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Dielectric anisotropy in the smectic phases of liquid crystals

L. Benguigui

Solid State Institute, Technion-Israel Institute of Technology, Haifa, Israel

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Résumé. — On a mesuré l'anisotropie diélectrique de deux composés (507 et 508) appartenant à la série p-pentoxybenzylidène-alkylaniline, dans les phases nématicques et smectiques : A et B pour le 508 ; A, B et C pour le 507. L'anisotropie croît fortement dans les phases smectiques. Cet effet est interprété par une augmentation des corrélations dipôle-dipôle.

Abstract. — We measured the dielectric anisotropy of two compounds (507 and 508) of the p-pentoxy-benzylidene-alkylaniline series, in their nematic and smectic phases : A and B for 508, A, B and C for 507. The anisotropy increases strongly in the smectic phases. We interpret this by an increase of the dipole-dipole correlations.

1. Introduction. — Recent works [1, 2] on liquid crystals have shown that the dielectric behaviour in the smectic phases is very different than that in the nematic phase. In this phase, the dielectric anisotropy comes essentially from the fact that the molecular dipoles cannot take all the possible orientations, as in the isotropic liquid. Because of the nematic order, some orientations are more probable and this gives a difference between \( \varepsilon_{||} \) (when the director \( n \) and the electric field \( E \) are parallel) and \( \varepsilon_{\perp} \) (\( n \) and \( E \) are perpendicular). It is the physical basis of the theory of Maier and Meier [3]. Extending the Onsager theory to the case of the nematic phase, they give the dependence of \( \varepsilon_{||} \) and \( \varepsilon_{\perp} \) with the temperature \( T \) and with the nematic order parameter \( S \). This theory describes with great success the dielectric properties of a nematic liquid crystal [4]. However, the measurements of materials with \( \varepsilon_{||} > \varepsilon_{\perp} \) in the nematic phase show that the dielectric anisotropy \( \Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp} \) decreases when the temperature \( T \) decreases and the material becomes smectic. With further decrease of \( T \), change in the sign of \( \Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp} \) is observed i.e. in the smectic phase one can observe \( \varepsilon_{\perp} > \varepsilon_{||} \), although in the nematic phase \( \varepsilon_{||} > \varepsilon_{\perp} \). De Jeu et al. [1] suggested an explanation to this phenomenon which takes into account the dipolar correlation [5], these had been completely neglected in the Maier and Meier theory. It is shown [1, 4] that the ordering in layers increase considerably the short range dipole-dipole correlations, giving an increase of \( \varepsilon_{\perp} \) and decrease of \( \varepsilon_{||} \).

We extended further this approach in order to give a more quantitative picture for the dielectric anisotropy in the smectic A, B and C phases [2]. If one supposes that the nematic order is perfect (\( S = 1 \)), one can obtain expressions of \( \varepsilon_{||} \) and \( \varepsilon_{\perp} \) as functions of the order parameters \( \psi \) and \( \delta \) (respectively the amplitude of the first harmonic of the density wave and the tilt angle). Physically, we can say that when the smectic ordering appears, there is tendency for the parallel components of the molecular dipole to form anti-parallel short range ordering and for the perpendicular components to form parallel ordering. From the theory of reference [2], we conclude :

a) If \( \varepsilon_{||} > \varepsilon_{\perp} \) in the nematic phase, we expect, in the smectic A or B phase, a decrease of the difference \( \varepsilon_{||} - \varepsilon_{\perp} \) and even a reversal of the dielectric anisotropy. This behaviour was actually observed in heptylazoxy-benzene [1] and in ethyl \( p-[p-\text{methoxy-benzylidene-amino}] \) cinnamate [2] (EMBAC).

b) If \( \varepsilon_{\perp} > \varepsilon_{||} \) in the nematic phase, we expect an increase of \( \varepsilon_{\perp} - \varepsilon_{||} \), when the material is in the smectic A or B phase.

c) In the smectic C phase, the molecular tilting reduces the antiparallel correlations (for \( \varepsilon_{||} \)) and parallel correlations (for the mean value of \( \varepsilon_{\perp} \)). In order words the tilting gives opposite effect to that of the layer ordering. In reference [2], we used this argument to explain why the dielectric anisotropy is smaller in the smectic C phase of heptylazoxy-azoxy-benzene than in the nematic phase (in this last phase \( \varepsilon_{||} > \varepsilon_{\perp} \)).

The points b and c have not been completely verified and it is the purpose of this paper to check these predictions [7].

We measured the dielectric constants \( \varepsilon_{||} \) and \( \varepsilon_{\perp} \) of...
two compounds of the p-pentoxybenzylidene alkyl-aniline series, with the following formula
\[ \text{C}_5\text{H}_4\text{O} - \bigcirc - \text{CH} = \text{N} - \bigcirc - \text{C}_m\text{H}_{2m+1} \].

The two compounds correspond to \( m = 7 \) (compound 507) and to \( m = 8 \) (compound 508). These two compounds are very good candidates for our purpose since they exhibit a nematic phase and several smectic phases (A and B for 508, and A, C and B for 507) [6]. Since the isotropic-nematic transition temperatures are relatively low, these Schiff bases do not exhibit noticeable unstability (no change in the transition temperatures in the course of this work).

