Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Characterization of the S_c Phase In a Liquid Crystal by Dielectric Relaxation

C. Druon [a] & J. M. Wacrenier [a]
[a] Equipe "Nouveaux Materiaux" du Centre Hyperfréquences & Semiconducteurs "C.H.S.", LA CNRS N° 287-Batiment P3-U.E.R. I.E.E.A.-Universite de Lille 1 59655 Villeneuve D'Ascq, Cedex, France
Version of record first published: 20 Apr 2011.

To cite this article: C. Druon & J. M. Wacrenier (1984): Characterization of the S_c Phase In a Liquid Crystal by Dielectric Relaxation, Molecular Crystals and Liquid Crystals, 108:3-4, 291-308

To link to this article: http://dx.doi.org/10.1080/00268948408078681

Mol. Cryst. Liq. Cryst., 1984, Vol. 108, pp. 291–308
0026-8941/84/1084–0291/$18.50/0

Printed in the United States of America

Characterization of the S_C Phase In a Liquid Crystal by Dielectric Relaxation

C. DRUON and J. M. WACRENIER

Equipe "Nouveaux Matériaux" du Centre Hyperfréquences & Semiconducteurs "C.H.S." LA CNRS N° 287-Bâtiment P3-U.E.R. I.E.E.A.-Universite de Lille 1 59655 Villeneuve D'Ascq Cedex (France)

(*Received February 2, 1984*)

The authors present a study of the dielectric relaxation of one compound with a S_C–N phase transition:

Octyloxyphenyl hexyloxybenzoate

The dielectric spectra observed clearly show that the S_C phase does not modify the reorientation motion of the molecules around their transversal axis. In the same way, they show that the rotational motion of the molecules around their longitudinal axis exists in S_C phase as well as in nematic phase. The use of a multi-domain model for the S_C phase enabled the authors to obtain the order of magnitude of the tilt angle of the molecules in the smectic layers. This angle is compared to the one yielded by the X-ray diffraction and a satisfactory agreement is obtained for this compound.

INTRODUCTION

The S_C phase in liquid crystals has been widely studied by many authors. This phase which is optically biaxial, exhibits a particular smectic structure since the molecules are tilted in the smectic layers. In particular, this structure can be characterized by the angle Ω of the average direction of the molecules with respect to the normal to the smectic planes. Several theoretical models have been proposed to

interpret the properties of this biaxial structure. These can be explained from dipole–dipole interactions[1] or from steric effects,[2] assuming that the rotation of the molecules around their long axis is frozen out. Other models, have been suggested which allow free rotation. They involve dipole–dipole interactions[3] or the second rank tensor orientational properties of smectic phases.[4] The influence of dipoles in the molecule[5] and the forces between dipoles and induced dipoles[6] have been studied. A model taking into account the orientation order of the chains in the molecule has also been proposed.[7]

The information concerning this structure has been obtained by means of several measurement methods.[8] The rotation of the molecules around their long axis in S_C phase has been shown by using the quasi-elastic diffusion of neutrons[9] or the nuclear quadripolar resonance.[10] Measurements of orientational order parameter and of transition enthalpy have been carried out by means of magnetic and calorimetric methods.[11] The measurement of the tilt angle of the molecules and its evolution versus temperature has been performed on various compounds by using optical methods,[12-15] Nuclear Magnetic Resonance,[16-17] X-ray diffraction,[18] Mössbauer spectroscopy[19] or the Electron Spin Resonance.[20-21] The angle Ω near the S_C–S_A transition has been obtained with a high resolution by using interferometer measurements.[22]

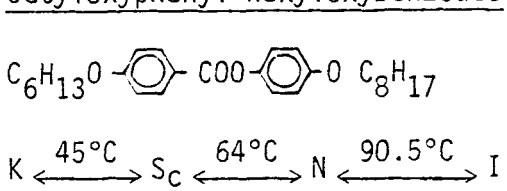
Dielectric relaxation has already yielded a few results on this S_C phase. The reorientation movement around the transversal axis of the molecules has been revealed on a series of four 4-*n*-alkyloxyphenyl 4-*n*-alkyloxybenzoate.[23] The measurement of the angle Ω of bis-(heptyloxy)-azoxybenzene has been performed at 1 MHz.[24] The static permittivity of various compounds has been measured and the value of Ω for the decyloxybenzoicacid-hexyloxyphenyl has been deduced from it.[25]

The measurement of dielectric absorption gives information on the anisotropic phases of the liquid crystals since this absorption is linked to the relaxation of the dipoles associated to the molecule. It is now well-known that dielectric spectra show absorption domains whose characteristics are linked to the rotational motions of the molecule around its longitudinal axis or its transversal axis.[26-28] To obtain sufficient information the study should not include merely the static permittivity. The wide frequency band dielectric absorption must be observed so that the various relaxation mechanisms can be revealed.

