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

A Study of the Dipolar Spin System in Selectively Deuterated Nematogens

Ronald Y. Dong [a] , B. Nakka [a] , E. Tomchuk [a] , J. J. Visintainer [b] & E. Bock [b]

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

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

To cite this article: Ronald Y. Dong , B. Nakka , E. Tomchuk , J. J. Visintainer & E. Bock (1977): A Study of the Dipolar Spin System in Selectively Deuterated Nematogens, Molecular Crystals and Liquid Crystals, 38:1, 53-59

To link to this article: http://dx.doi.org/10.1080/15421407708084374

Mol. Cryst. Liq. Cryst., 1977, Vol. 38, pp. 53–59

Printed in Holland

A Study of the Dipolar Spin System in Selectively Deuterated Nematogens†

RONALD Y. DONG, B. NAKKA 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 October 13, 1976*)

The proton spin dipolar relaxation times and dipolar echo responses were studied for the nematic phase of ring-deuterated *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA-d_8) as a function of temperature and frequency. Measurements of the proton dipolar echo responses were also made for methyl-deuterated *p*-azoxyanisole (PAA-d_6). The echo response was used to determine the inter-pair second moment M_2 (inter), while the total second moment M_2 was extracted from the echo shape. Both of these second moments were determined for the ring protons in PAA-d_6 and the end chain protons in MBBA-d_8 and are discussed in terms of the averaging caused by the internal motions of the molecules. The dipolar relaxation times measured for the side chain protons in MBBA-d_8 indicate a lower "effective" viscosity for this part of the molecule.

INTRODUCTION

Proton dipolar echo responses in thermotropic[1] and lyotropic[2] liquid crystals have recently been shown to be characteristic of spin-$\frac{1}{2}$ pairs, as observed in solids.[3] The quantity M_2 (inter), the interpair second moment of the absorption spectrum arising from dipolar interactions between the protons of two spin-$\frac{1}{2}$ *pairs*, is measured from the dipolar echo response.

---

† Presented at the Sixth International Liquid Crystal Conference, Kent, Ohio (1976).

Since M_2 (inter) is averaged by any internal motion of the vectors joining two spin-$\frac{1}{2}$ pairs, it is a useful parameter for probing the internal dynamics of mesogens. The total second moment M_2 for the nematic phase arises only from intramolecular dipolar interactions, since the intermolecular contributions are effectively averaged to zero by fast translational diffusion. Thus the intrapair contribution to the second moment, M_2 (intra), together with the interpair contribution, M_2 (inter), should sum to M_2. Intrapair spin–spin interactions can be differentiated from the interpair ones[3]; as an analogy consider the loosely coupled spin-$\frac{1}{2}$ pairs as equivalent to two dipolar coupled spin-1.

By using selectively deuterated nematogens, new insights into the segmental motions of a nematic molecule can be obtained. Our study of proton dipolar echo responses of the nematic phase of ring-deuterated *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA-d_8) and methyl-deuterated *p*-azoxyanisole (PAA-d_6) are reported in this paper.

A related study of the dipolar spin system involves the examination of the proton spin dipolar relaxation time T_{1D}. In a previous paper,[4] we had used proton T_{1D} measurements to show that orientational order fluctuations are a dominant relaxation mechanism for the dipolar system, and from its field dependence, the influence of the "effective" viscosity of MBBA and PAA can be compared. By suitable deuteration, this technique can be used to probe the relative viscosity of molecular fragments. In particular, end-chain flexibility is studied here by comparing the motions of the end-chain protons of MBBA-d_8 with the motions of the entire MBBA molecule. T_{1D} measurements as functions of temperature and frequency are reported and discussed.

EXPERIMENTAL

The MBBA-d_8 sample was obtained from Dr. J. W. Doane, Kent, Ohio, and the PAA-d_6 sample from Dr. C. G. Wade, Austin, Texas. All samples were degassed by the freeze-melt method and sealed in 7 mm o.d. tubes under vacuum. The clearing temperatures (T_c) of MBBA-d_8 and PAA-d_6 are respectively equal to ~34°C and ~136°C.

