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Tilt Angle Determination of a Smectic C Phase by Field-Induced Freedericksz Transition and X ray Investigations

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A smectic C liquid crystal exhibiting positive dielectric anisotropy was oriented with the director parallel to the glass substrates. When an electric field was applied normal to the director direction a dielectric reorientation (Freedericksz transition) occurred. Dissolving a dichroic dye in the smectic C phase and applying an electric field, a guest host effect similar to nematic phases was observed. From the dielectric reorientation the tilt angle of the smectic C phase was determined at different temperatures. The tilt angles obtained by the electrooptical measurements agree sufficiently with the values measured by X ray investigations.

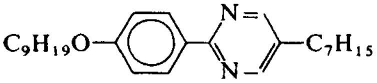
1 INTRODUCTION

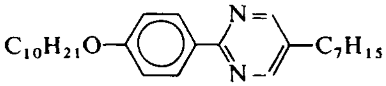
When a smectic C phase is formed by cooling a nematic phase in the presence of a strong magnetic field, the long molecular axes can be oriented uniformly in the direction of the field. In the orientation under discussion the layer normals are tilted by θ with respect to the preferred direction of the molecular long axes. Changing the direction of the magnetic field, the molecules rotate in such a manner around the layer normals, that they follow as far as possible the field direction, whereby the tilt angle remains constant.[1,2] A theoretical treatment of such a reorientation (Freedericksz transition) of smectic C phases was carried out by Rapini.[3]

We have studied the Freedericksz effect of a smectic C phase with positive dielectric anisotropy using an electric field. The orientation of the smectic phase was the same as described in Refs. 1 and 2.

2 SUBSTANCES

According to the dielectric investigations by Kresse *et al.*[4] the nematic phase of 5-*n*-alkyl-2-[4-*n*-alkyloxyphenyl]-pyrimidines first synthesized by Zaschke[5] possesses a positive dielectric anisotropy. A few of pyrimidine derivatives in addition to the nematic phase exhibit smectic A or C phases in a relatively low temperature range. Since the dielectric anisotropy of the smectic phases is quite likely to be also positive, these compounds appeared suitable for our investigations. We have used an equimolar binary mixture of the following substances:





The mixture exhibits the transition scheme:

$$\text{solid} \overset{43{,}5\text{-}44^\circ\mathrm{C}}{\bullet\!\!\relbar\!\!\relbar\!\!\relbar\!\!\bullet} \text{smectic C} \xleftrightarrow{52\text{-}52{,}5^\circ\mathrm{C}} \text{smectic A} \xleftrightarrow{56{,}5\text{-}57^\circ\mathrm{C}}$$

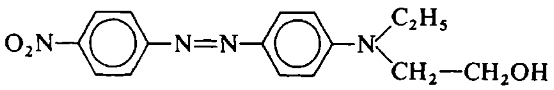
$$\text{nematic} \xleftrightarrow{70\text{-}70{,}3^\circ\mathrm{C}} \text{isotropic}$$

A binary mixture was used to obtain a liquid crystal with a larger smectic C region than in the pure compounds. Additionally, for the occurrence of a good planar orientation in the smectic phase the existence of a nematic phase was necessary.

3 EXPERIMENTAL

3.1 Preparation of uniformly oriented smectic layers

The nematic liquid crystal was oriented uniformly in a planar texture by use of two SnO_2 coated glasses which had been rubbed carefully on paper along the *y*-direction (see Figure 3) following the technique suggested by Zocher[6] and Chatelain.[7] In this planar texture the preferred orientation of the molecular axis—the director—lies along the *y*-direction in the plane of the glass substrate. The distance between the two plates was fixed by mylar spacers (17 μm). This arrangement was maintained at the required temperature by means of a polarizing microscope equipped with a heating stage. The oriented sample was slowly cooled down to the range of the smectic A resp. C phase. By microscopic observation the smectic A phase and similar the smectic C phase showed some poorly contrasted traces of focal conics with very elongated ellipses parallel to *y*. To detect the uniform alignment of the director in the sample, 0.8 weight-% of a dichroic dye (I)



(I)

were added to the liquid crystalline mixture. The absorption band of the dye in the visible range lies at 505 nm. The electronic transition moment responsible for this band is oriented parallel to the long molecular axis. In the nematic state the dye molecules are oriented parallel to the director. Therefore such samples show a distinct positive dichroism. According to our observations the direction of maximal absorption indicating the director orientation remains unchanged in the smectic A and C phases. The dichroic ratio—the quotient of extinction parallel and normal to the director—increases at the transition from the nematic to the smectic phases. These observations give evidence that the orientation of the director is the same in the nematic and the smectic phases.