In this paper, we present a dielectric study of one compound with a S_C–N transition. The formulae and the transition temperatures are as

follows:

Octyloxyphenyl hexyloxybenzoate



Before the experimental study, we present the model of the S_C phase developed by some authors for the S_C–N transition.[16,29] Then, we give the dielectric relaxation correlation functions proposed by Nordio *et al.*,[30] already used for the study of S_A phases.[31] We generalised these to deal with the case of any orientation of the director. The analysis of these functions enables us to specify the experimental conditions for the study of the S_C phase. The results obtained are given and we can deduce the information concerning the rotational motions of the molecules and the tilt angle of these molecules.

FINDING OUT THE EXPERIMENTAL CONDITIONS NECESSARY TO THE CHARACTERIZATION OF THE S_C PHASE

Characterization of S_C phase

Contrary to samples which show a well oriented monodomain when a nematic to smectic A phase transition occurs in the presence of a magnetic field $\mathbf{H}_0$, the compounds with transition N → S_C exhibit a more complex orientation in the S_C phase. Some authors have proposed a model for the structure obtained in the S_C phase when the sample is cooled from the N phase to the S_C phase in a magnetic field $\mathbf{H}_0$.[16,29]

In this case, the structure obtained is such that all the molecules remain in the direction of $\mathbf{H}_0$. However, as no orientation is imposed to the smectic planes, a multidomain structure appears at the transition S_C ← N.

These domains are formed by a set of molecules parallel to $\mathbf{H}_0$. Each domain is characterized by smectic planes with a normal making an angle Ω with the direction $\mathbf{H}_0$. This case is shown in Figure 1.†

†In this article, $\mathbf{D}_0$ will be the initial direction of the magnetic field $\mathbf{H}_0$ which was used to obtain the structure in multidomains.

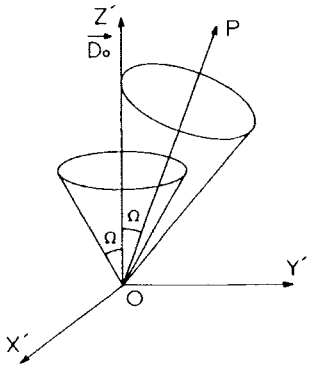


FIGURE 1 Geometry for the multi-domain model.

In the $X'Y'Z'$ coordinate system, $\mathbf{H}_0$ is parallel to $0Z'$. The normals to the different domains are assumed to be evenly and densely distributed on the surface of a circular cone having $0Z'$ as its axis and vertex half-angle Ω. In the S_C phase, if we consider a normal $0P$, when $\mathbf{H}_0$ is removed, the long axes of the molecules of the corresponding domains are the generating lines of an other cone having $0P$ as its axis and vertex half-angle Ω.

When a magnetic field $\mathbf{H}^{\ddagger}$ is applied to this structure, it can influence strongly the molecular arrangement. Thus, the following assumptions are suggested:

—**H** only acts on the orientation of the molecules and does not act on the orientation of the smectic planes.

—The molecules are free to reorient within the smectic layers and if **H** is sufficiently large, the director for a domain has a minimum angle with **H**.

—However, the direction of the molecules always makes an angle Ω with the normal to the smectic planes.

Correlation functions used in dielectric relaxation

Nordio *et al.* have developed a theory of the dielectric relaxation for the nematic phase.[30] In previous studies, we used this theory for the S_A phase as well.[31] They consider a first system of coordinates XYZ with $0Z$ parallel to the direction of the optical axis of the crystal and a second system of coordinates xyz linked to a molecule with $0z$ parallel

‡**H** will denote the direction of the magnetic field orienting the molecules in the smectic layers.

to the direction of the molecular axis. They showed that the correlation functions can be written as follows:

$$\langle \mu_Z(0)\mu_Z(t)\rangle = \langle D^1_{00}(0)D^{1*}_{00}(t)\rangle \cdot \mu_z^2 + \langle D^1_{01}(0)D^{1*}_{01}(t)\rangle \cdot \left(\mu_x^2 + \mu_y^2\right)$$

$$\langle \mu_X(0)\mu_X(t)\rangle = \langle D^1_{10}(0)D^{1*}_{10}(t)\rangle \cdot \mu_z^2 + \langle D^1_{11}(0)D^{1*}_{11}(t)\rangle \cdot \left(\mu_x^2 + \mu_y^2\right)$$

In these relations D^j_{lm} are the elements of Wigner's matrix and the terms between angular brackets are mean values.

The correlation functions $\langle D^1_{lm}(0)D^{1*}_{lm}(t)\rangle$ can be written as a summation of decreasing exponentials and moreover they can be represented by the first term with a very good approximation.

