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H. Ishikawa; A. Toda; H. Okada; H. Onnagawa

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# Relationship between order parameter and physical constants in fluorinated liquid crystals

by H. ISHIKAWA, A. TODA, H. OKADA*, H. ONNAGAWA
Toyama University, Faculty of Engineering, 3190 Gofuku, Toyama 930, Japan

and S. SUGIMORI
Toyama National College of Technology, 13 Hongo-cho, Toyama 939, Japan

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We have investigated the relationship between order parameter and physical constants (dielectric anisotropy and splay elastic constant) for fluorinated liquid crystals with a small temperature coefficient of the threshold voltage. In these special fluorinated liquid crystals, the dielectric anisotropy is proportional to the square of the order parameter. We have found that this anomalous dielectric behaviour affects the small temperature coefficient of the threshold voltage.

## 1. Background

The market for liquid crystal displays has grown markedly, for example for lap-top computers and portable display terminals, due to small size, light weight and low power consumption. Fluorinated nematic liquid crystals have good stability, high voltage holding ratio, high specific resistance, low threshold voltage ($V_{th}$) and small temperature coefficient of $V_{th}$, and are now widely used. We have already studied the temperature dependence of $V_{th}$, the dielectric anisotropy and the elastic constants of phenylbicyclohexane (PBC) compounds with one or two fluorine substituents in the benzene ring [1]. In this paper, we present the relationship between the order parameter and the physical constants of dielectric anisotropy and splay elastic behaviour for the fluorinated PBC compounds.

## 2. Experimental

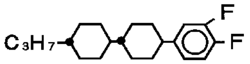
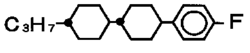
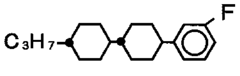
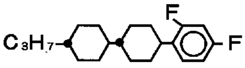
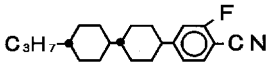
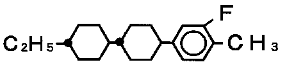
The liquid crystal cells were 10 μm in thickness, with polyvinyl alcohol (PVA) as alignment agent. The rubbing direction of the opposite glass substrate was antiparallel (antiparallel cell). The pre-tilt angle of typical nematic materials in the cell was 0·5°. The temperature of the cell was controlled by a hot stage (Mettler FP82HT). The molecular structures and phase sequences of the liquid crystal materials are shown in table 1.

Dielectric anisotropies and splay elastic constants were determined under an electric field, according to the measurement method reported by Gruler *et al.* [2]. An LCR meter (HP4274A) was used for capacitance ($C$) measurements with a small alternating voltage of 0·2 V and a frequency of 1 kHz superimposed on the d.c. voltage ($V$). The threshold voltage is described as

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

where $K_{11}$ is the splay elastic constant and $\varepsilon_0$ is the dielectric constant of a vacuum. The dielectric constant across the molecular short axis $\varepsilon_{\perp}$ was calculated from the capacitance below threshold voltage. The dielectric

Table 1.

| Compound | Structure | Transition Temp./°C<br>Cr | N | I |
|---|---|---|---|---|
| 3PBC$^{3,4}$F$_2$ |  | – 44·2– | 118 | – |
| 3PBC$^4$F |  | – 88·6– | 158·5 | – |
| 3PBC$^3$F |  | – 51·4– | 91 | – |
| 3PBC$^{2,4}$F$_2$ |  | – 47 – | 124 | – |
| 3PBC$^3$F$^4$C |  | – 54·7– | 207·5 | – |
| 2PBC$^3$F$^4$1 |  | – 63 – | 118·3 | – |

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*Author for correspondence.