3.2 The guest host effect in the smectic C phase

On applying an electric field above the threshold field, the planar oriented nematic mixture tends to align parallel to the field because of the positive dielectric anisotropy. In this way also the dissolved dye molecules, which are oriented parallel to the electric vector of the linearly polarized light in the original state, are reoriented in field direction and a colour change from red to colourless occurs. This effect is called "guest host " effect,[8] whereby the nematic liquid is the "host" and the dissolved dichroic dye is the "guest." The planar preparation of the nematic mixture was cooled down to the smectic C phase. In this state the mixture also showed a field-induced colour change due to the dielectric reorientation (Freedericksz transition) of the smectic C phase. In both the nematic and the smectic C phase the light intensity was measured for the wavelength of maximum absorption of the dye (505 nm) in dependence on the applied voltage at different temperatures. The incident light was polarized parallel to the *y*-direction. The intensity measurements were carried out with a photomultiplier which was mounted on the microscope eyepiece.

The results of the measurements are given in Figure 1. It is obvious from Figure 1 that for the nematic and the smectic C phase the light intensity increases up to a threshold voltage and approaches a saturation value at higher voltages. The threshold voltage of the smectic C phase is larger than

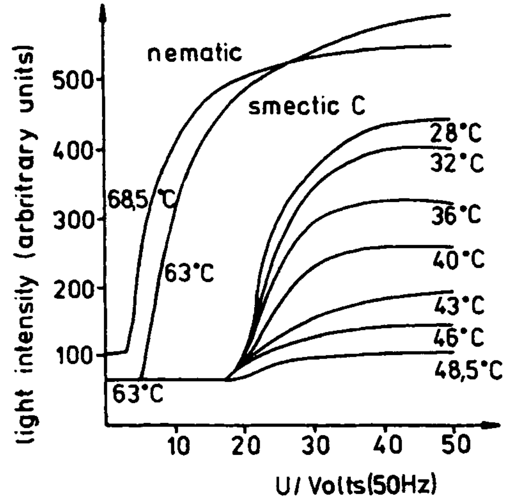


FIGURE 1 Intensity of monochromatic light (505 nm) in dependence on the applied voltage at different temperatures.

that observed in the nematic phase. In the smectic C phase the guest host effect is less pronounced and shows a higher temperature dependence.

3.3 Time behaviour of the effect

The rise and decay times in the nematic resp. smectic C phase were measured by the change of the intensity of the transient monochromatic light (505 nm), which was polarized parallel to the *y*-direction. The rate of the change was monitored by a photomultiplier, the output of which was fed to an oscilloscope. The impulse generator and a relay circuit enable the simultaneous voltage change in the cell and the start of the sweep of the oscilloscope. The

TABLE I

phase	t/°C	U (volts)	U/U_0	t_{rise}(ms)	t_{decay}(ms)	t_{delay}(ms)
nematic	66	15	3,7	19	24	16
	61	15	3,0	56	34	40
smectic C	44,5	50	2,8	28	26	20
	38,5	50	2,8	38	16	20
	33,5	50	2,8	52	16	21
	30	50	2,8	62	20	22

U: voltage
U_0: threshold voltage
layer thickness: 10 μm

oscillograms were registered photographically. The rise time and decay time are defined as those times in which on applying or removing the field, respectively, 90% of the intensity change is observed. The delay time is the time interval, in which after excitation the light intensity remains unchanged.

According to Table I the decay time in the smectic C phase is shorter than in the nematic state. For about the same ratio U/U_0 (U_0: threshold voltage) also the rise time in the smectic C phase is smaller than that measured in the nematic phase near to the nematic → smectic A transition (61°C).

For the dielectric reorientation of the nematic phase the rise time and the decay time, respectively, are given by the following equations:[9]

$$t_{\text{rise}} = \frac{\eta \cdot d^2}{\varepsilon_0 \cdot \Delta\varepsilon \cdot (U - U_0)^2} \tag{1}$$

$$t_{\text{decay}} = C \cdot \eta \cdot d^2/k \tag{2}$$

d : thickness of the specimen
η: viscosity coefficient
k: elastic constant
$\Delta\varepsilon$: dielectric anisotropy
ε_0: influence constant
C : constant

We can assume that for the dielectric reorientation of the smectic C phase analogous relations are valid.