Thus, we obtain:

$$\langle \mu_Z(0)\mu_Z(t)\rangle = \Phi_{00}\cdot\mu_z^2 + \Phi_{01}\left(\mu_x^2 + \mu_y^2\right)$$

$$\langle \mu_X(0)\mu_X(t)\rangle = \Phi_{10}\cdot\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right) \qquad (1)$$

with $$\Phi_{lm} = A_{lm}\exp\left(-\frac{t}{\tau_{lm}}\right)$$

The theoretical values of some parameters A_{lm} and τ_{lm} have been calculated with respect to $\langle P_2\rangle$ by the authors and we completed them.

To extend this theory to the case of the S_C phase, we consider a third system of coordinates $X'Y'Z'$. This laboratory system and the first coordinate system XYZ are linked by Euler's angles ϕ, ψ, θ (Figure 2).

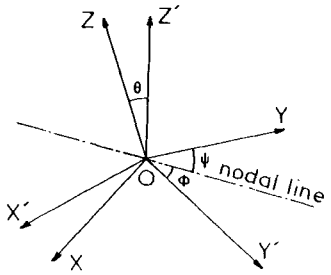


FIGURE 2 Coordinate system.

The components $\mu_{X'}$, $\mu_{Y'}$, and $\mu_{Z'}$ are obtained from the components μ_X, μ_Y and μ_Z by applying the rotation matrix $M(\phi, \psi, \theta)$.[32]

Thus, we obtain:

$$\mu_{X'} = (\cos\phi \cdot \cos\theta - \sin\phi) \cdot \mu_X + \cos\phi \cdot \sin\theta \cdot \mu_Z$$
$$\mu_{Y'} = (\sin\phi \cdot \cos\theta + \cos\phi) \cdot \mu_X + \sin\phi \cdot \sin\theta \cdot \mu_Z$$
$$\mu_{Z'} = -\sin\theta \cdot \mu_X + \cos\theta \cdot \mu_Z$$

We can deduce the correlation functions in a general case for a molecule with a main axis at a tilted angle θ with respect to $0Z'$.

$$\Phi_{Z'}(t) = \langle \mu_{Z'}(0)\mu_{Z'}(t)\rangle = \langle\cos^2\theta\rangle\left[\Phi_{00}\mu_z^2 + \Phi_{01}\left(\mu_x^2 + \mu_y^2\right)\right] + \langle\sin^2\theta\rangle\left[\Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)\right]$$

$$\Phi_{X'}(t) = \langle \mu_{X'}(0)\mu_{X'}(t)\rangle = \langle\cos^2\phi \cdot \sin^2\theta\rangle\left[\Phi_{00}\mu_z^2 + \Phi_{01}\left(\mu_x^2 + \mu_y^2\right)\right] + \left(1 - \langle\cos^2\phi \cdot \sin^2\theta\rangle\right)\left[\Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)\right]$$

$$\Phi_{Y'}(t) = \langle \mu_{Y'}(0)\mu_{Y'}(t)\rangle = \langle\sin^2\phi \cdot \sin^2\theta\rangle\left[\Phi_{00}\mu_z^2 + \Phi_{01}\left(\mu_x^2 + \mu_y^2\right)\right] + \left(1 - \langle\sin^2\phi \cdot \sin^2\theta\rangle\right)\left[\Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)\right] \quad (2)$$

In the right-hand part of these expressions, the terms between angular brackets are the mean value of the trigonometric functions for all the equivalent positions of the molecule according to the configuration studied.

Application of the formalism to the study of the S_C phase

Relations (1) and (2) allow the study of the experimental conditions which are to be taken into account according to the information wanted.

When only the characteristics of the relaxation domains are studied, we need to consider a structure where all the molecules are aligned according to a direction $0Z'$. For this purpose, the fields $\mathbf{H}_0$ and $\mathbf{H}$ placed parallel to $0Z'$ and relations (1) are used.

It is also possible to obtain information about the tilt angle Ω of the molecules. Indeed, the orienting field $\mathbf{H}$ can be applied in a direction different from the initial direction of $\mathbf{H}_0$ that we called $\mathbf{D}_0$. For instance, if $\mathbf{H}$ is applied perpendicularly to $\mathbf{D}_0$, the molecules will

orient in the smectic planes of each domain so as to be at a minimum angle with **H**.

In the case of $\mathbf{D}_0$ oriented parallel to $0Z'$ and **H** parallel to $0X'$, Figure 3 represents the position of a molecule in a domain.

