



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

### Diamagnetic Anisotropy Measurements of Nematic Liquid Crystals

Shin-Tson Wu<sup>a</sup>, Willis H. Smith<sup>a</sup> & Anna M. Lackner<sup>a</sup>

<sup>a</sup> Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, CA, 90265

Version of record first published: 20 Apr 2011.

To cite this article: Shin-Tson Wu, Willis H. Smith & Anna M. Lackner (1986): Diamagnetic Anisotropy Measurements of Nematic Liquid Crystals, *Molecular Crystals and Liquid Crystals*, 140:2-4, 83-93

To link to this article: <http://dx.doi.org/10.1080/00268948608080144>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Diamagnetic Anisotropy Measurements of Nematic Liquid Crystals

SHIN-TSON WU, WILLIS H. SMITH and ANNA M. LACKNER

*Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, CA 90265*

*(Received March 24, 1986; in final form May 16, 1986)*

Electro-optic effect of liquid crystals in the presence of a magnetic field was investigated. Two independent techniques: magnetic field dependent threshold voltage and magnetic field-assisted relaxation time, were used to evaluate the diamagnetic anisotropy for three nematic liquid crystals: BDH-E7, RO-TN-103 and ZLI-1132. Correlation between the diamagnetic anisotropy and the molecular structures was obtained. This information is particularly important for synthesizing liquid crystal components with desired diamagnetic anisotropy.

*Keywords: diamagnetic anisotropy, nematic liquid crystals, molecular structures, magneto-electro-optics*

## I. INTRODUCTION

Free relaxation of the electro-optic modulation effect using nematic liquid crystals (LCs) is determined by the intrinsic material properties (e.g., viscosity, elastic constant), LC layer thickness, and surface alignment, and is a relatively slow process. Several techniques<sup>1–8</sup> (we refer to them as the generalized dual field effect) have been developed for accelerating the LC decay time with the assistance of an additional field during the relaxation process. This second field (the first field refers to the excitation field) used in the dual field effect may be a pulsed or CW magnetic, electric, or optical field. The orientation of the second field depends on the sign of the dielectric anisotropy ( $\epsilon_a$ ), diamagnetic anisotropy ( $\chi_a$ ), and LC alignment, and may be parallel or perpendicular to the first field. Dual frequency effect,<sup>1,2</sup> bias voltage technique,<sup>3</sup> and magnetic field effect utilizing negative  $\epsilon_a$  liquid crystals<sup>4</sup> are the examples of the former (i.e., parallel fields); the

triode optical gate approach,<sup>5</sup> magnetic field,<sup>6,7,8</sup> and optical field effects<sup>8</sup> employing positive  $\epsilon_a$  liquid crystals are the examples of the latter (crossed fields). It has also been shown<sup>8</sup> that the decay time is remarkably independent of LC thickness in the dual field effect when the second field is sufficiently large (relative to the Freedericksz transition threshold).<sup>9</sup> This independence of the decay time from thickness is particularly attractive for the electro-optic modulation of infrared radiation using liquid crystals,<sup>10–13</sup> where normally a thick cell is required to achieve a high modulation efficiency and, hence, the response times are slow. For state of the art results in the dual field effect, a few tens of microsecond relaxation time has been achieved even though the nonuniform second field has been generated.<sup>5</sup>

In studies of the electro-optic behavior of liquid crystals in the presence of a magnetic field, two independent methods: magnetic field dependent threshold voltage and magnetic field-assisted relaxation time measurements, can be employed to evaluate the diamagnetic anisotropy ( $\chi_a$ ) of LCs, provided that the elastic constant is known. Unlike the phase transition<sup>14</sup> and nuclear magnetic resonance methods<sup>15</sup> for measuring the diamagnetic anisotropy of LCs, the magneto-electro-optic methods described in this paper are rather simple and convenient. Results for two nematic LCs, RO-TN-103 and ZLI-1132, are presented and compared to those for the BDH-E7 liquid crystal. The  $\chi_a$  of the LC mixture ZLI-1132 was about 3 times lower than that of the other two mixtures. Correlation between the diamagnetic anisotropy and the molecular structures of LCs was found. A brief discussion of the principles of diamagnetic anisotropy measurements is given in Section II. Detailed experiments on the magnetic field dependent threshold voltage and magnetic field-assisted relaxation time are described in Section III. Finally, the correlation between the value of diamagnetic anisotropy and LC molecular structures is discussed.

