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Dielectric measurements of liquid crystals

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Résumé. — Nous avons utilisé une nouvelle cellule permettant des mesures diélectriques sur de faibles quantités de cristal liquide. Cette cellule a été utilisée pour des mesures diélectriques du cyanobenzylidène p' octyloxyaniline (CBOOA). Nous avons déterminé la permittivité complexe sous l'action d'un champ électrique continu et alternatif, ainsi que sous champ magnétique et ceci dans un grand intervalle de fréquences et de températures en phase nématique et smectique.

Abstract. — A new measurement cell for very small quantities of liquid crystals is used for the determination of the complex permittivity of the cyanobenzylidene p' octyloxyaniline (CBOOA). The dielectric behaviour in the nematic and smectic-A phase is given as a function of an applied electric field (static and alternative) as well as of a magnetic one within a large frequency and temperature range.

1. Introduction.

The electrical behaviour is relatively scarcely studied in the numerous papers relative to liquid crystals. Maier and Meier were the pioneers in the domain [1]. Nematic compounds with cyano substituents along their long molecular axis were studied in order to have twisted nematic displays with low threshold voltages, and other electronics or non linear optics applications [2-4]. The organic molecules have the advantage to possess very high polarizabilities. Barnik *et al.* [5] were the first to study the effect of second harmonic generation with a liquid crystal.

The molecules of cyanobenzylidene p' octyloxyaniline (CBOOA) possess a high permanent dipole moment due to the presence of a cyano group at the edge of the chain. This compound can be oriented by an electric or magnetic field and become non-centrosymmetric in the nematic and smectic phases. It is therefore necessary to determine the optimum values of electric field frequency and intensity to be used for second harmonic generation.

Dielectric measurements reflect both electronic and orientational polarizations. The knowledge of

dielectric constants ϵ_{\parallel} and ϵ'_{\perp} gives fruitful informations about the structure of the mesophase.

It can be very interesting to get special cells in order to be able to have precise measurements on some liquid crystals with a very small amount of material (some mg).

The compound CBOOA is one of the most studied material for the smectic A \rightarrow nematic transition : the phase is smectic A between 73° and 83 °C and nematic between 83° and 109 °C. This material presents a quasi second order transition [6] to the nematic phase and has a partially bilayered structure [7, 8]. Many studies have been made with this compound : thermomechanical [6], elastic constant [9], transition nematic smectic and ultrasonic absorption [10, 11], mechanical intramolecular relaxation time, calorimetric and magnetic anisotropy [12], viscosity and magnetic measurements for N \rightarrow S_A transition [13], viscosity by NMR and DMR studies [13, 14]. The DC conductivity *versus* temperature was given by Mircea-Roussel *et al.* [15]. The value of dielectric anisotropy of CBOOA is positive ($\Delta\epsilon > 0$).

In the present work, the dielectric and elastic

constants, and their variations with AC or DC voltage amplitude, magnetic field intensity and with temperature are given.

2. Experimental.

Cells are constituted of two microscope glass plates. These plates are attacked by fluorhydric acid, the depth depends on the processing duration and the acid concentration. The glass plates are then coated with chromium and gold thin films evaporated successively. The adherence of these electrodes is very satisfactory.

The cell thickness is determined from capacity measurements without liquid crystal. Sometimes a glass lens of large focal distance (600 mm) is used as lower electrode. A small quantity of studied material is adequate : a thickness of about $5 \mu\text{m}$ is easily obtained (Fig. 1).

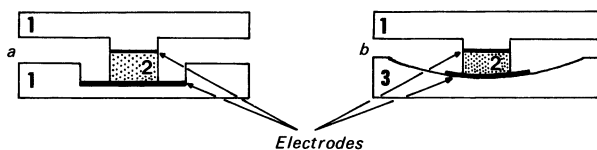


Fig. 1. — Measuring cells a) with two attacked glass plates, b) with an attacked glass plate and a lens, 1. glass plate, 2. liquid crystal, 3. lens.