The normal $0P$ to the smectic planes of the domain considered makes an angle Ω with $0Z'$. This is true for all the other domains of the sample. Therefore, ϕ' can have all the equiprobable values between 0 and 2π. In the domain considered, the molecule represented by $0M$ is located in the plane defined by $0X'$ and $0P$, and $0M$ makes an angle θ with $0Z'$. Therefore, $\cos^2\theta$ and $\cos^2\phi \cdot \sin^2\theta$ can be calculated as a function of Ω and ϕ'. The mean values $\langle\cos^2\theta\rangle$ and $\langle\cos^2\phi \cdot \sin^2\theta\rangle$ found in relations (2) can be calculated, taking into account the

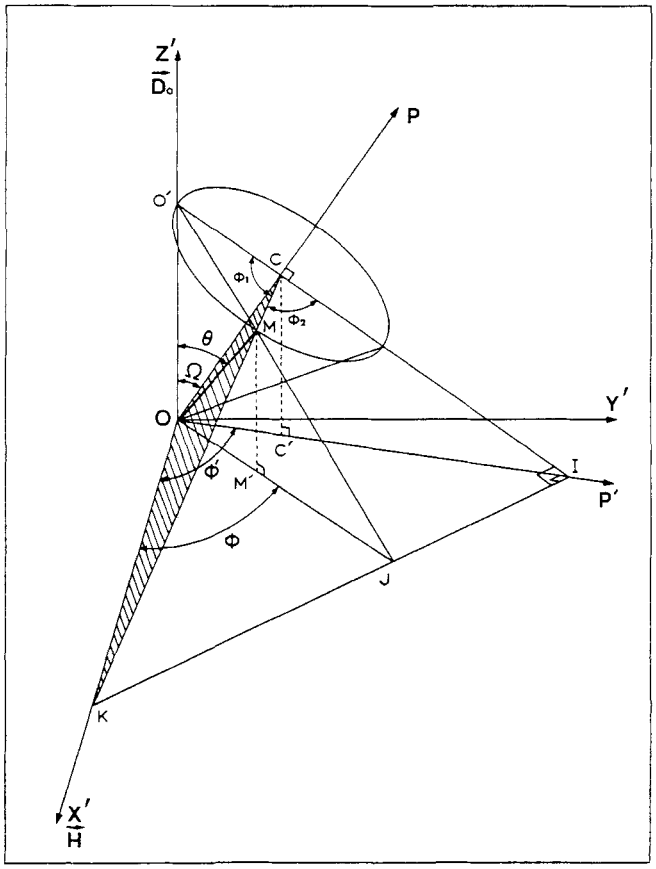


FIGURE 3 Coordinate system for the S_C model.

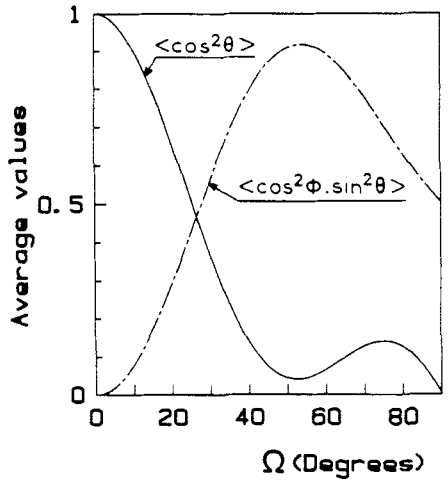


FIGURE 4 Evolution of $\langle \cos^2\theta \rangle$ and $\langle \cos^2\phi \cdot \sin^2\theta \rangle$ as a function of the tilt angle Ω.

previous remark about ϕ'. The relations obtained are as follows:

$$\langle \cos^2\theta \rangle = \cos^4\Omega + \sin^2\Omega \cdot \cos\Omega(1 - \cos\Omega) - \frac{2}{\pi}\sin\Omega \cdot \cos^3\Omega \cdot \log\left(\frac{1 + \sin\Omega}{1 - \sin\Omega}\right)$$

$$\langle \cos^2\phi \cdot \sin^2\theta \rangle = \frac{\sin^2\Omega}{2}(1 + 2\cos^2\Omega) + \frac{\sin^2\Omega}{\pi}\left[\sin\Omega + \cos^2\Omega \cdot \log\left(\frac{1 + \sin\Omega}{\cos\Omega}\right)\right]$$

The evolution of these mean values versus angle Ω is represented in Figure 4. Thus, the value of Ω can be obtained by measuring the complex permittivity for orientation of the electric field **E** and of the orienting magnetic field **H** either parallel or perpendicular to the direction $0Z'$.