## II. PRINCIPLE OF MEASUREMENT

When a parallel-aligned LC cell is under the influence of two crossed fields, electric field in the  $Z$  axis and magnetic field in the  $X$  axis (as shown in Figure 1), the equation of motion of the liquid crystal molecules in the small angle approximation is given by the following equation:<sup>8</sup>

$$K_{11} \frac{\partial^2 \phi}{\partial Z^2} + \left( \frac{\epsilon_a E^2}{4\pi} - \chi_a H^2 \right) \phi = \gamma_1 \frac{\partial \phi}{\partial t} \quad (1)$$

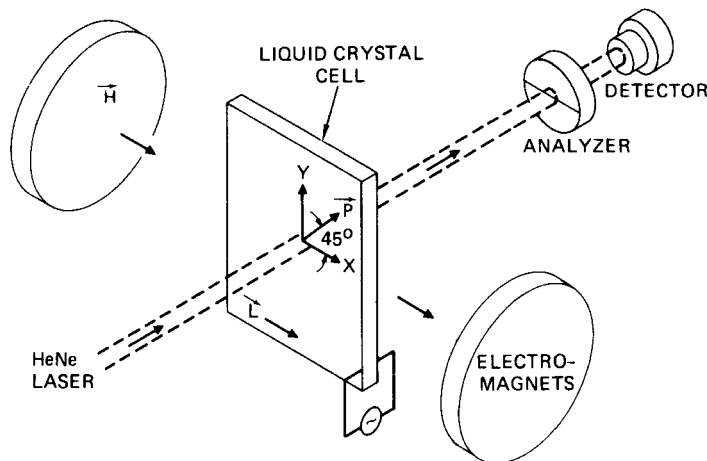


FIGURE 1 Schematic diagram of experimental apparatus for measuring the diamagnetic anisotropy of liquid crystals.

where  $\phi$  is the angle between the liquid crystal director and the applied E field,  $K_{11}$  is the splay elastic constant,  $\epsilon_a (= \epsilon_{\parallel} - \epsilon_{\perp})$  is the dielectric anisotropy,  $\chi_a (= \chi_{\parallel} - \chi_{\perp})$  is the diamagnetic anisotropy per volume, and  $\gamma_1$  is the rotational viscosity. The dual field effect is clearly seen from the second term of Eq. (1), where two fields are working against each other. From Eq. (1), assuming  $\phi$  is proportional to  $\sin \pi Z/d$ , the rise time and decay time are given by:

$$\tau_{\text{rise}} = \gamma_1 / \left( \frac{\epsilon_a E^2}{4\pi} - \chi_a H^2 - K_{11} \left( \frac{\pi}{d} \right)^2 \right) \quad (2)$$

$$\tau_{\text{decay}} = \gamma_1 / \left( K_{11} \left( \frac{\pi}{d} \right)^2 + \chi_a H^2 \right) \quad (3)$$

where  $d$  is the liquid crystal layer thickness. The new threshold voltage is obtained when the magnetic field is present:

$$V_{\text{th}}^2(H) = V_{\text{th}}^2(O) + \frac{4\pi\chi_a d^2}{\epsilon_a} H^2 \quad (4a)$$

where

$$V_{\text{th}}(O) = \pi \left( \frac{4\pi K_{11}}{\epsilon_a} \right)^{1/2} \quad (4b)$$

is the threshold voltage for Fredericksz transition in the absence of the magnetic field. The increased electric field is needed in order to overcome the additional aligning force exerted on the liquid crystals by the magnetic field. From the slope ( $S$ ) of the magnetic field dependent threshold voltage measurements (Eq. 4(a), where  $S = 4\pi\chi_a d^2/\epsilon_a$ ) and the measured  $V_{th}(O)$ , then  $H_c (= (\pi/d)(K_{11}/\chi_a)^{1/2})$  and  $\chi_a$  can be evaluated:

