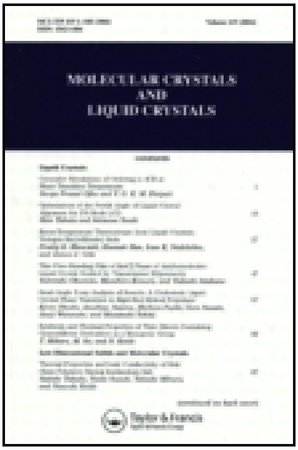

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A Study of 4 Nonanoate, 4′ Cyanobiphenyl Using Dielectric Relaxation Method

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A Study of 4 Nonanoate, 4′ Cyanobiphenyl Using Dielectric Relaxation Method

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In this paper, the results of a dielectric absorption study for 4 nonanoate 4′ cyanobiphenyl are presented. For electric field E perpendicular to director **n**, a very distributed domain can be observed. It can be interpreted as resulting from the superposition of rotation and libration movements of the molecule and of intramolecular movements. For E parallel to **n**, the reorientational movement of the molecule is observed. The activation energy of this mechanism is lower in SmA phase at $T > 30°C$ than in nematic phase. Moreover, if $T < 25°C$ the activation energy increases. These variations seem to be characteristic of a partially bilayer SmA phase with the appearing of monolayer S_C domains at $T < 25°C$.

INTRODUCTION

We present a dielectric study of 4 nonanoate, 4′ cyanobiphenyl (8 COOCB). This compound has been synthetized by Thomson Laboratory. Transition temperatures and formula of this compound are given in Figure 1.

The dipole moment of the molecule ($\mu \sim 3.8$ D) has an angle of about 25° with the CN bond axis. It is constituted mainly by the dipole moment of the cyano and nonanoate bonds.

Generally, dielectric studies for liquid crystals are carried out in rather narrow frequency band. Thus, the information obtained only shows a part of molecular dynamic phenomena. The results reported in this paper are the dielectric constants and the dielectric relaxations in a

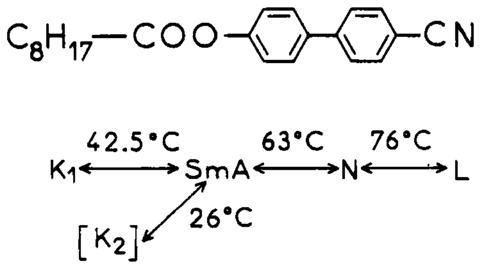


FIGURE 1 Structure of 8 COOCB

very wide frequency band (10 kHz–23 GHz). We also performed dielectric measurements for the smectic, nematic and liquid phases with both orientations of director **n** parallel or perpendicular to the electric field **E** applied.

EXPERIMENTAL

Measurements of real and complex parts of the complex permittivity $\epsilon^* = \epsilon' - j\,\epsilon''$ are simultaneously performed between 1 kHz and 26 GHz. A cell with 40 mg of sample is used in the frequency band ranging from 1 kHz to 1 GHz. It is constituted by a plan capacitor located at the end of a coxial line. Between 1 GHz and 18 GHz, a rectangular shaped coaxial cell with a short circuit extremity is used. Last, waveguide cells are used from 18 GHz to 26 GHz.

According to the frequency bands, various measurement methods are used: impedance bridges, resonance method,[1] amplitude and phase measurer, reflectometer devices, S.W.R. measurers. The sample temperature is stable within ±0.2°C. The orientation in nematic phase is obtained by placing the measurement cell in the gap of an electromagnet. The alignment in smectic phase is obtained by means of a slow decrease of the temperature of the substance submitted to a magnetic induction of 4 kG.

For the quasi-static permittivity, measurements are carried out with stable frequency and variable temperature. The dynamical measurements are obtained with stable temperature and variable frequency.