EXPERIMENTAL RESULTS

Experimental

The measurement of complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$ is performed within a wide frequency band (1 Hz–1 GHz). The cell used is a plane capacitor located at the end of a coaxial line.[33] The alignment of the

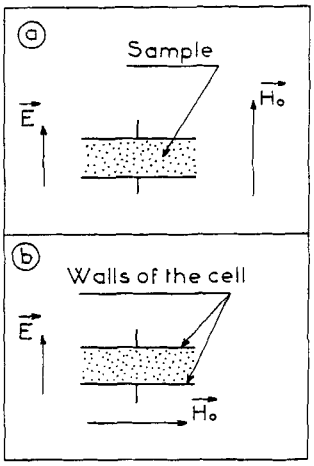


FIGURE 5 Geometry showing the direction of the measurement electric field **E** and of the alignment magnetic $\mathbf{H}_0$. (a) $\mathbf{E} \| \mathbf{H}_0$; (b) $\mathbf{E} \perp \mathbf{H}_0$.

sample is achieved according to a direction $\mathbf{H}_0$ parallel or perpendicular to the electric field using a magnetic field of 11 kG (Figure 5). The alignment in the smectic phase is achieved by a slow cooling from N phase in the magnetic field $\mathbf{H}_0$. The measurements in this S_C phase are performed with an orienting magnetic field **H** parallel or perpendicular to the initial direction $\mathbf{D}_0$.

The measurements are carried out at variable frequency and constant temperature for the study of the dynamic permittivity. The temperature remains stable with $\pm 0.1°C$. The accuracy on ϵ' and ϵ'' is 2% and 5%, respectively. The spectra obtained are limited to 1 GHz because experiments above this frequency would require too large quantities of material at the present time.

Static permittivity

The measurement of the static permittivity is performed at a low frequency inferior to the frequencies of the various relaxation phenomena. For the N phase, ϵ' is measured for two directions $\mathbf{E} \| \mathbf{D}_0 (\mathbf{E} \| \mathbf{n})$ and $\mathbf{E} \perp \mathbf{D}_0 (\mathbf{E} \perp \mathbf{n})$. For the S_C phase, the evolution of ϵ' is reported for **H** parallel to the direction $\mathbf{D}_0$.

We can see in Figure 6 that the dielectric anisotropy ($\Delta\epsilon' = \epsilon'_{\|} - \epsilon'_{\perp}$) is negative because the transversal component μ_t of the molecule dipole moment is superior to the longitudinal component. It can be noted that at the transition N – S_C, the plotting of the permittivity is continuous, which is an indication of the quality of the alignment of the molecules for the S_C phase with $\mathbf{H}_0$.

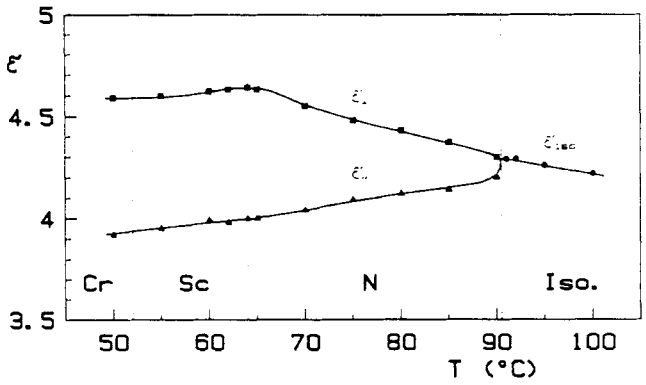


FIGURE 6 Static permittivity.

Dynamic permittivity for $\mathbf{E}\|\mathbf{D}_0$

In this case, the study of the dynamic permittivity is performed for $\mathbf{E}\|\mathbf{D}_0$ for the N and S_C phases and furthermore for $\mathbf{H}\|\mathbf{D}_0$ for the S_C phase. Figure 7 shows the spectra obtained for the S_C phase at $T = 55\,°C$ and for the N phase at $T = 80\,°C$. Three parts can be seen in the evolution of $\log \epsilon''$ versus $\log F$:

—a linear decrease, at low frequencies, due to the conductivity of the material,

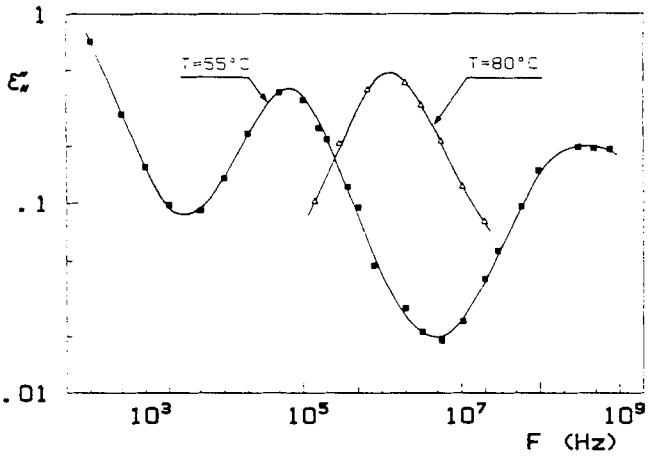


FIGURE 7 Evolution of $\epsilon''_{\|}$ versus frequency.