The magnetic anisotropy has been measured [6] and this quantity is proportional to \( S \). In the present case, it is observed that once in the SmA phase, \( S \) increases slowly when \( T \) decreases. Thus we conclude that the nematic order is almost perfect in the smectic phases of the two compounds. We can apply our ideas developed in reference [2]: The extra anisotropy in the smectic phases cannot be due to changes in \( S \).

2. Experiment. — The two compounds have been kindly furnished by the Liquid Crystals Group of the University of Bordeaux (Centre de Recherches Paul-Pascal).

The dielectric constants were measured by means of a bridge, built in our laboratory. The sensitivity is \( 10^{-2} \) pF, but the precision is about 5 %. The frequency we used is 10 kHz. It is below all the relaxation frequencies, except for \( \varepsilon_\parallel \) when the compound is in the SmB phase. In this case, we observed a relaxation in the SmB phase, in the range of 10-50 kHz. We get the corrected value of \( \varepsilon_\parallel \) using a Cole-Cole plot.

The alignment of the samples has been made by means of a magnetic field of 10 kG. For \( \varepsilon_\perp \), we did not observe relaxation and this shows that the alignment was good. For \( \varepsilon_\parallel \), we verified that the measurements are independent of the field for \( H > 3000 \) G.

In figures 1 and 2, we show \( \varepsilon_\parallel (T) \) and \( \varepsilon_\perp (T) \) of the two compounds. In figures 3 and 4, the dielectric anisotropies \( \Delta \varepsilon = \varepsilon_\perp - \varepsilon_\parallel \) are drawn. We remark that in the isotropic liquid phase the two compounds have equal values of \( \varepsilon \) (taking into account experimental errors). The transitions are easily observed by
discontinuities in $\varepsilon_{||}$ and $\varepsilon_{\perp}$; however the N-A and A-C transition of 507 are of first order but nearly of second order. The transition temperatures are in good agreement with reference [6], except for the C-B transition of 507; we found 49.5 °C and in reference [6], 51.8 °C.

3. Discussion. In the two compounds, $\Delta \varepsilon$ is low in the nematic phase, but it increases strongly in the smectic phases, as we expected. In particular, we can distinguish the particular behaviour of $\Delta \varepsilon$ in each of the three smectic phases: A, B and C. $\Delta \varepsilon$ increases quickly in the SmA and more slowly in the SmB phase (if $T$ decreases) in the two compounds 508 and 507. (Note that following reference [6], the SmB phases are uniaxial.) We see also that at the SmA-SmC transition there is a change in the slope of $\Delta \varepsilon$. As expected (see point c, in the introduction), the slope is lower in the SmC phase than in the SmA phase.

We can propose a more quantitative analysis using the results of reference [2]. We found that $\varepsilon_{||}$ and $\varepsilon_{\perp}$ can be expressed as

$$\varepsilon_{||} - \varepsilon_{||}^0 = \left( \frac{3 \varepsilon}{2 \varepsilon + \varepsilon^0} \right) \frac{4 \pi N \mu^2}{kT} \cos^2 \beta (1 + g_{||}) \quad (1)$$

$$\varepsilon_{\perp} - \varepsilon_{\perp}^0 = \left( \frac{3 \varepsilon}{2 \varepsilon + \varepsilon^0} \right) \frac{4 \pi N \mu^2}{2kT} \sin^2 \beta (1 + g_{\perp}) \quad (2)$$

where $g_{||}$ and $g_{\perp}$ are

$$g_{||} = -f(\psi^2, \delta) \frac{\mu^2 \cos^2 \beta}{kT} \quad (3)$$

$$g_{\perp} = h(\psi^2, \delta) \frac{\mu^2 \sin^2 \beta}{kT} \quad (4)$$

In (1) and (2), $\bar{\varepsilon}$ is the mean value of the dielectric constant, $\beta$ is the angle between the molecular dipole $\mu$ and the long axis of the molecules. In our case, the molecules have several dipoles and instead of $\cos^2 \beta$ and $\sin^2 \beta$ we have to use respectively the quantities $c^2$ and $s^2$ which are defined by

$$c^2 = \left( \frac{\sum_{i} \mu_i \cos \beta_i}{\sum_{i} \mu_i} \right)^2 \quad (5)$$

$$s^2 = \left( \frac{\sum_{i} \mu_i \sin \beta_i}{\sum_{i} \mu_i} \right)^2 \quad (6)$$

where $\mu_i$ and $\beta_i$ are the values of the moment and of the angle of the $i$th dipole [2].