The shorter decay times in the smectic C phase may be interpreted being due to lower viscosities. Indeed, Meiboom and Hewitt[10] were able to show in one substance that the viscosity in the nematic state near to the transition nematic → smectic C was higher than in the smectic C phase. Otherwise, larger elastic constants in the smectic C phase will also contribute to a decrease of the decay times.

3.4 Observation of the effect with a polarizing microscope

The Freedericksz transition in the oriented smectic C phase was studied with a polarizing microscope. To obtain a good homogeneous orientation, the sample thickness amounted only to 10 μm. On applying a voltage above the threshold value, large regions with uniform interference colour can be observed between crossed polarizers, indicating a uniform alignment of the molecules. With increasing voltage a change of the interference colour occurs, but the uniform regions are preserved. In most cases mainly two sets of regions appear, which show different interference colours and are divided by inversion walls. Occasionally almost the entire sample shows a uniform interference colour after applying the field (~ 0.5 cm^2). Because of the dichroic dye added to the liquid crystal the director direction can be determined from the vibration direction of linearly polarized light, for which the light intensity (505 nm) has a minimum.

For a fixed uniform region it was found, that by applying of an electric field the minimum of light intensity indicating the projection of the director orientation in the layer plane is shifted by a certain angle depending on the field strength. First an increase of this angle is observed with increasing voltage up to a maximal value. With further increasing voltage this angle decreases to zero (initial position). At very high voltages the minimum of light intensity is often shifted in the inverse direction. Simultaneously with the shift of the minimum an increase of the light intensity in the minimum position is observed with rising voltage. When mainly 2 sets of uniform regions exist, the minimum shift in both regions is about the same, but occurs in the inverse direction.

It must be noted, that after longer electric excitation the homogeneous uniform orientation disappears and is replaced by a texture of smectic C with small domains. By heating in the nematic state and after that cooling in the smectic state the original texture with large domains returns.

4 DETERMINATION OF THE TILT ANGLE BY THE GUEST HOST EFFECT

In the smectic C phase the molecules within the smectic layers are tilted by the tilt angle θ with respect to the layer normal. For an oriented sample with uniform director orientation the possible directions of the layer normal lie on the surface of a cone with the apex angle 2θ. The cone axis coincides with the director orientation (see Figure 2).

The oriented smectic C phase is placed into a rectangular coordinate system, whereby the direction of the director is parallel to the y axis. The origin of the coordinate system is defined by the centre of gravity of a definite molecule. The molecule vector **L** is parallel to the director and its amount is given by the half of the molecule length (Figure 3a). A small, but macroscopic region with fixed layer normal is considered. When an electric field is applied in the z direction, the molecules rotate around the layer normal because of the positive dielectric anisotropy of the smectic sample, so that they align as far as possible in field direction. The possible orientations of **L** lie on the surface of a cone with the apex angle 2θ and the corresponding layer normal as the cone axis. The dielectric reorientation is finished when (at higher voltages) the layer normal, the molecule vector **L** and the field direction are in the same plane. According to Wise *et al.*,[1] and also confirmed by our own observations

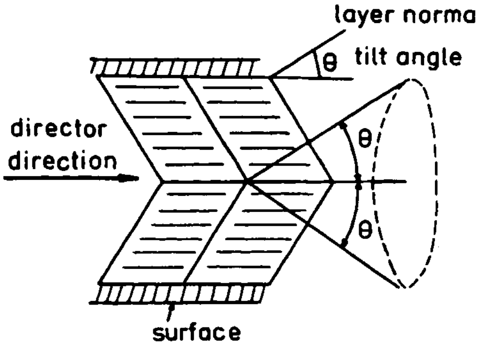


FIGURE 2 Orientation of the smectic C phase (schematically).

the smectic C planes neither distort nor shift on applying a magnetic or an electric field.