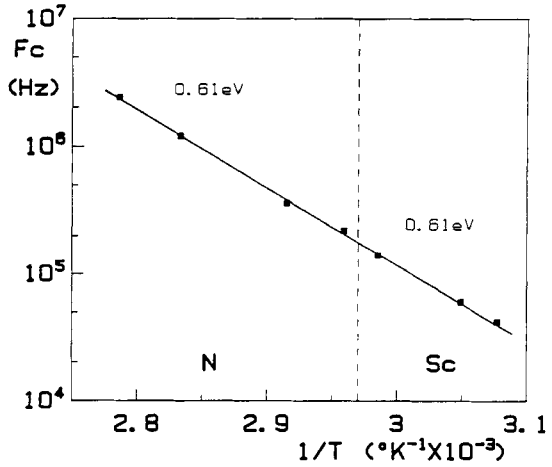


FIGURE 8 Evolution of F_c versus $1/T$.

—a relaxation domain at medium frequencies. This domain is of Debye type. This is due to the reorientation motions of the molecule around an axis perpendicular to the longitudinal axis L,[26,35]

—a relaxation domain at high frequencies, attributed to the libration motion of the molecule around its transversal axis and to the rotational motion around L.[31]

The evolution of the critical frequency F_c of the reorientation domain versus temperature yields information about the activation energy of this mechanism. Figure 8 shows that the variation of $\log F_c$ versus $1/T$ is linear. Using Arrhenius law $F_c = F_0 e^{-W/kT}$, we can deduce that the value of this energy is 0.61 eV for N and S_C phases.

Dynamic permittivity for $\mathbf{E} \perp \mathbf{D}_0$

In this case, the study of the dynamic permittivity is performed for $\mathbf{E} \perp \mathbf{D}_0$ for the N and S_C phases and furthermore for $\mathbf{H} \| \mathbf{D}_0$ for the S_C phase.

Figure 9 shows the spectrum obtained for the S_C phase at $T = 55\,^\circ C$. Again, a conductivity mechanism is observed at low frequencies. The absorption at high frequencies which is due to the rotational and librational motion of the molecule has a high amplitude. A very slight absorption can also be noticed at medium frequencies. The corresponding domain is partly hidden by the conductivity. The order of magnitude of the amplitude can be obtained by subtracting the value of the conductivity from the maximum value of this absorption. It can be deduced that this amplitude (ϵ''_{max}) is about 0.02.

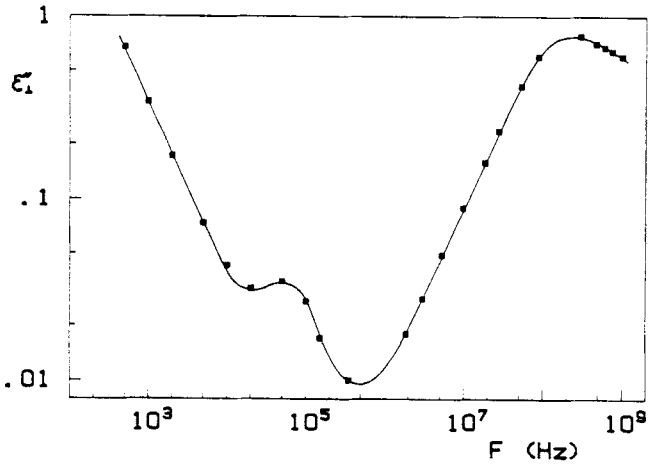


FIGURE 9 Evolution of $\epsilon''_{\perp}$ versus frequency.

This small domain is located in the frequency band corresponding to the reorientation motion of the molecules. It can be attributed to a very small part of molecules which are wrongly oriented. We can notice that the measurement of the complex permittivity for this type of alignment gives immediate information on the quality of the alignment of the sample. In the case of a perfect alignment, there is zero amplitude of this domain.

Influence of the orienting magnetic field H

As seen previously, information on the angle Ω can be obtained by changing the direction of the orienting magnetic field **H**. This study has been carried out for the medium and high frequency domains. We have measured the amplitude of these domains according to the direction of **H** for a sample oriented with either $\mathbf{E}\|\mathbf{D}_0$ or $\mathbf{E} \perp \mathbf{D}_0$.