The sample cell is fixed in a flat copper box heated with paste fixed resistances (Foil Minco). The whole system is of reduced dimensions and can be introduced between the poles of an electromagnet.

The temperature of the cell is thermostated to $\pm 0.2^\circ\text{C}$ and a platine resistance is used to test the liquid crystal temperature. The electrical connections are carefully realized to avoid parasitic impedances.

Dielectric measurements are performed using the cell as a capacitor of area $S = 7.06 \text{ mm}^2$ and of thickness $d = 30 \mu\text{m}$ in a large frequency range (10^{-3} to $2 \times 10^6 \text{ Hz}$) on cooling the sample.

The complex permittivity is given by :

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

with : $\varepsilon' = Cd/\varepsilon_0 S$ and $\varepsilon'' = \varepsilon'/RC\omega = \sigma/\omega$.

Measurements of the components of the complex permittivity in nematic and smectic phases are performed in two geometries : $\mathbf{E}, \mathbf{H} // \mathbf{n}$ and $\mathbf{H} \perp \mathbf{n}$.

In the lower frequency range (10^{-3} to 10 Hz) the capacitance and conductance are measured with a semi-automatic apparatus achieved in our laboratory [16].

From 100 Hz to 100 kHz , we used a General Radio 1610 bridge and from 10 kHz to 2 MHz an automatic HP 4275 bridge controlled by a microcomputer HP 85F.

3. Results and discussion.

The transition temperatures were determined from capacitance measurements for frequencies between 10 kHz and 2 MHz with heating and cooling rates of $0.5^\circ\text{C}/\text{mn}$ and from differential scanning calorimetry (D.S.C.). Capacity *versus* temperature is given in figure 2 for $f = 10 \text{ kHz}$.

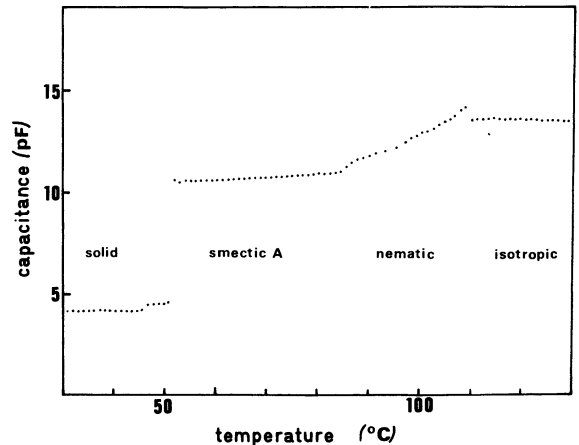


Fig. 2. — Capacity as a function of temperature at $f = 10 \text{ kHz}$.

The correspondence between both methods is very satisfactory. Moreover the capacitance measurements allow the detection of the smectic $A \rightarrow$ nematic transition.

The variation of the conductance $G(\omega)$ and capacity $C(\omega)$ are given *versus* frequency for some temperatures in figure 3. The amplitude of the measurement electric field was about 100 mV in order to avoid any orientation of the sample.

$\bar{\varepsilon}'$ and $\bar{\sigma}(\omega)$ are given for the different phases in table I at a frequency $f = 10 \text{ kHz}$.

Table I.

Phase	Isotropic	Nematic	Smectic A	Crystal
$T (^\circ\text{C})$	130	105	60	20
$\bar{\varepsilon}$	6	5	4.2	2.2
$\bar{\sigma} (\Omega \cdot \text{cm})^{-1}$	1.2×10^{-7}	5.9×10^{-8}	9×10^{-9}	1.7×10^{-12}

We observe two distinct domains in the curves : the high frequency range (10^3 - 10^5 Hz) where the capacitance and conductance are constant, which reflects the bulk properties and the lower frequency range (10^{-3} - 10^3 Hz) corresponding to ionic phenomena. In fact, the important increase of the capacitance at low frequencies is due to the presence of ionic impurities near the electrodes (blocking effect). To avoid this blocking effect, the dielectric