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constant parallel to the molecular long axis $\varepsilon_{\parallel}$ was calculated from an extrapolation in capacitance as a function of the inverse voltage characteristics, i.e. the value $1/V$ approaches zero. From these experimental results, the dielectric anisotropy $\Delta\varepsilon$ was calculated as $\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$. The splay elastic constant $K_{11}$ was calculated as

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

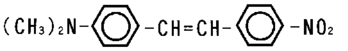
The order parameter was measured from absorbance measurements using various wavelengths in a guest–host (GH) cell [3]. 4-Dimethylamino-4′-nitrostilbene (DANS) was used as a dichroic dye as shown in table 2. The order parameter $S$ was calculated as [4]

$$S=\frac{A_{\parallel}-A_{\perp}}{A_{\parallel}+2A_{\perp}} \tag{3}$$

where $A_{\parallel}$ and $A_{\perp}$ are the maximum absorption coefficients of light polarized parallel and perpendicular to the liquid crystal alignment, respectively, and varied with the wavelength. The absorption coefficients were measured with a spectroscope (Hitachi 330).

In a preliminary experiment, the order parameters of the liquid crystal 7CB were measured in the presence of 0·2, 0·5, 1 and 2 wt % of dichroic dye. The experimental results are shown in figure 1. The order parameters show the same value below the dye concentration of 0·5 wt % and are in good agreement with those reported by Karat *et al.* [5]. Therefore, the dye concentration of 0·5 wt % was used in this study.

Table 2.

| Compound | Structure |
|---|---|
| DANS |  |

## 3. Results and discussion

In our previous paper, we reported details of the threshold voltages and the dielectric anisotropies of the fluorinated liquid crystal compounds [1]; however, we did not discuss the order parameter. In this paper, we measure the order parameters and reinvestigate all the data for the threshold voltages, dielectric anisotropies and splay elastic constants of the liquid crystal compounds listed in table 1. Figure 2 shows the temperature dependence of the threshold voltage for the various kinds of liquid crystal compound. For the liquid crystal compounds 3PBC$^{3,4}$F$_2$ and 3PBC$^3$F$^4$C with *meta*- and *para*-fluorines and with *meta*-fluorine and *para*-cyano substituents in the benzene ring, respectively, small temperature coefficients of the threshold voltage were obtained over a wide temperature range. Figure 3 shows the temperature dependence of the dielectric constant parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) to the molecular axes. Figure 4 shows the experimental results for the dielectric anisotropy for the various kinds of liquid crystal compounds. In general, the dielectric anisotropy of the liquid crystal compounds exhibiting a low threshold voltage was larger than that of common liquid crystal compounds. The dielectric anisotropy increased in the order 2PBC$^3$F$^4$1, 3PBC$^3$F, 3PBC$^{2,4}$F$_2$, 3PBC$^4$F, 3PBC$^{3,4}$F$_2$ and 3PBC$^3$F$^4$C, i.e. in the order of *ortho*-, *ortho*- & *para*-, *para*-, and *meta*- & *para*-fluorine

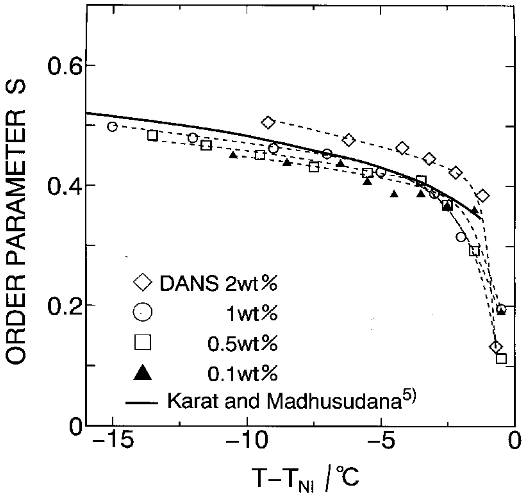


Figure 1. Measured order parameters of the liquid crystal 7CB with varied concentration of dichroic dye (0·2, 0·5, 1 and 2 wt %).