$$H_c = V_{th}(O)/S^{1/2} \quad (5)$$

$$\chi_a = \pi^2 K_{11} S / [d^2 V_{th}^2(O)] \quad (6)$$

where  $H_c$  represents the threshold magnetic field for observing the splay deformation of the LC directors. In this case, the magnetic field is normal to the parallel-aligned LC cell. This configuration requires, in addition, that the magnetic field be parallel to the optical probe beam; this cannot be achieved in our setup. Nevertheless, in our configuration (Figure 1),  $H_c$  can still be evaluated through Equation (5). It is worth while mentioning here that if we align the LC directors in the direction of the  $Y$  axis (perpendicular to magnetic field), then the resulting deformation has two thresholds depending on the magnetic and electric fields.<sup>6</sup> In the interest of studying dual field effect in improving the LC decay time and measuring the diamagnetic anisotropy, our discussion is limited to the geometry shown in Figure 1. Note that  $\chi_a$  can also be determined through the relationship  $\chi_a = \epsilon_a S / (4\pi d^2)$ . Caution must be taken in that  $\epsilon_a$  may depend on the frequency of the applied electric field. When a short square pulse is used to excite the liquid crystal (in this case, fast rise time can be achieved), it contains different Fourier components of frequencies and makes  $\epsilon_a$  difficult to evaluate. Thus, evaluation of  $\chi_a$  by utilizing Eq. (6) is recommended.

Another method for determining  $\chi_a$  is through the measurement of magnetic field-assisted LC relaxation time. As seen in Eq. (3), the relaxation time is governed by two factors: the intrinsic elastic torque (the first term in the denominator), and the external field induced torque (the second term). In the presence of a magnetic field, the decay time is improved by the following factor:

$$\frac{\tau_{decay}(H)}{\tau_{decay}(O)} = \frac{1}{1 + \left(\frac{H}{H_c}\right)^2} \quad (7)$$

where  $\tau_{\text{decay}}(O) = \gamma_1 d^2 / K_{11} \pi^2$  is the free relaxation time of the homogeneous aligned liquid crystals. Through the magnetic field-assisted relaxation time measurements  $H_c$  is determined, and therefore  $\chi_a$  can be obtained:

$$\chi_a = \left( \frac{\pi}{d} \right)^2 \frac{K_{11}}{H_c^2} \quad (8)$$

### III. EXPERIMENTAL

In our experiments, two commercially available nematic LCs, RO-TN-103 and ZLI-1132, were investigated. The LC cell is composed of glass substrates which are coated with 800 Å layers of transparent conductive metal film (indium-tin-oxide) and are separated by a mylar spacer. Surface parallel LC alignment is achieved by evaporating SiO<sub>2</sub> layers onto the substrates at medium and shallow angles.<sup>16</sup> The pretilt angle of the LC cell was characterized to be  $\sim 1^\circ$ . For the diamagnetic anisotropy measurements, the LC cell is situated in an electro-magnet such that the LC director is parallel to the magnetic field, as depicted in Figure 1. To measure the threshold voltage and response times under the influence of a magnetic field, a 1-KHz AC voltage burst was applied to the cell. Rise and decay time measurements of liquid crystal cells, as shown in Figure 1, were accomplished using a weak, polarized HeNe laser to probe the cell under study. The laser polarization was arranged to be at  $45^\circ$  to the liquid crystal director. Only one component of the outgoing beam was analyzed. Before the voltage was applied to the cell, each LC cell thickness was tuned by compressing the mylar spacer so that either the maximum or minimum transmission of the HeNe laser beam was detected; i.e., the total phase retardation of the LC cell is equal to  $N\pi$ ,  $N$  is an integer. Knowing the birefringence value of the liquid crystal at room temperature, the cell thickness can be determined by measuring the total phase retardation of the given LC cell.<sup>17</sup> Since all the LC cells used are thicker than 4  $\mu\text{m}$ , the surface effect on birefringence as reported recently<sup>18</sup> can be neglected and accurate LC thickness can be determined. In the decay time measurements, only a small voltage,  $(V - V_{\text{th}}(H))/V_{\text{th}}(H) \ll 1$ , was applied to the LC cell so that the small angle approximation as discussed in Equation (1) is valid.