As mentioned before, the rotation of the director can be detected by the addition of a dichroic dye to the liquid crystal. The dye molecules are oriented parallel to the director in the liquid crystalline phase. The electronic transition moment of the dye responsible for the absorption in the visible region is oriented in the direction of the long molecular axis. When linearly polarized light of the wavelength of maximal absorption is incident perpendicular to the x, y plane, a maximal absorption is observed, if the vibration direction is parallel to the director projection in the x, y plane. As shown in Figure 3a, the final points of the vector $\mathbf{L}_{xy}$ produce an ellipse in the x, y plane, the shape of which is determined by the orientation of the layer normal and by the tilt angle θ. The vector $\mathbf{L}_{xy}$ is the projection of $\mathbf{L}$ in the x, y plane: $\mathbf{k}_{xy}$ is the projection of $\mathbf{k}$ in the x, y plane, where the vector $\mathbf{k}$ is parallel to the layer normal and its amount is $|\mathbf{L}| \cos \theta$. As can be seen from Figure 3a and 3b, only a part of the ellipse is obtained under our experimental conditions. The points 2 and 3 on the ellipse correspond to the maximal deflections of $\mathbf{L}_{xy}$ with respect to the initial position (point 1), which are characterized by the angles ε_1 and ε_2 respectively, where $\varepsilon_1 + \varepsilon_2 = \varepsilon$ (see Figure 3b). From the angles ε_1 and ε_2, which are available from the experiment, the tilt angle θ of the smectic C phase may be calculated. It is readily seen from Figure 3b that

$$\tan \varepsilon_2 = \frac{|\mathbf{k}_x|}{|\mathbf{k}_y|} = \frac{|\mathbf{L}| \cdot \sin \theta \cos \theta \sin \alpha}{|\mathbf{L}| \cdot \cos^2 \theta} = \frac{\sin \theta \sin \alpha}{\cos \theta} \tag{3}$$

where α is the rotation angle of the layer normal around the y axis in the x, z plane. The orientation of the layer normal is fixed by the angle α. According to Figure 3b the axes of the coordinate system ξ, η are parallel to the main axes of

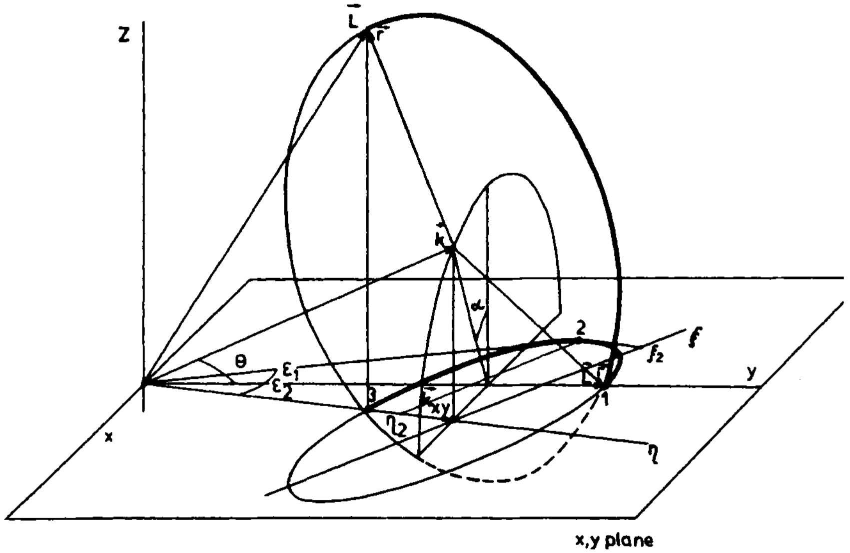


FIGURE 3a Orientation of the molecule vector **L** on applying of an electric field above the threshold value for a fixed orientation of the layer normal (**k**).

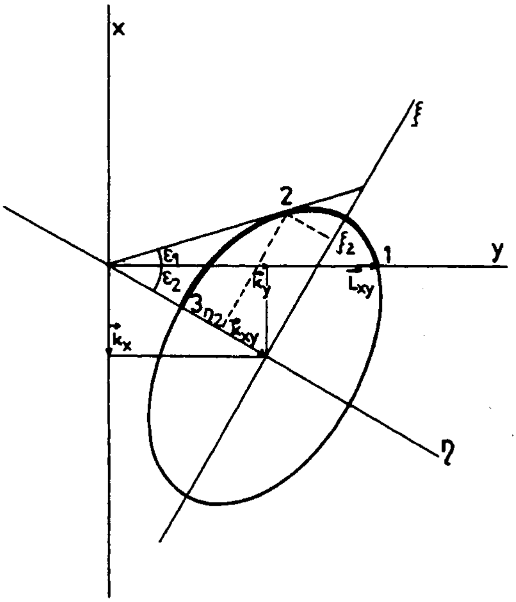


FIGURE 3b Projection of the molecule vector **L** in the xy plane

the ellipse and the origin of the coordinate system is given by the vector $\mathbf{k}_{xy}$.

