Correlation of magnetic anisotropy with dielectric anisotropy in fluorinated phenyl bicyclohexane liquid crystal

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Temperature dependence of magnetic anisotropy of homologous nematic fluorinated phenyl bicyclohexane liquid crystals is measured by a magneto-electric method. The result shows that the diamagnetic property is slightly influenced by the positions and the numbers of fluorine atoms substituted at the phenyl ring. By investigating the correlation of the dielectric anisotropy with the magnetic anisotropy, a novel explanation is proposed for the behaviour of the molecular dipole–dipole dimerization in the polar liquid crystal compounds.

Keywords: fluorine, liquid crystal, magnetic, dielectric
PACC: 6130G, 7000

1. Introduction

In recent years, full colour and flat screen liquid crystal displays (LCDs) have gained growing interest and are now almost indispensable in everyday life. Because of the fluorine large electronegativity, the presence of fluorine in a liquid crystal (LC) molecule exerts a strong electron withdrawing effect and hence causes a large influence on permittivity.[1,2] Furthermore, due to low rotational viscosity, wide nematic phase range and long term stability, the fluorinated LC compounds are widely used as materials for the active LC matrix display.[3] Therefore, novel fluorinated LC materials have been synthesized and studied continually by many groups.[4−7]

A series of phenyl bicyclohexane (PBC) fluorinated LCs was invented by one of the authors in the early 1980s.[8] Our research group has studied the physical properties of the compounds with one, two, and three fluorine atoms substituted at the phenyl ring. Particularly, the temperature dependences of the physical parameters, such as the threshold voltage, dielectric permittivity, splay elastic constant, birefringence, and order parameters have been investigated in detail.[9−12] From our studies, a systematic relationship between fluorine atom positions on the benzene ring and some physical properties has been clarified. It is shown that the positions and the numbers of the fluorine substituent strongly influence dielectric permittivity and threshold voltage, but hardly influence other physical characteristics, such as elastic constant and refractive index.

The susceptibility anisotropy of LC is also an important physical property. However, few researches have aimed to measure the magnetic properties of the PBC fluorinated LCs till recent literature to our knowledge. In order to study thoroughly the fluorine substituent effect and physical property of the materials, the determination of the dielectric permittivity and magnetic properties is practically as well as theoretically very interesting. Therefore, the authors measure the temperature dependence of the magnetic anisotropy, in addition, study the correlation of the magnetic anisotropy with dielectric anisotropy. The target molecular configuration is shown in Fig. 1, and the NI phase transition temperature is listed in Table 1.

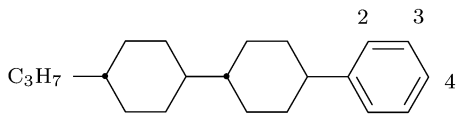


Fig. 1. Studied molecular structure of 3PBC fluorinated nematic LC compounds. At positions 2, 3 and 4 of the phenyl ring, hydrogen atoms are substituted by one or two fluorine atoms, separately.

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Table 1. Phase behaviour and abbreviation of liquid crystal compounds corresponding to the molecular structure shown in Fig. 1.

compounds	2	3	4	$T_{\mathrm{CrN}}/^{\circ}\mathrm{C}$	$T_{\mathrm{NI}}/^{\circ}\mathrm{C}$
$3\mathrm{PBC}^{2,4}\mathrm{F}_2$	F	H	F	47.0	130.0
$3\mathrm{PBC}^{3,4}\mathrm{F}_2$	H	F	F	40.2	121.0
$3\mathrm{PBC}^{3}\mathrm{F}$	H	F	H	51.4	90.2
$3\mathrm{PBC}^{4}\mathrm{F}$	H	H	F	88.6	153.1

2. Experimental measurement

In the previous studies,[9−11] we have investigated the dielectric constants and the splay elastic constants for these compounds, experimentally. Based on the known of the above data, a method, where the magnetic filed is added perpendicularly to the LC layer, is employed to determine magnetic anisotropy in this study. The surface of the glass substrate of LC cells is aligned with polyvinyl alcohol (PVA). According to the rubbing direction, the glass substrate is bound reversely to build an antiparallel cell. As splay deformation is induced by the magnetic field, threshold field can be measured to determine the magnetic anisotropy.[13−16]