TABLE I

Amplitude of the M.F. and H.F. domains with various molecular orientations

Alignment	$\mathbf{E}\|\mathbf{D}_0$				$\mathbf{E} \perp \mathbf{D}_0$			
Orientator field	$\mathbf{H}\|\mathbf{D}_0$		$\mathbf{H} \perp \mathbf{D}_0$		$\mathbf{H}\|\mathbf{D}_0$		$\mathbf{H} \perp \mathbf{D}_0$	
Amplitude → Temperature (°C)	$\delta_{\|}$	$\Delta_{\|}$	$\delta^H_{\|}$	$\Delta^H_{\|}$	$\delta_{\perp}$	$\Delta_{\perp}$	$\delta^H_{\perp}$	$\Delta^H_{\perp}$
52	0.4	—	0.18	—	—	—	—	—
55	0.4	0.18	0.195	0.41	0.02	0.78	0.25	0.48
62	0.4	—	0.175	—	—	—	—	—

Table I gives the results obtained for the various configurations. We have denoted δ and Δ the amplitude of M.F. and H.F. domains respectively.

INTERPRETATION

Motions of the molecule

The reorientation motion of the molecules is observed in N phase as well as in S_C phase. Moreover, we found out that the activation energy of this mechanism was the same in both phases. The value obtained (.61 eV) is of the same order of magnitude as the one found out for other compounds in N or S_A phases.[35-36] Thus, the appearance of the S_C phase do not change this type of motion. The rotational motion of the molecule around its longitudinal axis in the S_C phase is revealed. This experimental result agrees with other studies performed for various compounds.[9-10] Moreover, the amplitude of the corresponding domain does not appreciably change when the $N \rightarrow S_C$ transition occurs. Therefore, for this compound, there does not exist any tendency to the freezing out of the rotation of the molecule in S_C.

Calculation of the tilting angle Ω of the molecules

From the dielectric spectra and from the model adopted for the S_C phase, the tilting angle Ω in the smectic layers can be calculated. At the most four determinations are possible by taking into account the characteristics of the M.F. and H.F. relaxation domains for the various molecular orientations.

1. Determination from the M.F. domain for $\boldsymbol{E} \| \boldsymbol{D}_0$. First, Ω can be calculated from the measurements of amplitude of the M.F. domain and from the correlation functions given above. It can be noted that for this M.F. domain, only the term depending upon μ_z^2 is involved. The terms linked to Φ_{10} are characteristic of the H.F. domain and $\tau_{10} \ll \tau_{00}$.[30-31] Thus, we can write for the M.F. domain:

$$\Phi z'(t) = \Phi_{00}\langle \cos^2\theta \rangle \mu_z^2$$

$$\Phi x' = \Phi_{00}\langle \cos^2\phi \cdot \sin^2\theta \rangle \mu_z^2$$

For $\mathbf{H} \| \mathbf{D}_0$, $\quad \theta = 0 \quad$ thus $\Phi z'(t) = \Phi_{00} \cdot \mu_z^2 = A_{00} e^{-t/\tau_{00}} \cdot \mu_z^2$

For $\mathbf{H} \perp \mathbf{D}_0$, $\quad \Phi^H z'(t) = \Phi_{00}\langle \cos^2\theta \rangle \mu_z^2 = A_{00} e^{-t/\tau_{00}} \langle \cos^2\theta \rangle \cdot \mu_z^2$

The ratio of the amplitudes of the domains for these two orientations is directly linked to $\langle\cos^2\theta\rangle$. Thus, for $T = 55\,^\circ$C, $\delta_{\|}^H/\delta_{\|} = \langle\cos^2\theta\rangle = 0.488$. In Figure 4, the curve shows that $\Omega = 26\,^\circ$.

This determination is probably the most accurate because the measurement of the amplitude of the relaxation domain and the calculation of Ω are carried out in better conditions. Indeed:

—The relaxation domain is of Debye type.

—The measurements are performed with the same alignment. Therefore, the wall effect, if it exists, is the same for the two measurements necessary to this determination.

—The amplitude ratio measured does not depend upon the details of the dielectric relaxation theory used.

2. Determination from the M.F. domain for $\boldsymbol{E} \perp \boldsymbol{D}_0$.

$$\text{For } \mathbf{H} \perp \mathbf{D}_0, \qquad \Phi^H x' = \Phi_{00}\langle\cos^2\phi \cdot \sin^2\theta\rangle \cdot \mu_z^2$$

By using the expression obtained in the case of the previous alignment $(\mathbf{E}\|\mathbf{D}_0, \mathbf{H}\|\mathbf{D}_0)$: $\Phi z' = \Phi_{00}\mu_z^2$. At $T = 55\,^\circ$C we obtain: $\delta_{\perp}^H/\delta_{\|} = \langle\cos^2\phi \cdot \sin^2\theta\rangle = 0.625$. In Figure 4, the curve shows that $\Omega = 32.5\,^\circ$.