The equation of the ellipse in the ξ, η system may be expressed by:

$$\frac{\xi^2}{a^2} + \frac{\eta^2}{b^2} = 1 \tag{4}$$

The main axes of the ellipse are given by the following relations:

$$a = |\mathbf{r}| = r \qquad \text{and} \qquad b = |\mathbf{r}| \cdot \sin\theta \cos\alpha \tag{5}$$

where $|\mathbf{r}|$ is the radius of the circle, with which $\mathbf{L}$ rotates around the layer normal (Figure 3a): $|\mathbf{r}| = |\mathbf{L}| \cdot \sin\theta$. In the point 2 ($\eta = \eta_2, \xi = \xi_2$) $\tan\varepsilon$ may be expressed in the following way:

$$\tan(\varepsilon_1 + \varepsilon_2) = \tan\varepsilon = \left.\frac{d\xi}{d\eta}\right|_{\substack{\eta=\eta_2 \\ \xi=\xi_2}} = \frac{-\eta_2}{\xi_2 \cdot \sin^2\theta \cos^2\alpha} \tag{6}$$

and

$$\tan\varepsilon = \frac{\xi_2}{|\mathbf{k}_{xy}| + \eta_2} \tag{7}$$

with $|\mathbf{k}_{xy}|^2 = |\mathbf{k}_x|^2 + |\mathbf{k}_y|^2$.

Together with Eqs. (6) and (7) we obtain with Eq. (4):

$$|\mathbf{k}_{xy}|^2 \tan^2\varepsilon(1 + \sin^2\theta \cos^2\alpha \tan^2\varepsilon) - r^2(1 + \tan^2\varepsilon \sin^2\theta \cos^2\alpha)^2 = 0 \tag{8}$$

Using $r^2 = |\mathbf{L}|^2 \cdot \sin^2\theta$ and

$$\frac{|\mathbf{k}_{xy}|^2}{|\mathbf{L}|^2} = \frac{|\mathbf{k}_x|^2 + |\mathbf{k}_y|^2}{|\mathbf{L}|^2} = \cos^2\theta(\sin^2\theta \sin^2\alpha + \cos^2\theta)$$

Eq. (8) can be put in the form

$$\tan^2\varepsilon(2\cos^2\theta - 1 + \sin^2\theta \sin^2\alpha) - \sin^2\theta = 0 \tag{9}$$

Substituting Eq. (3) into Eq. (9) we obtain

$$\cos^2\theta = \frac{1}{1 + \dfrac{\sin^2\varepsilon}{\cos^2\varepsilon_2}} \tag{10}$$

There are 2 boundary cases

1) The layer normal is in the y, z plane ($\alpha = 0°$). The projection of $\mathbf{L}$ in the x, y plane ($\mathbf{L}_{xy}$) describes an ellipse whose minor axis is parallel to the y axis

and is given by $b = r \cdot \cos\theta$. In this case $\varepsilon_2 = 0, \varepsilon = \varepsilon_1$ and Eq. (8) is reduced to

$$\cos^2\theta = \frac{1}{1 + \sin^2\varepsilon_1} = \frac{1}{1 + \sin^2\varepsilon} \qquad (11)$$

2) The layer normal is in the x, y plane ($\alpha = 90°$). In this case the ellipse degenerates to a straight line of the length $2r$ and $\varepsilon_2 = \varepsilon$ is identical with the tilt angle θ.

In not too great distance from the transition smectic C → smectic A always the first boundary case ($\alpha = 0°$) was observed. For lower temperatures the angle α, which characterizes the orientation of the layer normal, was not larger than 30° according to our measurements. The second case was not observed in our studies.

5 DETERMINATION OF THE TILT ANGLE BY X RAY MEASUREMENTS

Two methods based on X ray measurements were used for the determination of the tilt angle in the smectic C phase. First, the tilt angles were determined in a direct way using the pattern of the oriented samples. To obtain an oriented smectic sample, the X ray camera was fitted in a magnetic field of about 13000 Gauss. The camera consisted of an adjustable support on which was mounted a collimator, an electrical heated sample holder and the film holder. The temperature was measured with a thermocouple. A small-bore glass tube with a internal diameter of 0.8 mm was used to obtain a nearly parallel