2.1. Dielectric anisotropy and splay elastic constant

Capacitance versus voltage measurement with a antiparallel aligned LC cell is used for determining the dielectric constant and the splay elastic constant which is employed in our previous studies.[9−11] An LCR meter (HP4274A) is used for capacitance (C) measurement. The measurement process involves applying DC voltage in steps of 0.2 V and holding time of 5 s. A small alternating voltage with 1 kHz frequency is superimposed. The small dielectric anisotropy leads to a high threshold voltage that is described as

$$V_{\mathrm{th}} = \pi \left(\frac{K_{11}}{\varepsilon_0 \Delta\varepsilon} \right)^{1/2}, \tag{1}$$

where K_{11} is the splay elastic constant, V_{th} is the threshold voltage, ε_0 is the permittivity of vacuum, and $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is the dielectric anisotropy. The dielectric constant in the direction of the molecular short axis, $\varepsilon_{\perp}$, is obtained from the capacitance below threshold voltage. The dielectric constant in the direction parallel to the molecular long axis, $\varepsilon_{\parallel}$, is obtained from an extrapolation in capacitance as a function of inverse voltage, i.e. the value $1/V$ approaches zero. The splay elastic constant K_{11} can be determined from Eq. (1).

2.2. Magnetic anisotropy

A magnetic field is applied perpendicularly to the director of a uniform nematic layer with thickness d. In the present study, it is assumed that the strong anchoring condition of the molecules at the substrates is not influenced by the magnetic field. Therefore, the director pattern will be distorted only when the magnetic field is above a threshold B_c.[13−16] When the splay deformation is induced by the magnetic field, the magnetic anisotropy $\Delta\chi$ can be obtained from the following equation:

$$B_{\mathrm{c}} = \frac{\pi}{d} \left(\frac{\mu_0 K_{11}}{\Delta\chi} \right)^{1/2}, \tag{2}$$

where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$. With magnetic field increasing gradually, the characteristic curve of capacitance versus field is measured at a frequency of 1 kHz. The threshold B_{c} value is determined by the intersection of linear section ($B < B_{\mathrm{c}}$) with curved section ($B > B_{\mathrm{c}}$) to be the field at which $\Delta C/C_0$ is about $0.1\% - 0.5\%$, where, C_0 is the capacitance value at $B < B_{\mathrm{c}}$ and ΔC is the increment of capacitance at $B > B_{\mathrm{c}}$. From Eqs. (1) and (2), the magnetic anisotropy can be determined. According to our experience and advice in Ref. [14], the gaps of the cells used in this work are of $15 - 90$ μm.

3. Results and discussion

3.1. Dielectric anisotropy and splay elastic constant

The dielectric anisotropy and the splay elastic constant have been reported in detail in our previous studies.[9−11] These results are shown, respectively, in Figs. 2 and 3 as a function of reduced temperature. As already explained in the previous reports,[9−11] the dielectric anisotropy is mainly determined by the strong dipole moment of $C - F$ bonds of the phenyl ring. Therefore, the values of the dielectric anisotropy show an order as follows:

$$3\mathrm{PBC}^{3,4}\mathrm{F}_2 > 3\mathrm{PBC}^{4}\mathrm{F} > 3\mathrm{PBC}^{2,4}\mathrm{F}_2 > 3\mathrm{PBC}^{3}\mathrm{F}.$$

For the splay elastic constants, there are not marked differences in temperature dependence because of the resemblant molecular geometries and dimensions of the LC materials. For $3\mathrm{PBC}^{2,4}\mathrm{F}_2$, the elastic constant decreases rapidly close to T_{NI}, however, for $3\mathrm{PBC}^{4}\mathrm{F}$, it decreases slowly and possesses

a large value close to $T_{\rm NI}$. A tiny difference at the transition point is possible in that the splay constant is influenced by the molecular rotation. In our another study of LC mechanical rotation model,[17] we have investigated the critical angular velocity around the molecular long axis at the transition temperature. The velocities are obtained as below (in 10^{11} rad/s): $3{\rm PBC}^4{\rm F}(9.31), 3{\rm PBC}^{3,4}{\rm F}_2(8.21), 3{\rm PBC}^3{\rm F}(8.01)$, and $3{\rm PBC}^{2,4}{\rm F}_2(7.94)$.

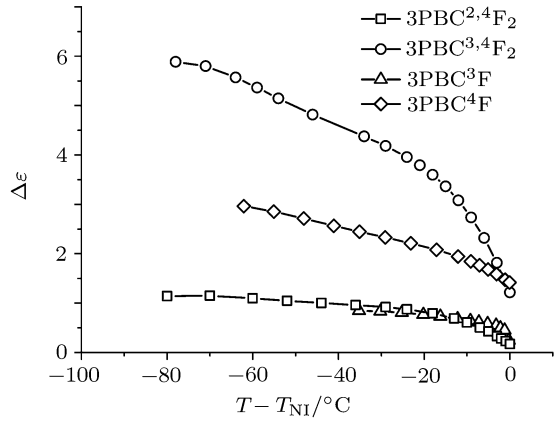


Fig. 2. Temperature dependences of dielectric anisotropy, where reduced temperature $T - T_{\rm NI}$ is used.