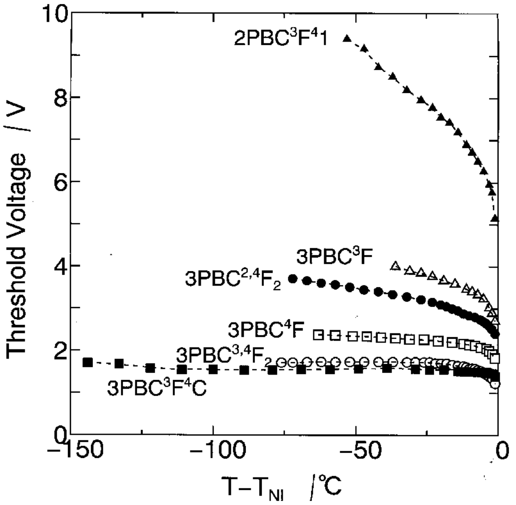


Figure 2. Temperature dependence of the threshold voltage for the various kinds of liquid crystal compounds reported (see table 1 for structures).

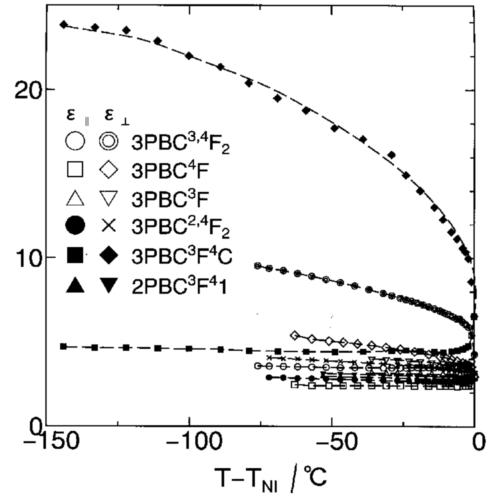


Figure 3. Temperature dependence of the dielectric constant parallel to the molecular long- ($\varepsilon_\parallel$) and short- ($\varepsilon_\perp$) axes for the liquid crystal compounds in table 1.

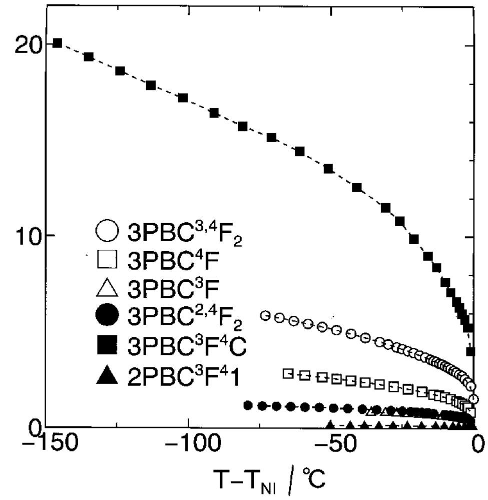


Figure 4. Temperature dependence of the dielectric anisotropy for the liquid crystal compounds in table 1.

substituents and in the order of CH$_3$, F and CN in terms of the kind of *para*-substituent in the benzene ring.

As already shown in the previous paper [1], the values of $\varepsilon_\perp$ and $\varepsilon_\parallel$ are explained in a similar manner. The centre of the benzene ring is set as the origin and the dielectric vector components which depends on the direction of the fluoro, cyano and methyl substituents are considered. If the compounds have two fluorines in the benzene ring, the sum of two dielectric vector components is assumed. In 2PBC$^{3}$F$^{4}$1, the dielectric anisotropy of the methyl substituent is relatively neutral. In 3PBC$^{2,4}$F$_2$, 3PBC$^{3}$F, 3PBC$^{4}$F and 3PBC$^{3,4}$F$_2$, the $\varepsilon_\perp$ and $\varepsilon_\parallel$ are determined by the short- and long-axial components of the dielectric vectors, respectively. The increase in dielectric vector arising from one fluorine substituent $\varepsilon_F$ is considered. Ideally, $\varepsilon_\perp$ is not changed in 3PBC$^{4}$F and increased $0{\cdot}866\varepsilon_F$ in 3PBC$^{2,4}$F$_2$, 3PBC$^{3}$F, 3PBC$^{4}$F and 3PBC$^{3,4}$F$_2$; and $\varepsilon_\parallel$ is also increased $0{\cdot}5\varepsilon_F$, $0{\cdot}5\varepsilon_F$, $1{\cdot}0\varepsilon_F$ and $1{\cdot}5\varepsilon_F$ in 3PBC$^{2,4}$F$_2$, 3PBC$^{3}$F, 3PBC$^{4}$F and 3PBC$^{3,4}$F$_2$, respectively. The dielectric vector components in 3PBC$^{2,4}$F$_2$, 3PBC$^{3}$F and 3PBC$^{4}$F are well explained by the $\varepsilon_F$. In 3PBC$^{3,4}$F$_2$, however, the $\varepsilon_\perp$ and $\varepsilon_\parallel$ are two or three times larger than the calculated value. The reason is given by the inductive effects of fluorine and cyano, i.e. electrons are concentrated in the neighborhood of *meta*- and *para*-fluorine substituents. In 3PBC$^{3}$F$^{4}$C, the dielectric component of the cyano substituent is larger than that of fluorine, so the values of $\varepsilon_\perp$ and $\varepsilon_\parallel$ are larger compared with 3PBC$^{3,4}$F$_2$.