We want to calculate the correlations factors $g_{||}$ and $g_{\perp}$, but for this purpose, we need to know: $N \mu^2$, $c^2$, $s^2$, $\varepsilon_{||}^0$ and $\varepsilon_{\perp}^0$. We can easily get, from the results in the isotropic phase two quantities, namely $N \mu^2$ and $\varepsilon_{||}^0 = (\varepsilon_{||}^0 + 2 \varepsilon_{\perp}^0)/3$ with the help of Onsager formula

$$\varepsilon - \varepsilon_{\infty} = \left( \frac{3 \varepsilon}{2 \varepsilon + \varepsilon_{\infty}} \right) \frac{4 \pi N \mu^2}{3kT} \quad (7)$$

It is generally believed that this formula is a very good approximation for an isotropic liquid [8]. In fact we need $\varepsilon_{||}^0$ and $\varepsilon_{\perp}^0$, which can be known only by direct measurement of the refractive index. Since their differences is small we can neglect it, but this procedure is not always justified. In fact, within this approximation, we get reasonable results only for the compound 507. Thus we give the calculation of $g_{||}$ and $g_{\perp}$, only for this compound. Using the formulas (1) and (2), we are able to calculate the two quantities $Tc^2(1 + g_{||})$ and $Ts^2(1 + g_{\perp})/2$. In the smectic B, $\psi \approx 1$ and $\delta = 0$, and from (3) and (4), we see that $g_{||}$ and $g_{\perp}$ are proportional to $T^{-1}$. Thus we have to find that $Tc^2(1 + g_{||})$ and $Ts^2(1 + g_{\perp})/2$ are straight lines, in the SmB phase, with slopes equal respectively to $c^2$ and $s^2/2$. This is the way to deduce these two last quantities.

In the isotropic phase, we found $\varepsilon_{||}^0 = 1.8$ and $4 \pi N \mu^2/k = 1400$ K. In figure 5, we draw $Tc^2(1 + g_{||})$

![Fig. 5.](image)

and $Ts^2(1 + g_{\perp})/2$. These two quantities are effectively linear with $T$ in the SmB phase (more precisely, for $T < 47$ °C). We find $c^2 \sim s^2/2 \sim 0.5$. This result associated to the approximation $\varepsilon_{||}^0 \sim \varepsilon_{\perp}^0$ means that in the nematic phase the dielectric anisotropy should be null. This is clearly not true and seems to be a consequence of the assumed equality $\varepsilon_{||}^0 = \varepsilon_{\perp}^0$. Nevertheless, $\Delta \varepsilon$ is low in the nematic phase, and this implies that $s^2/2$ is slightly larger than $c^2$. Clearly our procedure is not precise enough to get very good values of $c^2$ and $s^2$.

The variations of $Tg_{\perp}$ and $T | g_{||}$ with $T$ are given in figure 6 (in agreement with (3), we found $g_{||} < 0$). $Tg_{\perp}$ and $T | g_{||}$ are proportional to the correlation functions $f(\psi^2, \delta)$ and $h(\psi^2, \delta)$. These correlation functions increase if $T$ decreases, as expected from the theoretical analysis of references [1] and [2]. In the SmB phases, these functions are almost constant.
Correlation functions $T_{g_1}$ and $T |g_1|$ versus $T$. (if $T < 47 \, ^\circ C$). We note that in the SmC phase, the two correlation functions are nearly equal, in contrast to the situation in the SmA and B phases. The effect of the tilt angle on the correlation function is more easy to visualize if we draw

$$T(g_1 - g_{II}) \propto f(\psi^2, \delta) + h(\psi^2, \delta)$$

as a function $T$ (Fig. 7). We note the close similarity of this curve with the curve of $\Delta \varepsilon$.

However, we have to precise the limitation of the theoretical predictions of reference [2]. We give explicit expression for $g_{II}$ and $g_1$ in the SmB phase.

$$g_{II} = \frac{6 \mu^2 \cos^2 \beta}{r^3} \frac{1}{kT}$$

$$g_1 = \frac{3 \mu^2 \sin^2 \beta}{2 r^3} \frac{1}{kT}$$

where $r$ is the mean distance between the molecules. At the same temperature, we must have $|g_{II}||g_1| = 2$, taking into account that $c^2 = s^2/2$. But, from figure 6, we have $g_1 > |g_{II}|$, in the SmB phase. Clearly, the theory of reference [2] gives correctly the temperature dependence of $\Delta \varepsilon$, but we have to improve the model, in order to give more realistic expressions for $g_{II}$ and $g_1$.

4. Conclusion. — We measured the dielectric anisotropy of two compounds in their nematic, and smectic phases. $\Delta \varepsilon$ is low in the nematic phase and increases strongly when the samples are in the smectic phases. In our case $\varepsilon_{II} < \varepsilon_1$ in the nematic and this inequality is true also in the smectic phases. This is in contrast to the case where $\varepsilon_{II} > \varepsilon_1$ in the nematic phase [1, 2], where there is a reversal of the dielectric anisotropy in the smectic phase. All these behaviours are very well explained by the dipole-dipole correlations which become to be important in a layered structure. We get in general good agreement with the theoretical predictions of reference [2].

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References and notes

[8] There are another procedure, like measurements on dilute solutions, to get the dipole moment. However, in (7) $\mu$ is the dipole moment of the molecule in its own medium, which is different from the dipole moment $\mu_a$ of the molecule in vacuum and from the dipole moment $\mu_d$ in dilute solution. Only for spherical molecules it is easy to get relations between these different dipole moments. See in reference [5], ch. 2 and Appendix 2, for a detailed discussion for this very delicate point.