**A. Magnetic field dependent threshold voltage**

Results of threshold voltage ( $V_{th}$ ) measurements at different magnetic field intensities are shown in Figure 2 for two liquid crystals: ZLI-1132 (Figure 2a) and RO-TN-103 (Figure 2b). The linear relationship between  $V_{th}^2$  and  $H^2$ , as predicted by Eq. (4a), is verified. Figures 2(c) and 2(d) show the magnetic field dependent excitation voltage required to achieve a  $\pi$  phase change for the LCs RO-TN-103 and ZLI-1132, respectively. From Figure 2(a) or 2(b) and Equations (5) and (6), two important physical parameters of liquid crystals, diamagnetic anisotropy ( $\chi_a$ ) and threshold magnetic field ( $H_c$ ), can be obtained. Results of  $\chi_a$  and  $H_c$  for liquid crystals ZLI-1132 and RO-TN-103 are listed and compared with E-7 (measured by the same technique)<sup>8</sup> in Table I. The elastic constants  $K_{11}$  used for the calculation are taken from Ref. 19. Please note that the threshold magnetic fields obtained from the above method can also be obtained independently from the magnetic field-assisted relaxation time measurements as described in

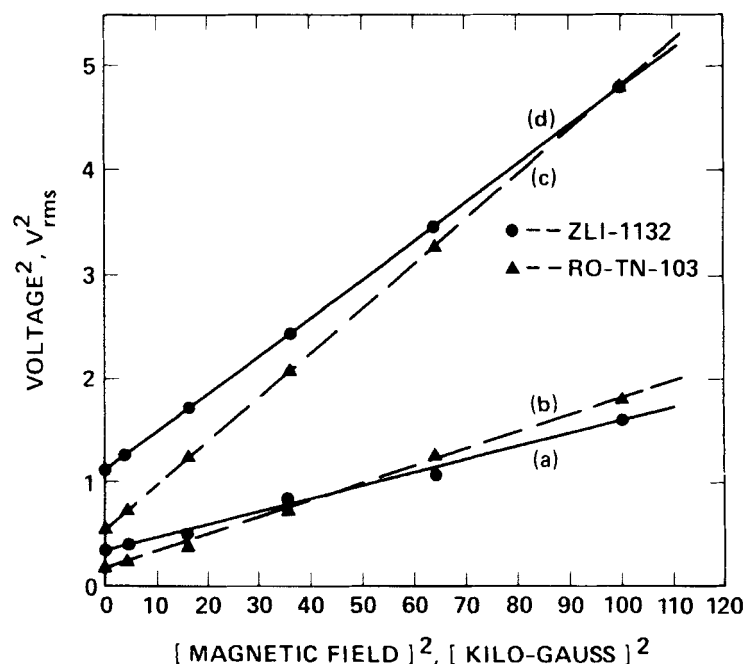


FIGURE 2 Experimental results for the magnetic field dependent threshold voltage (curves (a) and (b)) and voltage required to achieve a  $\pi$  phase change (curves (c) and (d)). Data points on solid lines and dashed lines correspond to the ZLI-1132 and RO-TN-103 LC cells, respectively.

TABLE I  
Measured diamagnetic anisotropy ( $\chi_a$ ) of three nematic LCs

Liquid Crystal	$d$ ( $\mu\text{m}$ )	$K_{11}$ (dyne)	$H_c$ (KG)	$\chi_a$ ( $\text{erg G}^{-2} \text{cm}^{-3}$ )
BDH-E7 <sup>a</sup>	22.4	$10.7 \times 10^{-7}$	4.40	$1.09 \times 10^{-7}$
RO-TN-103 <sup>b</sup>	25.8	$11.4 \times 10^{-7}$	3.40	$1.46 \times 10^{-7}$
ZLI-1132 <sup>c</sup>	28.1	$8.7 \times 10^{-7}$	4.96	$4.42 \times 10^{-8}$

<sup>a</sup>BDH Chemicals, England.

<sup>b</sup>Hoffman La-Roche Chemicals, Switzerland.

<sup>c</sup>E. Merck, Germany.

Eq. (7). As will be discussed later, good agreement in the determination of  $H_c$  was obtained between these two techniques.