Figure 5 shows the temperature dependence of the splay elastic constants for the various kinds of liquid crystal compounds. There were small differences with the position and nature of the substituents, except for the compound 3PBC$^{3}$F$^{4}$C. Many research groups have reported on the association of liquid crystal compound with a *para*-cyano substituent in the benzene ring giving antiparallel alignment in non-polar solvents [6–10]. However, Toriyama *et al.* [11] reported parallel ordering for the liquid crystal compound 3PBC$^{3,4}$F$_2$ in a non-polar nematic liquid crystal solvent. It is assumed therefore that antiparallel ordering of 3PBC$^{3}$F$^{4}$C probably explains why it exhibits a larger splay elastic constant than that arising from the parallel ordering of the fluoro substituted liquid crystal compounds under consideration.

Figure 6 shows the temperature dependence of the order parameters for the various kinds of liquid crystal

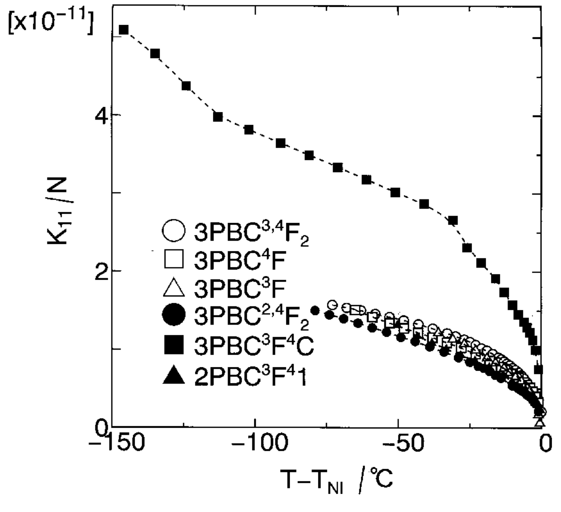


Figure 5. Temperature dependence of the splay elastic constant for the liquid crystal compounds in table 1.

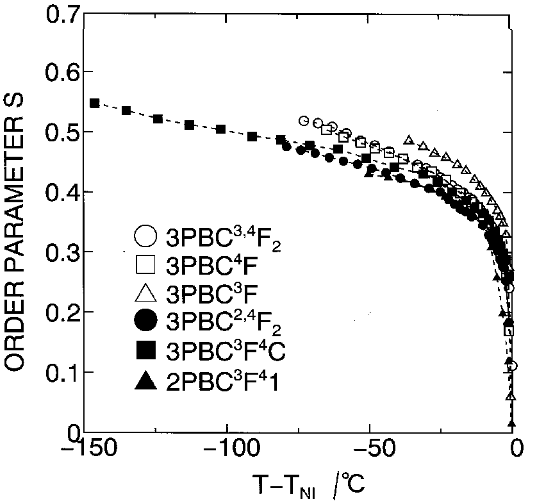


Figure 6. Temperature dependence of the order parameter for the liquid crystal compounds in table 1.

