Steenwinkel, *Z. Naturforsch*, **24a**, 1526 (1969).
11. J. J. Visintainer, R. Y. Dong, E. Bock and E. Tomchuk, Proc. 6th Int. Sym. Mag. Reson., Banff (1977), p. 215.
12. R. A. Wise, D. H. Smith and J. W. Doane, *Phys. Rev.*, **A7**, 1366 (1973).
13. C. P. Slichter and D. Ailion, *Phys. Rev.*, **135**, 1099 (1964).