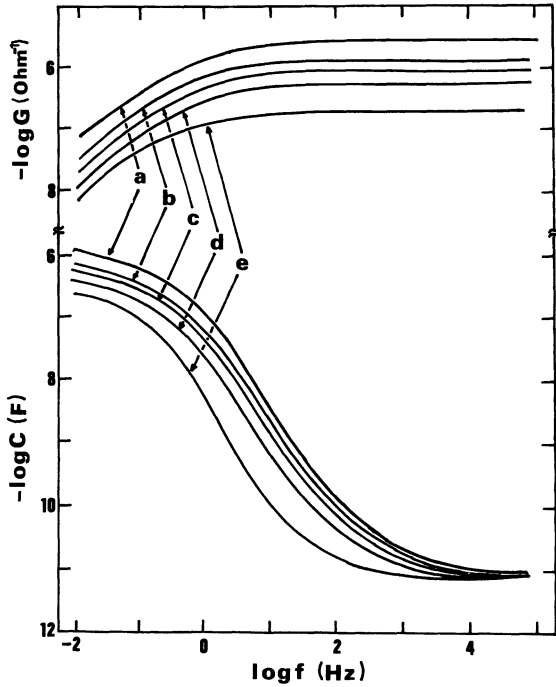


Fig. 3. — Dielectric spectra (conductance and capacitance) for various temperatures a) $T = 130^\circ\text{C}$; b) $T = 105^\circ\text{C}$; c) $T = 95^\circ\text{C}$; d) $T = 80^\circ\text{C}$; e) $T = 60^\circ\text{C}$.

measurements were performed in the following work at $f = 10\text{ kHz}$.

The variations of ϵ'_l and ϵ''_l are given in figures 4, 5, 6 and 7 versus the amplitudes of DC and AC applied electric fields respectively at $T = 105^\circ\text{C}$ and $f = 10\text{ kHz}$.

The variation of the two dielectric constant components ϵ'_l and ϵ'_\perp versus magnetic field intensity are given in figure 8 at $T = 105^\circ\text{C}$ and $f = 10\text{ kHz}$.

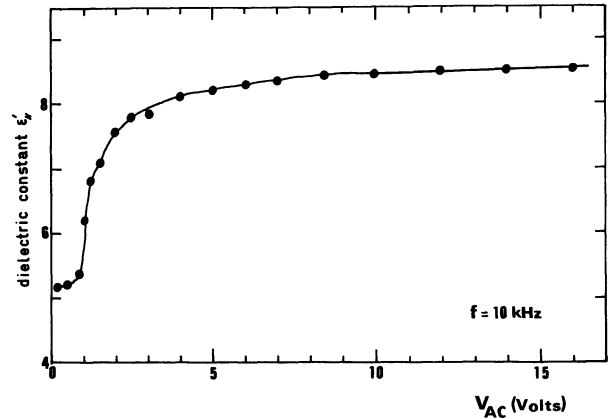


Fig. 6. — ϵ'_l as a function of V_{AC} at $T = 105^\circ\text{C}$.

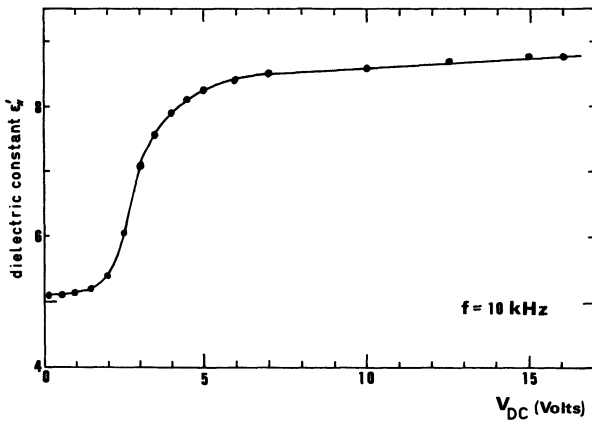


Fig. 4. — ϵ'_l as a function of V_{DC} at $T = 105^\circ\text{C}$.