All measurements were performed on a Bruker B-KR 322s spectrometer. The T_{1D} measurements were made using the three pulse Jeener–Broekaert sequence.[5] The $90°\text{-}\tau\text{-}90°_{90°}$ pulse sequence was used to obtain a dipolar echo whose peak amplitude $E(\tau)$ was fitted to the following Gaussian expression

$$E(\tau) = E(0)\exp[\tfrac{1}{2}M_2\,(\text{inter})\,\tau^2] \qquad (1)$$

from which M_2 (inter) was determined. The Gaussian dependence on τ^2 arises solely from the refocussing of the interpair dipolar interactions. The linear fit of ln $E(\tau)$ vs. τ^2 was good to 75% of the decay for both nematogens. The dipolar echo signals at a fixed τ of 20 μsec were either recorded by a Bruker boxcar integrator or a Nicolet 1090AR Explorer Digital Oscilloscope. M_2 was then determined from the shape of half a dipolar echo by fitting it to the usual moment expansion

$$f(t) = f(0) \sum_{j=0}^{n} M_j \frac{(it)^{2j}}{(2j)!} \tag{2}$$

A least square fit APL program, with $n = 10$, was used.

The dipolar echo was used to determine M_2 because values of $f(t)$ for very short t can be observed whereas with free induction decays (FID), the dead time obliterates these important points so that the FID shape must be extrapolated to $t = 0$ with loss of accuracy. On the other hand the observed broadening of the dipolar echo as τ becomes larger introduces errors in M_2. However, at $\tau = 20$ μsec, $f(t)$ was found to be sufficiently close to the shape of the FID that the echo technique was preferable.

Both M_2 (inter) and M_2 were determined at 60 and 14 MHz for PAA-d_6 and MBBA-d_8, and found to be frequency independent within experimental error.

The temperatures of the sample were maintained either with a nitrogen or air flow, with a gradient across the sample of the order of 0.5°C. The reduced temperature, T_{red}, is defined as $T(°\text{K})/T_c(°\text{K}) \times 100$ where $T(°\text{K})$ is the temperature of the sample in degrees Kelvin.

RESULTS AND DISCUSSION

The M_2 and M_2 (inter) data for PAA-d_6 versus T_{red} are presented in Figure 1, with similar data for MBBA-d_8 in Figure 2. In previous studies of thermotropic liquid crystals,[1] M_2 (inter) includes interpair contributions from the methylene protons, the phenyl protons and possibly contributions from interactions between these two types of proton pairs. The interpretation of M_2 (inter) for long chain molecules assumed that the major contribution came from methylene proton pairs because of their proximity. To check this experimentally, we therefore chose selectively deuterated PAA and MBBA to study only the phenyl proton pairs in PAA-d_6, and the methylene proton pairs in MBBA-d_8 where they should be an important contributor.

M_2 (inter) is given by[1]

$$M_2\,(\text{inter}) = \frac{9}{16}\frac{\gamma^4\hbar^2 S^2}{N} \sum_{i>j}{}' \left\langle \frac{3\cos^2\phi_{ij} - 1}{r_{ij}^3} \right\rangle_{\text{av.}}^2 \alpha(\phi_{ij}) \tag{3}$$

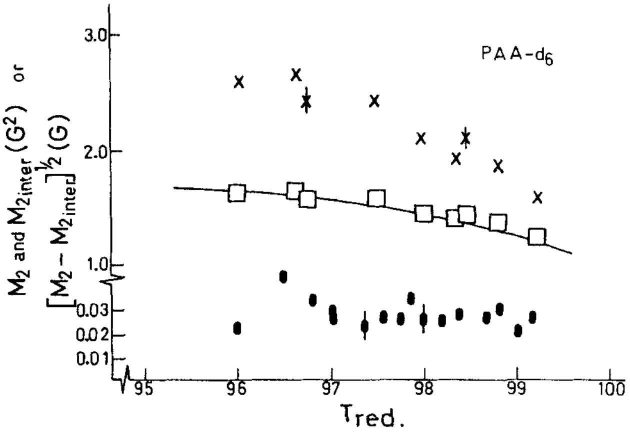

FIGURE 1 Plot of M_2 and M_2 (inter) versus T_{red} for PAA-d_6. ● and X denote M_2 (inter) and M_2 respectively. □ denotes $\{M_2 - M_2 \text{ (inter)}\}^{1/2}$ and the solid curve the normalized S (see text).

where S is the order parameter for the long molecular axis relative to the nematic director, $\mathbf{r}_{ij}$ is the distance vector between different proton *pairs*, ϕ_{ij} is the orientation of $\mathbf{r}_{ij}$ relative to the long molecular axis, the double sum is restricted to protons in different pairs within the same molecule, and N is the total number of protons in the molecule. $\alpha(\phi_{ij})$ is a numerical factor of the order of unity. The $\langle \quad \rangle_{\text{av.}}$ implies an average over the internal segmental motions of the molecule. As seen in Figure 1 and 2, M_2 (inter) for