The measurement of the quasi-static permittivity is performed at 200 kHz in three phases. Figure 2 shows the evolution of $\epsilon'_{\parallel}$, $\epsilon'_{\perp}$ and ϵ'_{iso} versus measurement temperature. It can be noted that the permittivity variations do not correspond to a $1/T$ law for all phases. Variations obtained can be the consequence of interactions between neighbouring molecules. These interactions exist in all phases and lead to strong correlations in orientation motions of molecules.[2]

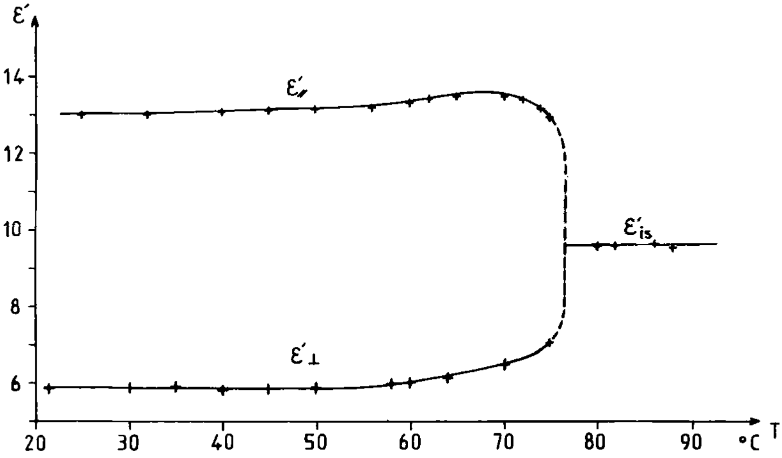


FIGURE 2 Variation of $\epsilon'_{\parallel}$, $\epsilon'_{\perp}$ and ϵ'_{is} versus temperature

The measurements of dynamic permittivity components are performed in the following conditions:

- $T = 85°C$ for isotropic phase
- $T = 45°C$ and $70°C$ for measurement direction $\mathbf{E} \perp \mathbf{n}$
- $17°C < T < 76°C$ for measurement direction $\mathbf{E} \parallel \mathbf{n}$

It can be noted that temperatures lower than 25°C correspond to the supercooled range of the S_A phase.

The evolution of the permittivity versus frequency depends on the measurement direction. This type of behavior has already been found for other compounds.[3]

For the measurement direction $\mathbf{E} \parallel \mathbf{n}$, whatever the temperature, the Cole and Cole diagrams obtained are half-circles shaped and centred on the abscissa axis (Figure 3). The critical frequencies F_c of these domains are 6 MHz and 1.7 MHz for nematic phase ($T = 70°C$) and smectic phase ($T = 45°C$), respectively.

Figure 4 shows the evolution of the critical frequency of this mechanism versus temperature. In this Figure, we can observe three parts characterized by straight lines with different slopes. From the latter, we can calculate the activation energy W of the mechanism observed. We obtain:

— $W = 0.76$ eV for the nematic phase

— $W = 0.50$ eV for the smectic phase at $T > 30°C$

— $W = 0.69$ eV for the smectic phase at $T < 25°C$

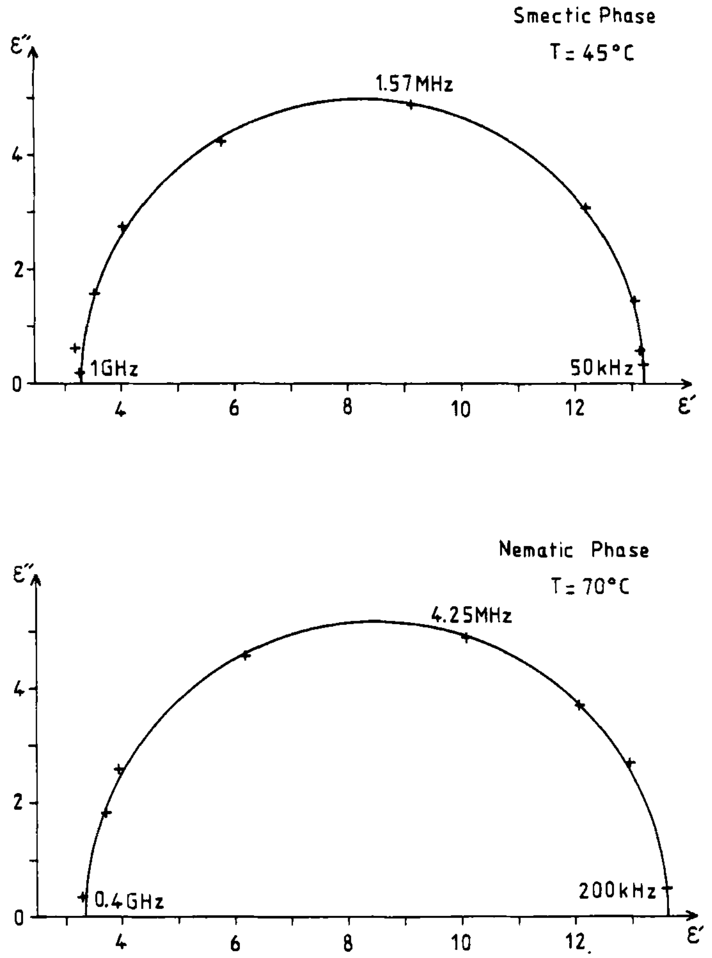


FIGURE 3 Cole and Cole diagrams obtained for E || n

Variations of activation energy at the transition N-S have already been pointed out in our laboratory,[3] then by other authors.[7,11] Besides, we note a variation of energy at $T < 25°C$. It is to be noted that there is no absorption domain in solid phase within this frequency range.