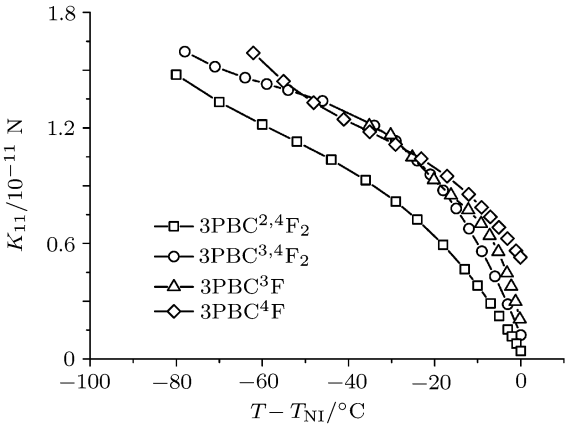


Fig. 3. Temperature dependences of splay elastic constant, where reduced temperature $T - T_{\rm NI}$ is used.

In the study,[17] we have found that the long molecular rotation axis passes through the line connecting positions 3 and 4, but close to position 4. When the molecule rotates around the molecular axis, the molecule whose fluorine atom is substituted at position 4 will be in a slim shape compared with other molecules. Therefore, the slim molecule $3{\rm PBC}^4{\rm F}$ rotates at a higher speed than $3{\rm PBC}^{2,4}{\rm F}_2$ does at NI phase transition point. In other words, the molecular rotation condition of $3{\rm PBC}^4{\rm F}$ is steadier than $3{\rm PBC}^{2,4}{\rm F}_2$ in the nematic phase range. The steady molecular rotation maybe results in a larger elastic constant value and higher order parameter close to NI transition point, and hence a larger magnetic anisotropy which will be shown in the next section.

3.2. Magnetic anisotropy

3.2.1. Density of compounds

In order to obtain mass magnetic anisotropy $\Delta\chi^{(m)} = \Delta\chi/\rho$, where ρ is the mass density, the density of the LCs is measured using an Anton Paar Model 602 HT digital density meter. The values are extrapolated from a solution, where the LC compounds are dissolved in an apolar solvent p-xylene according to the weight proportion. The temperature dependence of the density is shown in Fig. 4.

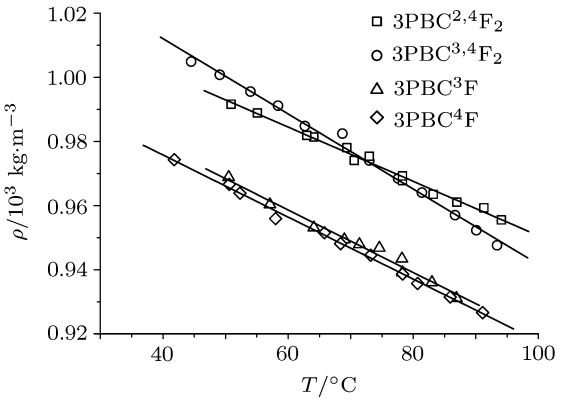


Fig. 4. Temperature dependence of density of compounds. The density value is extrapolated from LC solution in which p-xylene serves as solvent by weight proportions.

3.2.2. Magnetic anisotropy

The mass magnetic anisotropy $\Delta\chi^{(m)}$ as a function of temperature is illustrated in Fig. 5. The data of magnetic anisotropy are weakly temperature dependent at lower temperatures but strongly temperature dependent near the nematic-isotropic transition temperature point.

In the magnetic measurement, we find that the electric capacity of the anti-parallel LC cell increases with the applied magnetic field increasing. Because we have known that the studied PBC LCs are dielectrically positive, we can judge that the diamagnetic anisotropy observed in this experiment is positive, i.e. $\Delta\chi^{(m)} = \chi_{\parallel}^{(m)} - \chi_{\perp}^{(m)} > 0$.