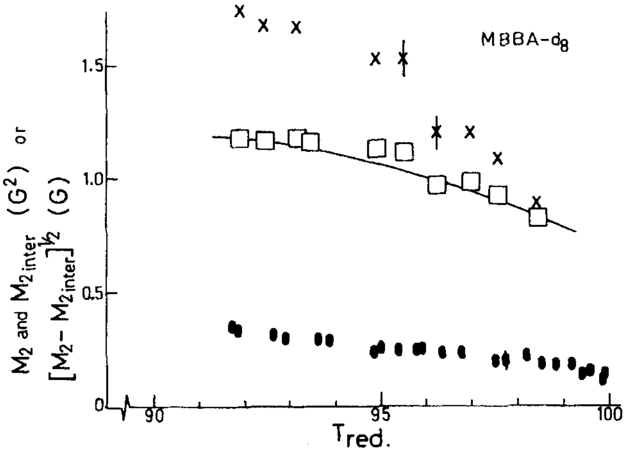

FIGURE 2 Plot of M_2 and M_2 (inter) versus T_{red} for MBBA-d_8. ● and X denote M_2 (inter) and M_2 respectively. □ denotes $\{M_2 - M_2 \text{ (inter)}\}^{1/2}$ and the solid curve the normalized S (see text).

the phenyl proton pairs is indeed very small compared with the M_2 (inter) of the end chain proton pairs. This is expected since $\mathbf{r}_{ij}$ is large for phenyl pairs. Furthermore M_2 (inter) is negligibly small compared with M_2 for PAA-d_6. It is of interest to note that M_2 is much larger for PAA-d_6 than for MBBA-d_8.

The M_2 (intra) expression is similar to Eq. (3) and is given by[1]

$$M_2\,(\text{intra}) = \frac{9}{16}\frac{\gamma^4\hbar^2 S^2}{n_\alpha}\sum_\alpha \frac{\langle 3\cos^2\phi_\alpha - 1\rangle^2_{\text{av.}}}{a_\alpha^6} \tag{4}$$

where the sum is carried out over the n_α proton pairs in the molecule and ϕ_α is the angle between the intrapair vector $\mathbf{a}_\alpha$ and the long molecular axis. It is noted that while both M_2 (inter) and M_2 (intra) are proportional to S^2, their different motional averages lead to different temperature dependences. To a first approximation, one may take M_2 (intra) as proportional to $\{M_2 - M_2\,(\text{inter})\}$. The $\{M_2 - M_2\,(\text{inter})\}^{1/2}$ are shown as a function of T_{red} in Figures 1 and 2, and compared with the respective temperature dependences of the order parameters[6] which are normalized at the lowest T_{red} and denoted by the solid curves in these figures. It is seen that the temperature dependence of $\{M_2 - M_2\,(\text{inter})\}^{1/2}$ is identical to that of S for both the phenyl protons (PAA-d_6) and the end-chain protons (MBBA-d_8). However, the temperature dependences of M_2 (inter) and $\{M_2 - M_2\,(\text{inter})\}$ are clearly different for MBBA-d_8 since M_2 (inter) is sensitive to segmental motional averaging along the long end-chain.

Proton T_{1D} were measured as functions of temperature for MBBA-d_8 at $\omega_L/2\pi = 5$, 9.2, 15, 30 and 60 MHz. The data are presented in Figure 3.

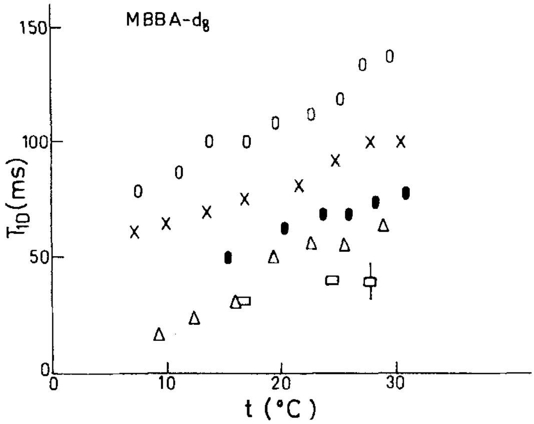

FIGURE 3 The proton dipolar spin relaxation time versus temperature in the nematic phase of MBBA-d_8. 0, X, ●, △ and ☐ denote measurements at 60, 30, 15, 9.2 and 5 MHz respectively.