For measurement direction E ⊥ n, we obtain a widely distributed relaxation domain (Figure 5). The shape of this domain is due to the existence of several mechanisms of elementary dipole reorientation.

We tried to analyse these results using numerical analysis from the theory of Nordio *et al.*[4] This method has already been published.[5,6] Figure 6 shows the results obtained. We can note that a rather good

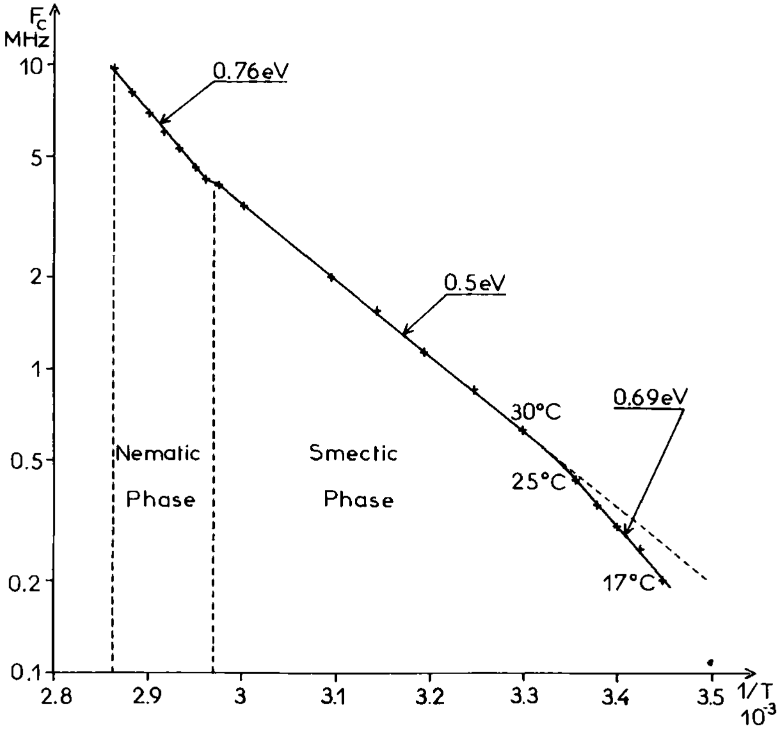


FIGURE 4 Evolution of the critical frequency versus temperature

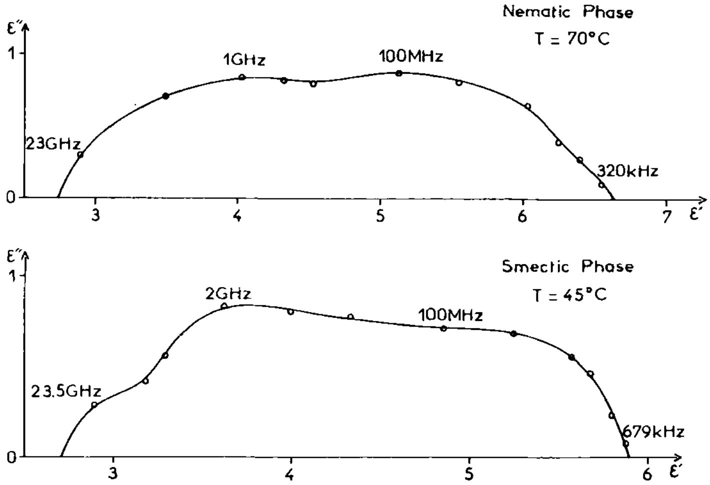


FIGURE 5 Cole and Cole diagram obtained for E ⊥ n

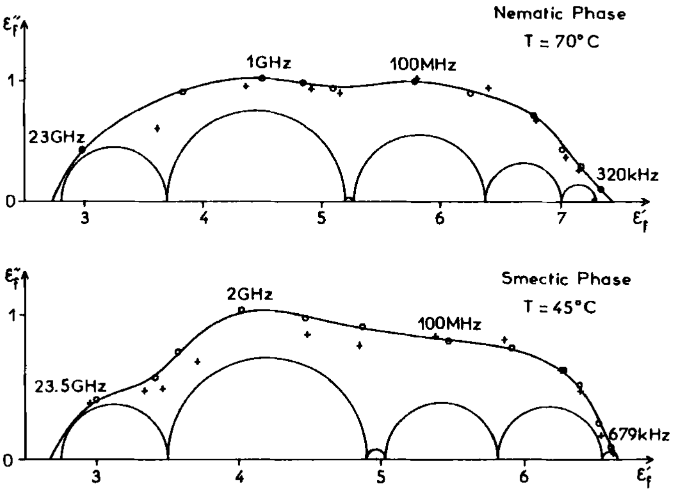


FIGURE 6 Results of the numerical analysis for E ⊥ n
○ : experimental points
+ : calculated points

agreement is obtained for lower frequencies. In the other hand, for higher frequencies important deviations exist between calculated and experimental points. The results obtained, then, are only qualitative. However, they show that there exist two elementary domains at least in this high frequency part. Therefore, the distribution of the whole spectrum is the superposition of four elementary domains at least. Every domain comes from a dipole movement.

For the isotropic phase, the Cole and Cole diagram obtained is distributed (Figure 7). However, we can see that the lower frequency part is of Debye type.

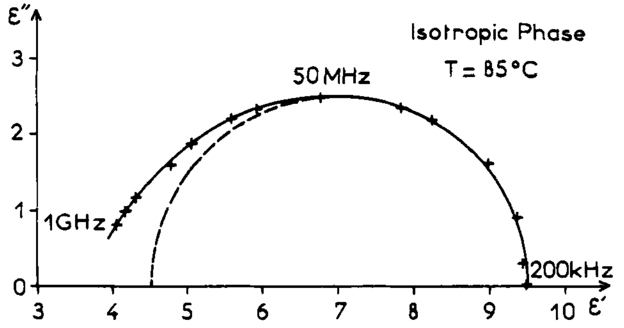


FIGURE 7 Cole and Cole diagram obtained for isotropic phase

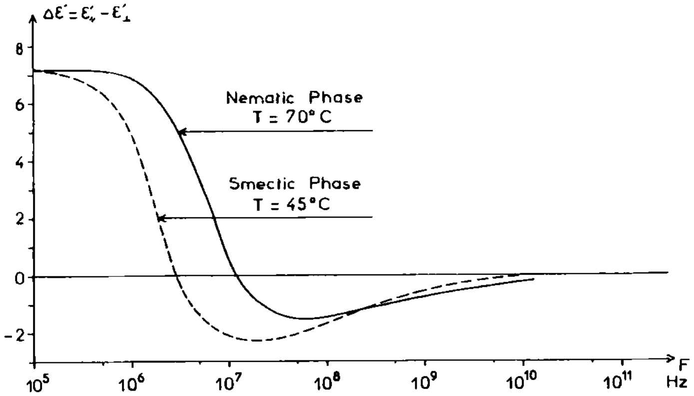


FIGURE 8 Evolution of the dielectric anisotropy versus frequency

Last, Figure 8 shows dielectric anisotropy $\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp}$ versus frequency for both phases. We note an inversion of this anisotropy within frequency range as large as two decades.

INTERPRETATION

To interpret the results obtained in anisotropic phases, it is to be remembered that the forces orienting molecules are linked to a nematic or smectic potential according to the corresponding phase. It orientates the molecular axis with a direction parallel to director **n**. Molecules can show, with respect to this mean position, various rotation or libration movements. In particular, there can be a reorientation motion round an axis perpendicular to the director, over the potential barrier "seen" by the molecule.

This latter motion is the cause of the relaxation mechanism of Debye type observed when **E** is parallel to **n**. The existence of the potential barrier explains the low value of the critical frequency ($F_c < 10$ MHz). The importance of the dipolar moment of the molecule (3.8 D) is the cause of the high amplitude of this domain ($\epsilon''_{\max} = 5$). The lack of distribution only results from the mechanism previously mentioned. Lastly, changes of activation energy observed can be due to two causes: it can come from a change of orientator potential. This is linked to interaction effects between molecules. It can also be due to a change of diffusion coefficient $D_{\perp}$. This is linked to steric effects. It can also be due to both.