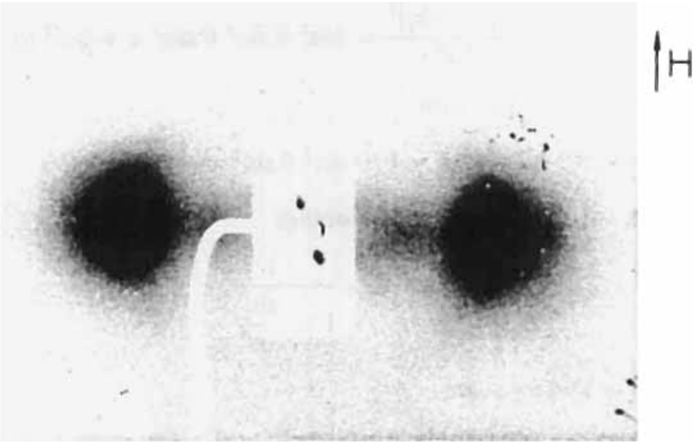


FIGURE 4 X ray pattern of the smectic C phase oriented by a magnetic field.

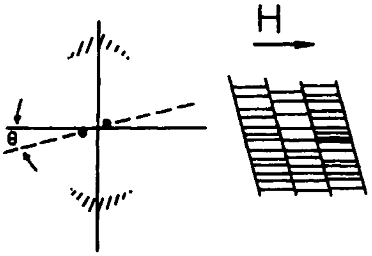


FIGURE 5 Determination of the tilt angle from the X ray pattern of a oriented smectic C liquid crystal (schematically).

primary beam. The samples were heated into the nematic state and subsequently cooled down to the smectic state and the magnetic field was maintained also during the exposure. The picture of the obtained patterns is given in Figure 4. The middle part of the pattern is covered after an exposure time of 30 min because of the great intensity of the inner spots. A schematic interpretation of the pattern is given in Figure 5. It can be seen that the long axes of the molecules are parallel to the magnetic field, whereas the normals of the layers give a definite angle. By the relative position of the spots the tilt angle θ can be measured.

Since the first determination is somewhat rough, we used also a second method. The layer spacings d of non-oriented samples were measured in dependence on the temperature with a goniometer equipment.[11] With the assumption that the molecules in the smectic A phase are arranged perpendicular to the layer planes and the chain conformation in the smectic C phase as well as in the smectic A phase is not too different, the tilt angle is given by the following relation:

$$d_C = d_A \cdot \cos\theta \tag{12}$$

(d_C, d_A: layer spacing in the smectic C and smectic A phase, respectively).

6 EXPERIMENTAL RESULTS

In Figure 6 the tilt angle obtained by different methods is plotted against the temperature difference $T - T_{CA}$, where T_{CA} is the transition temperature smectic C → smectic A. This plot is advantageous for the comparison of the values, because by addition of 0.8 weight-% of the dye to the liquid crystalline mixture T_{CA} is depressed by about 2 degrees.

The values determined by the electro-optical measurements are mean values of several series of measurements. The deviations of the measured values from the mean value amount about 1–2 degrees. It is seen from Figure 6

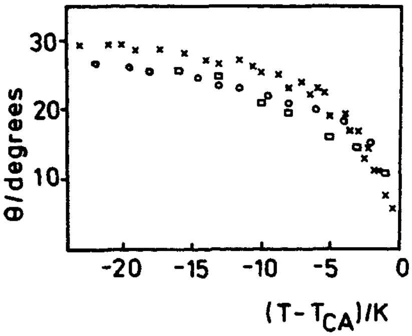


FIGURE 6 The tilt angle of the smectic C phase obtained by different methods in dependence on the temperature difference $T - T_{CA}$ (T_{CA}: transition temperature smectic C → smectic A)

× optical measurements

□ } X ray investigations oriented samples
○ } layer spacing

that the data of the electro-optical measurements are generally 2–3° larger than those obtained by X ray investigations.

According to Ref. 1 the temperature dependence of the tilt angle is a general property of compounds which have a smectic A phase above the temperature range of smectic C. It has been predicted by de Gennes[12] that for such compounds the tilt angle should vary as $(T_{CA} - T)^{0.35}$. Near the smectic C → smectic A transition a temperature dependence of the tilt angle of about $(T_{CA} - T)^{0.4}$ can be derived from the slope of the $\ln \theta/\ln (T_{CA} - T)$-curve.

Finally it can be noted that for smectic C phases with positive dielectric anisotropy the guest host effect based on the Freedericksz transition is a useful and simple method for the tilt angle determination, provided that the director of the C phase can be oriented parallel to the glass substrate.

Acknowledgement

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