MBBA[4] and MBBA-d_8 have similar T_{1D} temperature dependences but the MBBA-d_8 magnitudes are slightly higher than the MBBA T_{1D} values at the same temperature and frequency. By examining the field dependence of T_{1D} one can determine how the dipolar system of the end-chain is influenced by orientational order fluctuations.[7] This is the case for MBBA and PAA.[4] Theory based on the modulation of the dipolar interaction by orientational order fluctuations gives [4,8]

$$T_{1D}^{-1} \propto H^{-1} \tag{5}$$

under the condition

$$H^2 \frac{\Delta\chi}{\eta} \gg \omega_L \tag{6}$$

where $\Delta\chi$ is the anisotropic part of the diamagnetic susceptibility, H the applied magnetic field, and η the viscosity.

A plot of T_{1D}^{-1} for MBBA-d_8 versus the reciprocal of the external field strength is shown in Figure 4 for several temperatures. The MBBA data reported earlier[4] at 297°K is also included. For MBBA the deviation from linearity below ~5 kgauss was explained as due to the violation of the condition given by Eq. (6). For MBBA-d_8 Eq. (6) is satisfied down to a field of ~2 kgauss. This is an indication that the "effective" viscosity for the end chain protons is a factor of four or five times smaller than that of the entire MBBA molecule. Moreover, as seen in Figure 4, the deviations from linearity

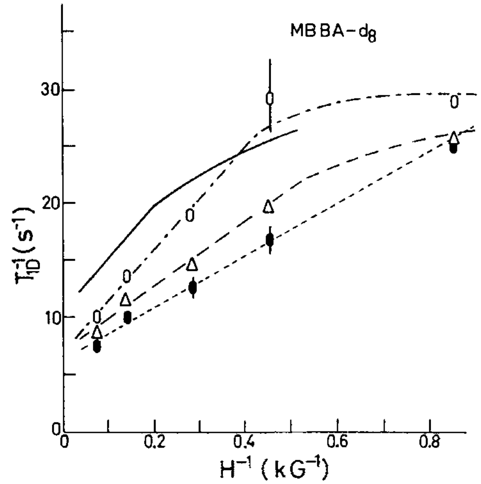

FIGURE 4 The reciprocal of the proton dipolar spin relaxation time versus the reciprocal of magnetic field strength in MBBA-d_8. 0, △ and ● denote measurements at 289°K, 297°K and 301°K respectively. The solid line is a data plot for MBBA at 297°K.

set in at higher fields with lower temperatures since viscosity increases with temperature decrease.

In conclusion, the dipolar spin system can be used to study not only long-range order fluctuations but also the internal motions of mesogens. M_2 (inter) is sensitive to internal segmental motions, such as alkyl chain flexibility, which may occur with the onset of various mesomorphic phase transitions. Furthermore M_2 (inter) and M_2 (intra) are affected differently by end-chain motion. Finally, end-chain flexibility can be investigated by studying the effect of the external magnetic field on dipolar spin relaxation times where orientational order fluctuations dominate.

Acknowledgment

We are grateful to Dr. J. W. Doane and Dr. C. G. Wade for the deuterated samples. The financial assistance of the National Research Council of Canada, the University of Winnipeg, and the Faculty of Graduate Studies of the University of Manitoba is gratefully acknowledged. We also thank Mr. E. Samulaitis and Mr. K. Krebs for their technical assistance.

References

1. N. Boden, Y. K. Levine, D. Lightowlers and R. T. Squires, *Chem. Phys. Lett.*, **31**, 511 (1975); **34**, 63 (1975).
2. N. Boden, P. Jackson, Y. K. Levine and A. J. I. Ward, *Chem. Phys. Lett.*, **37**, 100 (1976).
3. N. Boden, Y. K. Levine, D. Lightowlers and R. T. Squires, *Mol. Phys.*, **29**, 1877 (1975).
4. R. Y. Dong, M. Wiszniewska, E. Tomchuk and E. Bock, *Mol. Cryst. Liq. Cryst.*, **27**, 259 (1974).
5. J. Jeener and P. Broekaert, *Phys. Rev.*, **157**, 232 (1967).
6. a) G. H. Brown, J. W. Doane and V. D. Neff, *Rev. Solid State Sci.*, **1**, 303 (1970).
   b) R. Chang, *Mol. Cryst. Liq. Cryst.*, **30**, 155 (1975).
7. P. G. de Gennes, "The Physics of Liquid Crystals," Oxford University Press, (1974).
8. R. Blinc, D. L. Hogenboom, D. E. O'Reilly and E. M. Peterson, *Phys. Rev. Lett.*, **23**, 969 (1969).