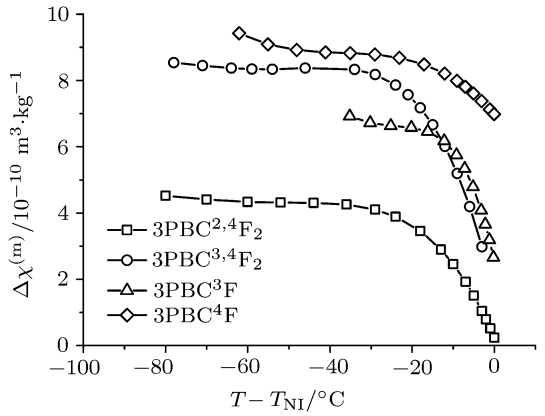


Fig. 5. Temperature dependences of magnetic anisotropy, where reduced temperature $T - T_{\rm NI}$ is used.

According to the experience and Refs. [16], [18] and [19], phenyl ring makes main positive contribution to magnetic anisotropy; however, bicyclohexane makes a lower negative contribution to magnetic anisotropy. Based on the molecular structure, it is easy to understand that the fluorinated PBC LCs possess smaller positive magnetic anisotropic values. One can obtain an order according to the $\Delta\chi^{(m)}$ magnitude as follows:

3PBC^{4}F > 3PBC^{3,4}F$_2$ > 3PBC^{3}F > 3PBC^{2,4}F$_2$.

The compounds 3PBC^{4}F and 3PBC^{2,4}F$_2$ possess the largest and the smallest magnetic anisotropies, respectively. Along with the direction of the molecular long axis (position 4 of the phenyl ring), a polar fluorine substitution of hydrogen atom produces a positive effect on the magnetic anisotropy. On the other hand, fluorine substitution on position 2 or 3 of the ring brings about a negative effect on the magnetic anisotropy. The magnetic anisotropy of 3PBC^{3,4}F$_2$ is larger than that of 3PBC^{2,4}F$_2$, which indicates that the reducing effect on magnetic anisotropy of position 2 is more prominent.

3.2.3. Correlation of magnetic anisotropy with dielectric anisotropy

Before investigating correlation between dielectric anisotropy and magnetic anisotropy, it is necessary to consider an effect of order parameter S of LCs on those two anisotropic quanta.

Generally, mean diamagnetic polarizability in ordered LC compounds is independent of temperature. When the LC sample sets in a magnetic field, the local magnetic field in the nematic layer is equal to the external field, and the molecular magnetic polarization is not influenced by the magnetic dipolar moments of the surrounding molecules. The magnetic polarization of the sample is basically determined by the macroscopic order of the molecular polarizability tensor.[18] Thus, an equation is established from which the order parameter can be deduced.

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} = (\chi_l - \chi_{\rm t})S, \tag{3}$$

where, $\chi_l - \chi_{\rm t}$ is molecular absolute anisotropy, S is the order parameter which is temperature dependent. From the equation, the anisotropic diamagnetic susceptibility is a function of order parameter only. For the dielectric anisotropy, the temperature dependence is presented by the Maier–Meier theory and shown as follows:[20]

$$\Delta\varepsilon = \frac{NhF}{\varepsilon_0}\left[\Delta\alpha - F\mu^2\frac{(1-3\cos^2\beta)}{2k_{\rm B}T}\right]S. \tag{4}$$

Therefore, $\Delta\varepsilon$ is dependent not only on order parameter S, but also on the term that varies with the inverse of absolute temperature increasing. However, this term contributes very little, even negligible at high temperatures, if we consider that most of LCs possess relatively narrow nematic phase ranges.

Correlations between dielectric anisotropy and magnetic anisotropy are plotted in Fig. 6. Attending to the high temperature region, both the dielectric anisotropy and the magnetic anisotropy possess small values, and they form a linear relationship. At high temperatures, the dielectric anisotropy is proportional to the magnetic anisotropy. As temperature decreases, the magnetic anisotropy increases slowly, or almost stops increasing. Contrastively, the dielectric anisotropy increases markedly with temperature decreasing.

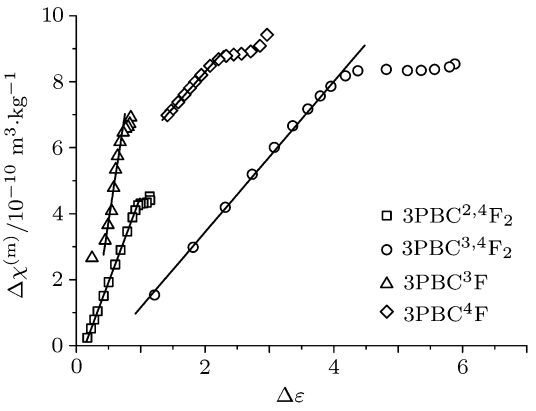


Fig. 6. Correlation between dielectric anisotropy and magnetic anisotropy at the same temperature. In direction of grid origin, data correspond to the values at high temperatures.