#### B. Magnetic field-assisted LC relaxation

As seen in Eq. (3), the relaxation time of liquid crystal is improved by the presence of a magnetic field. The improvement factor,  $[1 + (H/H_c)^2]^{-1}$ , is related to the threshold magnetic field of the given cell. The lower the  $H_c$ , the larger the improvement factor at a given magnetic field strength. Therefore, by measuring the magnetic field dependent relaxation time of a LC cell,  $H_c$  can be determined. Relaxation times (at  $1/e$  intensity of the transmitted HeNe laser beam intensity) of two LC cells, RO-TN-103 (25.8  $\mu\text{m}$  thick) and ZLI-1132 (28.1  $\mu\text{m}$  thick), were measured at different magnetic field intensities and normalized to the free relaxation time,  $\tau_{\text{decay}}(0)$  for each cell. The experimental results (indicated by dots) of the normalized decay times are shown in Figure 3 for these two liquid crystals. The solid lines represent the theoretical values (Eq. (7)), using  $H_c$  as the variable parameter. It is readily seen that  $H_c$  (where  $\tau(H)/\tau(0) = 1/2$  or  $H = H_c$ ) is 3.6 KG and 5.0 KG for the 25.8  $\mu\text{m}$  RO-TN-103 and 28.1  $\mu\text{m}$  ZLI-1132 LC cells, respectively. Very good agreement is found between these values and those listed in Table I (measured by the magnetic field dependent threshold voltage method,  $H_c = 3.40$  and 4.96 KG for RO-TN-103 and ZLI-1132, respectively).

#### IV. DISCUSSION

As described in Eq. (7), liquid crystal material with larger diamagnetic anisotropy benefits from lower threshold, and results in a larger improvement in decay time. It is, therefore, important to establish a correlation between the molecular structures and the dia-



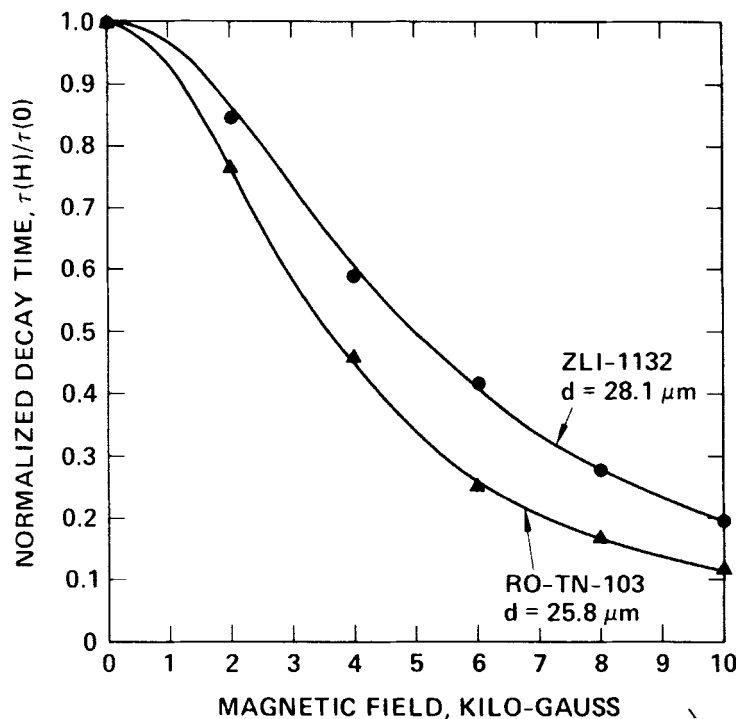


FIGURE 3 Theoretical and experimental results of the normalized decay times of liquid crystal cells. Parameters used for calculation are:  $H_c = 3.6$  KG,  $\tau_{\text{decay}}(0) = 1.4$  s for the  $25.8 \mu\text{m}$  RO-TN-103 cell, and  $H_c = 5.0$  KG,  $\tau_{\text{decay}}(0) = 720$  ms for the  $28.1 \mu\text{m}$  ZLI-1132 cell.

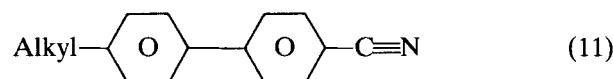
magnetic anisotropy. In order to understand the difference in  $\chi_a$  values for three positive liquid crystals as listed in Table I, the contribution of individual compounds of LC mixtures has to be evaluated. A general discussion of magnetic susceptibility can be found in Ref. 20.