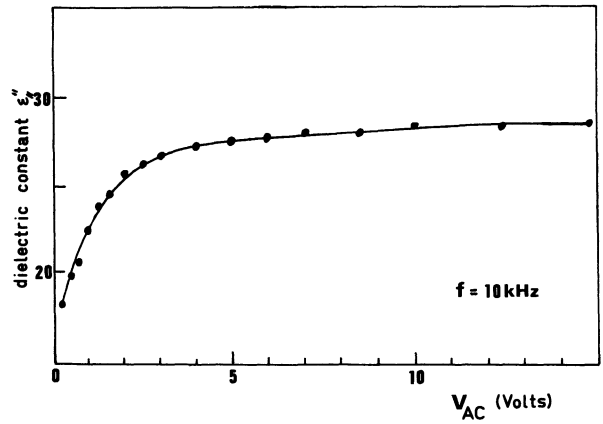


Fig. 7. — ϵ''_l as a function of V_{AC} at $T = 105^\circ\text{C}$.

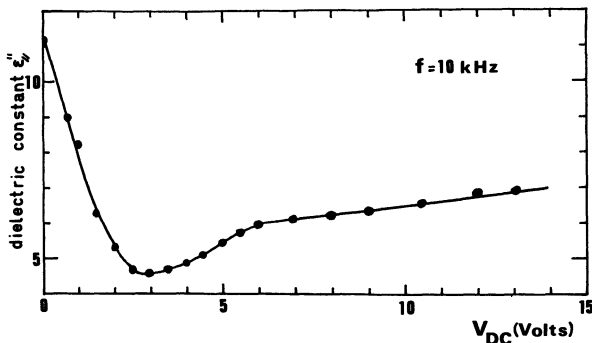


Fig. 5. — ϵ''_l as a function of V_{DC} at $T = 105^\circ\text{C}$.

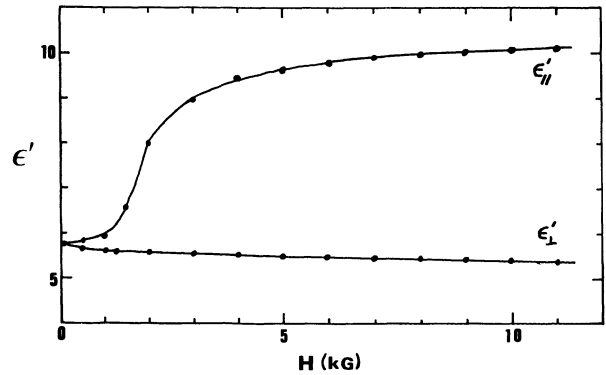


Fig. 8. — ϵ'_l and ϵ'_\perp as a function of magnetic field at $T = 105^\circ\text{C}$ and $f = 10\text{ kHz}$.

The variation of constants ϵ_{\parallel}' and ϵ_{\perp}' are given versus temperature at $f = 10$ kHz under a magnetic field of $H = 9$ kGauss in figure 9.

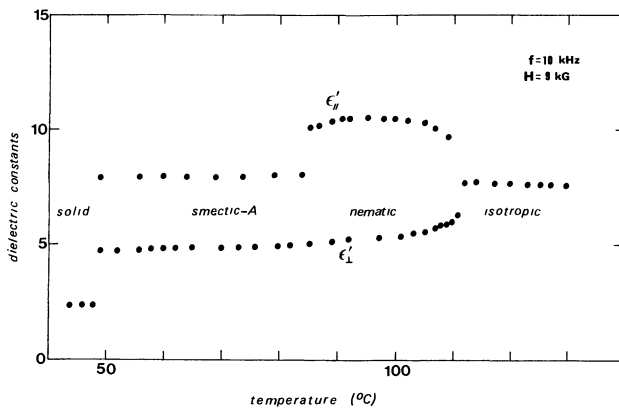


Fig. 9. — ϵ_{\parallel}' and ϵ_{\perp}' as a function temperature at $f = 10$ kHz and $H = 9$ kG.