To understand the correlation diagram, we consider molecular associations, i.e. the dipole–dipole interaction that might exists in the polar nematic LC compounds.

In high frequency condition, the dielectric anisotropy is directly proportional to the order parameter. Hence the dielectric anisotropy is analogous to the magnetic anisotropy shown in Eq. (3). Therefore, the magnetic anisotropy and the dielectric anisotropy should present a linear correlation.[13,21] At a low frequency, e.g. 1 kHz measured in this experiment, both the relative motions between molecules and the random motions of molecules themselves contribute together to the static dielectric anisotropy. The dielectric property strongly depends on the permanent dipole of molecules. The molecular dipole–dipole interactions perpetually take place in the polar PBC LCs. In the previous studies,[22−24] it was found that the polar molecules could easily form parallel or antiparallel dimers.

For magnetic susceptibility, the magnetic dipolar moments of the surrounding molecules have no effective influence on the considered molecule.[18] The dimerization caused by electric dipolar–dipolar interactions can enhance magnetic dipolar interaction between the molecules in the dimer organization, but such an interaction is weak and has no influence on the magnetic anisotropy of system. One reason is that the magnetic dipole-strength is negligibly small compared with electric dipole-strength. The other reason is that positive diamagnetic susceptibility $\Delta\chi$ of the studied LCs is produced mainly from the large quantity of $|\Delta\chi_{\perp}|$, which is determined by the phenyl ring orientation in the dimerization. Thus, there is little chance to establish a molecular-level system or dimerizations that change the magnetic anisotropy markedly.

Having known the different dimerization effects on the dielectric anisotropy and magnetic anisotropy, we can easily understand why the dimerization does result in the nonlinear correlation in the two anisotropic quantities at low temperatures. In Fig. 6, the nonlinear curves show different grades of slope for different compounds. For $3PBC^{3,4}F_2$ and $3PBC^4F$, the curves show strong and large deviation from the linear correlation than those for $3PBC^{2,4}F_2$ and $3PBC^3F$ when temperature decreases. In other words, when the nematic phases of $3PBC^{3,4}F_2$ and $3PBC^4F$ approach to a crystal phase, the dimerization processes are pronounced and stronger than those of $3PBC^{2,4}F_2$ and $3PBC^3F$, which is consistent with the previous results that the former is stronger than the latter in molecular polarity.[22−24]

Generally, molecular association is pronounced at lower temperatures, and contrarily, it is weak at higher temperatures.[22,23] The authors have investigated the molecular dipole–dipole association and its temperature dependence for fluorinated PBC LC compounds.[22−24] The results revealed that these molecules could form parallel molecular dimers, i.e. Kirkwood factor $g > 1$ in isotropic and anisotropic environments at lower temperatures separately. Therefore, the parallel dimers increase at lower temperatures where they induce the expansion of the dielectric anisotropy; however, the dimers do not increase the magnetic anisotropy proportionally with order parameter increasing.

For these compounds, we can find the marked inflexion on the correlation curves of magnetic anisotropy versus dielectric anisotropy at temperatures (approximation values) of 124.0 ($3PBC^4F$), 87.0 ($3PBC^{3,4}F_2$), 74.0 ($3PBC^3F$), and 94.0^oC ($3PBC^{2,4}F_2$). Below the temperatures, the molecular association becomes powerful and swarming. Therefore, the presumption that the pronounced increasing of the dielectric anisotropy accompanied with the normal or even weak increasing of the magnetic anisotropy is due to the molecular dimerization, has a high priority.

4. Conclusion

Temperature dependences of the magnetic anisotropy of PBC fluorinated LCs are studied. The compounds possess diamagnetic properties and positive magnetic anisotropies ($\Delta\chi^{(m)} > 0$). The magnetic anisotropy shows weak temperature dependence at low temperatures, but strong temperature dependence near the nematic isotropic phase transition point. Along the molecular long axis, the polar fluorine substitution makes an effective contribution to the magnetic anisotropy. On the molecular short axis, the fluorine atoms bring about a canceling effect on the magnetic anisotropy. For the dielectric anisotropy and the magnetic anisotropy, each of the two anisotropic quantities presents a linear correlation at high temperatures, but deviates from the linear course at lower temperatures. We consider that the pronounced molecular dipole–dipole dimerization gives rise to the above correlative properties in polar PBC LCs.

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