Quantum mechanically, the diamagnetism of atoms originates from the change of electron precession around the nuclei by the applied magnetic field. Usually, the diamagnetic anisotropies of molecules are rather small because the atomic susceptibility is isotropic. However, for many liquid crystal mixtures, the  $\chi_a$  is positive and the value is about three orders of magnitude higher than that of the hydrogen atom, due to the presence of conjugated  $\pi$ -electrons in the

phenyl rings  $\left( \text{—} \text{C}_6\text{H}_4 \text{—} \right)$ .<sup>21</sup> In addition, the  $\chi_a$  of a compound

which contains phenyl rings is linearly proportional to the number of phenyl rings. For example, the  $\chi_a$  value is two times higher for the

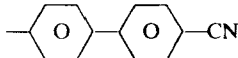
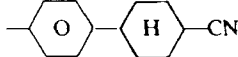
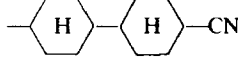
biphenyl ring than for the single phenyl ring. Besides the phenyl rings, the triple bond (e.g.  $\text{C}\equiv\text{N}$  bond) and alkyl chains<sup>22-24</sup> are also found to have some contribution (negative  $\chi_a$ ) to the diamagnetic anisotropy of liquid crystals. This fact can be understood from the following examples:<sup>7</sup> When a phenyl ring of the compound



is replaced by a cyclohexane ring  $\left(\text{C}_6\text{H}_{12}\right)$ , the value of  $\chi_a$  drops but is still positive. When both rings are saturated  $\left(\text{C}_6\text{H}_{12}-\text{C}_6\text{H}_{12}\right)$ ,  $\chi_a$  becomes negative and the numerical value

is small. This is explained by the negative anisotropy of the  $\text{C}\equiv\text{N}$  bond; the  $\chi_a$  values for alkyl chains are small and can be neglected. Therefore, the diamagnetic anisotropy of positive liquid crystals can be approximately determined by the total number of phenyl rings and  $\text{C}\equiv\text{N}$  bonds. From the measured  $\chi_a$  values of BDH E-7 (cyano-biphenyl mixtures) and ZLI-1132 (cyano-phenyl-cyclohexanes mixtures) (the difference between E-7 and RO-TN-103 is too small due to similar structures), and from the number of phenyl rings and CN bonds in each LC mixture,<sup>25</sup> the individual  $\chi_a$  value for these two units can be determined. Our calculated values of the volume diamagnetic anisotropy are  $+7.0 \times 10^{-8}$  and  $-3.7 \times 10^{-8}$  (CGS unit) for the phenyl ring and the CN bond, respectively. Based on these results, the value of  $\chi_a$  for the molecules described in Formula (11), the cyano biphenyl LC mixtures, is calculated to be  $1.03 \times 10^{-7}$  (i.e.,  $2 \times 7.0 \times 10^{-8} + 1 \times (-3.7 \times 10^{-8})$ ). When a phenyl ring in Formula (11) is replaced by a cyclohexane ring (this ring has little contribution to the diamagnetic anisotropy due to the lack of  $\pi$ -electrons),  $\chi_a$  drops to  $3.3 \times 10^{-8}$  ( $7.0 \times 10^{-8} - 3.7 \times 10^{-8}$ ). Finally, when all the phenyl rings are replaced by the cyclohexane rings, the contribution to  $\chi_a$  is primarily from the unsaturated  $\text{C}\equiv\text{N}$  bond so that the  $\chi_a$  value becomes negative,  $-3.7 \times 10^{-8}$ . Compared to the reported data<sup>20</sup> on the mass diamagnetic anisotropy  $\chi_a^m$  (which is equal to  $\chi_a/\rho$ , where  $\rho$  is the density of liquid crystal and its value is close to unity) of the above compounds in the nematic phase (see Table II) the agreement is fairly good. Furthermore, the extrapolated  $\chi_a$  ( $\sim 1.4 \times 10^{-7}$  CGS unit) for liquid crystal MBBA

TABLE II  
Comparison of the measured  $\chi_a$  values for three compounds commonly used in LC mixtures

Compounds	$\chi_a$ (this work)	$\chi_a^m$ (Ref. 20)
	$1.0 \times 10^{-7}$	$1.3 \times 10^{-7}$
	$3.3 \times 10^{-8}$	$4.7 \times 10^{-8}$
	$-3.7 \times 10^{-8}$	$-5.7 \times 10^{-8}$

$\left( \text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{C}_4\text{H}_9 \right)$  is in very good agreement with the measured value of  $1.36 \times 10^{-7}$  (at room temperature) from the NMR experiment.<sup>15</sup> Please note that in this extrapolation, only the contributions of two phenyl rings are taken into account, and the contribution of the  $\text{CH}=\text{N}$  bond is neglected.