These dielectrical measurements allow the determination of the values of dielectric anisotropy $\Delta\epsilon$, elastic constants and transport properties.

The parallel component of conductivity $\sigma_{\parallel} = \epsilon_{\parallel}' \omega$ decreases up to voltages higher than the Fredericksz transition when a DC electric field or magnetic field induces a deformation in liquid crystal, and then increases slowly above a threshold field. A different behaviour is observed with AC voltage in this case, σ_{\parallel} increases whatever this voltage may be.

The values of the dielectric constant ϵ' in the isotropic phase and the dielectric anisotropy $\Delta\epsilon$ one in the nematic phase are similar to those found by Billard *et al.* [17] (at $T = 85$ °C, $\Delta\epsilon = 5.5$ in the present work).

In the smectic range, however, these authors did not detect any dielectric anisotropy; this fact was probably due to desorientation in the sample. In our case, we observe continuity of ϵ_{\perp}' at the $S_A \rightarrow N$ transition while ϵ_{\parallel}' decreases strongly.

The same behaviour has been observed by Nagabhushan *et al.* [18] in the compound 4 OBCAB. The sharp drop in constant ϵ_{\parallel}' is due to the effect of dimerisation [19]: in the smectic phase of CBOOA, the antiparallel correlation is stronger than in the nematic phase. In fact, a fraction of the molecules form quadripolar dimers by head to head association and cannot participate to dipolar effects. Engelen *et al.* [8] estimated the fraction of dipolar correlation at 0.5.

It can be noticed that the slope of ϵ_{\parallel}' versus $(V_{DC})^{-1}$ is linear and close to the slope of ϵ_{\parallel}' versus

$(V_{DC})^{-1}$ with a much larger linearity range. This allows us to determine with accuracy the asymptotic value $\epsilon_{\parallel}'(V \rightarrow \infty) = 8.8$ and to obtain $\Delta\epsilon = 4.8$ at $H \rightarrow 10$ kG, $T = 105$ °C and $f = 10$ kHz.

With an applied magnetic field, the experimental results show that ϵ_{\perp}' is almost constant and very near $\bar{\epsilon}$ (without orientation). It can be deduced that the molecules are in the planar alignment (director parallel to the electrodes) in the nematic phase without external force (see Fig. 8).

The value of the threshold voltage for the Fredericksz transition is $V_{th} = 0.9$ V and is rather weak for nematic compounds with cyano substituents along their long molecular axis.

The Fredericksz transition allows the calculation of the splay elastic constant K_{11} from the threshold potential, with $\Delta\epsilon > 0$

$$V_{th} = \pi (K_{11}/\epsilon_0 \Delta\epsilon)^{1/2}$$

$$K_{11} = 3.99 \times 10^{-12} \text{ N}$$

$$\text{and } (K_{11}/\Delta\chi) = 5.33 \text{ (C.G.S.) .}$$

This value is close to that of Cheung *et al.* [20] obtained by optical measurements with an homeotropic orientation. These authors found $K_{11} = K_{33}$ (bend constant) at temperatures from 93 °C to the nematic-isotropic transition ($T = 109$ °C).

Finally, from our measurements, we can deduce that the compound CBOOA possesses a high polarizability ($\Delta\epsilon \approx 4.8$), it can be completely oriented with an electric field strength higher than 3 000 V/cm (AC or DC) or by a magnetic field. On the other hand, we can avoid ionic phenomena with frequencies higher than ≈ 10 kHz.

4. Conclusion.

We presented in this paper the results of dielectric measurements of cyanobenzylidene *p'* octyloxy-aniline obtained with a new measurement cell, which allows us to determine dielectric constants with satisfactory precision. Our data for the nematic phase are in good agreement with these reported by Billard [17] but we observe a different behaviour in the smectic-A phase which may be explained by the partial dimerisation of the molecules. We have determined the optimum conditions of orientation and utilisation of the compound CBOOA as an organic material suitable for second harmonic generation.

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