Recently, results have been obtained from X-ray diffraction.[8] These results bring about information about the smectic phase. They show that:

i) The layer thickness of the SmA phase is approximately 1.4 L (L is the molecular length)

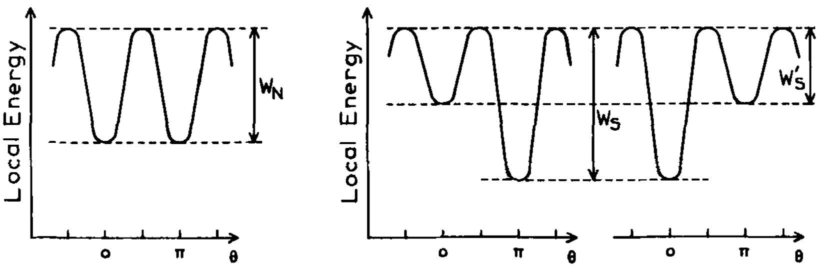
ii) At $T < 25°C$, there appears skewed cybotatic groups in SmA phase. The size of these groups corresponds approximately to eight molecules in all directions. The tilt angle is about 35°.

The results show that at $30°C < T < 76°C$, the smectic phase is partially bilayer. This behavior is often seen in the case of molecule with cyano end group.[9,10] The existence of antiferroelectric order in bilayer structure[12,13] shows that interaction forces applied on the dipole of each molecule tend to orientate it according to a preferential direction. We assume, in first approximation, that these forces are derivative of an orienting potential. Therefore, for each molecule, this potential is asymmetrical according to both preferential directions. The smectic potential shape in bilayer structure then is given in Figure 9.

It can be shown using dielectric relaxation theory that, in the case of large asymmetrical shape, the activation energy of relaxation mechanism resulting from the motion of molecule from a minimum potential to the other one is connected with the lower potential barrier (W'_S in Figure 9).[14] This can explain the change of activation energy to the transition N-S_A. This variation seems to be the result of deformation in shape of the potential "seen" by a molecule.

In nematic phase, this potential is symmetrical shape on an average and the activation energy is equal to W_N. In bilayer S_A the potential is asymmetrical shape and the activation energy is equal to W'_S.

The increase of activation energy in smectic phase at $T < 25°C$ can



NEMATIC PHASE BILAYER SMECTIC A PHASE

FIGURE 9 Potential shapes in anisotropic phases be explained in the same way if we consider the formation of monolayer S_C groups. Indeed, in this case, the potential "seen" by each molecule is symmetrical again.

This mechanism can also be used to explain changes of activation energy observed elsewhere[12] in the case of compound showing monolayer and bilayer S_A phases according to temperature.

In the case of electric field **E** is perpendicular to director **n**, the absorption obtained, is due to four mechanisms at least corresponding to different dipole motions. These mechanisms can come from the movement of the molecule constituted as a stiff rod or movement of parts of this molecule.

Our analysis using Nordio *et al.* theory shows that the low frequency domain is probably due to the rotation motion of the molecule round its mean axis. It also shows that the second domain comes from the libration motion of the molecule round both resting positions determined by two minimum of the smectic or nematic orienting potential. The numerical calculations we performed (Figure 6) using this theory are rather in good agreement with experimental results obtained in lower frequencies. We can note that the corresponding mechanisms are due to the whole molecule. This latter can be seen as a stiff rod in this frequency range.

In the case of higher frequencies, our analysis shows two domains but these results are qualitative. These domains seem to be linked to intramolecular movements. These motions lead to libration and rotation of dipolar moment applied on different parts of the molecule. They are the cause of the absorption observed in this frequency range. In particular, there can be a domain, with a critical frequency in the gigahertz range corresponding to the rotation of the nonanoate chain round the mean axis of the molecule.[15]

The observation of rotational motions of the molecule in lower frequencies, and of the nonanoate chain can be explained only if the CN bond has an angle with the molecular axis.

The existence of these movements of polar groups of the molecule explains the inversion of the dielectric anisotropy within a wide frequency band.

For the isotropic phase, the lower frequency part of the absorption observed is of Debye type. It comes from the rotational diffusion motion of the molecule. The distorsion observed in high frequencies is probably due to the intramolecular movements responsible for the high frequency domains observed for the measurement direction $\mathbf{E} \perp \mathbf{n}$ in anisotropic phases.

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