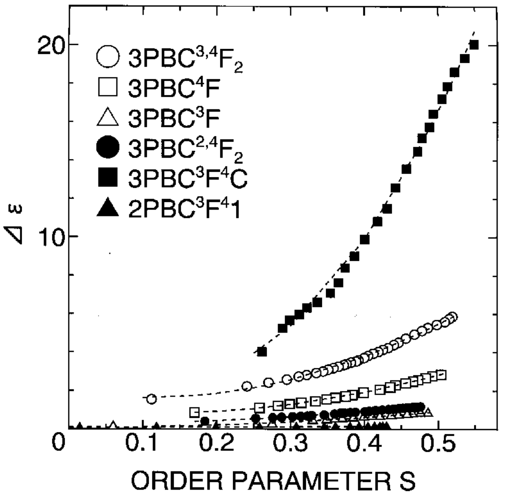


Figure 7. Dielectric anisotropy versus order parameter characteristics.

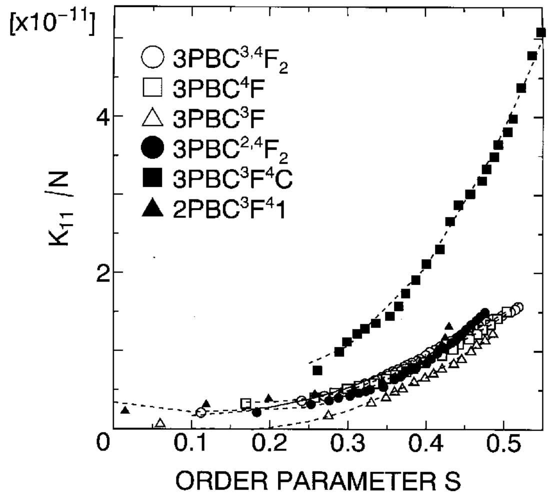


Figure 8. Splay elastic constant versus order parameter characteristics.

compounds. When the temperature was raised, the order parameters decreased and changed discontinuously near the nematic–isotropic transition temperature. The values of the order parameter itself and the temperature dependences of the order parameters were not markedly different from those of other liquid crystal compounds, that is, with different dielectric anisotropies, splay elastic constants and molecular structures.

Maier and Meier reported the relationship between the dielectric anisotropy and the order parameter to be theoretically [12]

$$\Delta\varepsilon \sim S \qquad (4)$$

The relationship between the splay elastic constant and the order parameter was theoretically shown by Kimura *et al.* to be [13]

$$k_{11} \sim S^2 \qquad (5)$$

From the temperature dependence of the dielectric anisotropies, the splay elastic constants and the order parameter in figures 3–6, the relationships between dielectric anisotropy and splay elastic constant and order parameter were compared at the same temperature. Figure 7 shows the dielectric anisotropy versus order parameter characteristics. The dielectric anisotropies of the liquid crystal compounds 2PBC$^3$F$^4$1, 3PBC$^3$F and 3PBC$^{2,4}$F$_2$ are almost proportional to the order parameter; this relationship is in good agreement with equation (4). However, the dielectric anisotropies of the compounds 3PBC$^4$F, 3PBC$^{3,4}$F$_2$ and 3PBC$^3$F$^4$C show a quadratic relationship to the order parameter; the dielectric anisotropy appeared to change from linear to parabolic with the increase in dielectric anisotropy. Figure 8 shows the splay elastic constant versus order parameter characteristics. The value of the splay elastic constant is different in 3PBC$^3$F$^4$C, as already shown in figure 5, but the splay elastic constants of all the compounds are proportional to the square of the order parameter. The splay elastic constants therefore show a typical behaviour as compared with equation (5). The anomalous behaviour of the dielectric anisotropy versus the order parameter reflects the tendency to a small temperature dependence of the threshold voltage, as seen in equation (1).

## 4. Conclusion

We have investigated the relationship between certain physical constants and the order parameter in fluorinated phenylbicyclohexane compounds, and observed anomalous behaviour of the dielectric constant against the order parameter in $3PBC^4F$, $3PBC^{3,4}F_2$ and $3PBC^3F^4C$. The origin of this peculiarity remains to be studied.

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