## V. CONCLUSION

Two magneto-electro-optic methods, magnetic field dependent threshold voltage and magnetic field-assisted relaxation time, were used to characterize the volume diamagnetic anisotropy of nematic liquid crystals. Good agreement is found between these two techniques. The value of  $\chi_a$  is determined primarily by the contents of the phenyl ring and triple bond in a given LC mixture. This information is particularly useful for formulating LC mixtures with desired diamagnetic anisotropy.

## References

1. H. K. Bucher, R. T. Klingbiel and J. P. VanMeter, *Appl. Phys. Lett.*, **25**, 186 (1974).
2. M. Schadt, *Mol. Cryst. Liq. Cryst.*, **89**, 77 (1982).
3. P. D. Berezin, L. M. Blinov, I. N. Kompanets and V. V. Nikitin, *Sov. J. Quant. Electron.*, **3**, 78 (1973).
4. M. Hareng, G. Assouline and E. Leiba, *Appl. Opt.*, **11**, 2920 (1972).
5. D. J. Channin and D. E. Carlson, *Appl. Phys. Lett.*, **28**, 300 (1976).
6. H. J. Deuling, E. Guyon and P. Pieranski, *Solid State Commun.*, **15**, 277 (1974).

7. L. Pohl, R. Eidenschink, J. Krause and G. Weber, *Phys. Lett.*, **65A**, 169 (1978).
8. S. T. Wu, *J. Appl. Phys.*, **58**, 1419 (1985).
9. P. G. de Gennes, "*The Physics of Liquid Crystals*," (Clarendon, Oxford, 1974).
10. S. T. Wu, U. Efron and L. D. Hess, *Appl. Phys. Lett.*, **44**, 1033 (1984).
11. S. T. Wu, U. Efron and L. D. Hess, *Appl. Phys. Lett.*, **44**, 842 (1984).
12. S. T. Wu, *Phys. Rev.*, **A 33**, 1270 (1986).
13. S. T. Wu, U. Efron, J. Grinberg, L. D. Hess and M. S. Welkowsky, *Proc. SPIE*, **572**, 94 (1985).
14. F. Hardouin, M. F. Achard, G. Sigaud and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **39**, 241 (1977).
15. P. I. Rose, *Mol. Cryst. Liq. Cryst.*, **26**, 75 (1974).
16. D. Meyerhofer, *Appl. Phys. Lett.*, **29**, 691 (1976).
17. S. T. Wu, U. Efron and L. D. Hess, *Appl. Optics*, **23**, 3911 (1984).
18. S. T. Wu and U. Efron, *Appl. Phys. Lett.*, **48**, 624 (1986).
19. M. Schadt and F. Muller, *IEEE Trans. Electron Devices*, **ED-25**, 1125 (1978).
20. W. H. DeJeu, "*Physical Properties of Liquid Crystalline Materials*," Chapter 3, Gordon and Breach Science Publishers, New York, 1980.
21. W. Haberdizl, "*Theory and Applications of Molecular Diamagnetism*," Section 3.5 E, L. N. Mulay and E. A. Boudreaux, Eds., Wiley, New York, 1976.
22. Hp. Schad, G. Baur and G. Meier, *J. Chem. Phys.*, **70**, 2770 (1979).
23. B. J. Forrest and L. W. Reeves, *Chem. Rev.*, **81**, 1 (1981).
24. T. Haven, D. Armitage and A. Saupe, *J. Chem. Phys.*, **75**, 352 (1981).
25. J. Cognard, *Mol. Cryst. Liq. Cryst.*, Supplement 1, pp. 1–78 (1982).