The value of Ω obtained here is markedly higher than the one calculated in the determination 1. This difference can be explained by the fact that the calculation involves the two directions of alignment $\mathbf{E}\|\mathbf{D}_0$ and $\mathbf{E} \perp \mathbf{D}_0$. We should therefore take into account a correcting factor occurring in the expression linking the permittivity measured to the correlation function.[37] However, we verified that, taking into account the amplitude of the domain studied, this factor is almost equal to 1 and thus does not appreciably modify the value calculated for Ω. The discrepancy observed can also come from the influence of the walls upon the orientation of the molecules. This influence is different in both directions of alignment. If this effect is important, it can lead to strong errors in the calculation of Ω performed by using this second determination.

3. Determination from the H.F. domain for $\mathbf{E}\|\mathbf{D}_0$. For the H.F. relaxation, the terms linked to Φ_{00} are not involved. Thus, we can write:

$$\Phi z'(t) = \langle\cos^2\theta\rangle\Phi_{01}\left(\mu_x^2 + \mu_y^2\right) + \langle\sin^2\theta\rangle\left[\Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)\right]$$

$$\Phi x'(t) = \left(1 - \langle\cos^2\phi \cdot \sin^2\theta\rangle\left[\Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)\right]\right.$$
$$+ \Phi_{01}\langle\cos^2\phi \cdot \sin^2\theta\rangle\left(\mu_x^2 + \mu_y^2\right)$$

$$\text{For } \mathbf{H}\|\mathbf{D}_0, \qquad \theta = 0, \qquad \Phi z' = \Phi_{01}\left(\mu_x^2 + \mu_y^2\right)$$

For $\mathbf{H} \perp \mathbf{D}_0$,

$$\Phi^{H}z' = \Phi_{10}\langle\sin^2\theta\rangle\mu_z^2 + \left[\Phi_{01}\langle\cos^2\theta\rangle + \Phi_{11}\langle\sin^2\theta\rangle\right]\left(\mu_x^2 + \mu_y^2\right)$$

Consider the ratio:

$$\frac{\Phi^{H}z'}{\Phi z'} = \frac{\Phi_{10}\langle\sin^2\theta\rangle}{\Phi_{01}} \cdot \frac{\mu_z^2}{\mu_x^2 + \mu_y^2} + \langle\cos^2\theta\rangle + \frac{\Phi_{11}}{\Phi_{01}}\langle\sin^2\theta\rangle$$

The terms A_{10} and A_{01} are equal and τ_{10}, τ_{01} and τ_{11} are nearly similar.[30-31] Moreover $\Phi_{z'}^{H}/\Phi_{z'}$ is equal to $\Delta_{\|}^{H}/\Delta_{\|}$ with a first approximation. Then, this ratio can be writen as follows:

$$\frac{\Delta_{\|}^{H}}{\Delta_{\|}} = \langle\sin^2\theta\rangle\frac{\mu_z^2}{\mu_x^2 + \mu_y^2} + \langle\cos^2\theta\rangle + \frac{A_{11}}{A_{01}}\langle\sin^2\theta\rangle$$

$$\langle\cos^2\theta\rangle = \frac{\dfrac{\Delta_{\|}^{H}}{\Delta_{\|}} - \left[\dfrac{\mu_z^2}{\mu_x^2 + \mu_z^2} + \dfrac{A_{11}}{A_{01}}\right]}{1 - \left[\dfrac{\mu_z^2}{\mu_x^2 + \mu_y^2} + \dfrac{A_{11}}{A_{01}}\right]}$$

The term $\mu_z^2/(\mu_x^2 + \mu_y^2)$ can be calculated from the spectra measured for the alignment $\mathbf{E}\|\mathbf{D}_0$, $\mathbf{H}\|\mathbf{D}_0$. We obtain:

- for the M.F. domain: $\Phi^{MF}z' = \Phi_{00} \cdot \mu_z^2$
- for the H.F. domain: $\Phi^{HF}z' = \Phi_{01}(\mu_x^2 + \mu_y^2)$

Using the amplitude ratio of these domains, we can write:

$$\frac{\mu_z^2}{\mu_x^2 + \mu_y^2} = \frac{A_{01}}{A_{00}} \cdot \frac{\delta_{\|}}{\Delta_{\|}}$$

Finally:

$$\langle\cos^2\theta\rangle = \frac{\dfrac{\Delta_{\|}^{H}}{\Delta_{\|}} - R}{1 - R} \text{ with } R = \frac{A_{01}}{A_{00}} \cdot \frac{\delta_{\|}}{\Delta_{\|}} + \frac{A_{11}}{A_{01}}$$

The theoretical values of the amplitude A_{lm} are calculated versus $\langle P_2\rangle$.[30-31] If $\langle P_2\rangle = 0.65$,[38] we obtain at 55 °C: $\langle\cos^2\theta\rangle = 0.65$ and consequently $\Omega = 20.5°$.

4. Determination from the H.F. domain for $\boldsymbol{E} \perp \boldsymbol{D}_0$.

$$\text{For } \mathbf{H} \| \mathbf{D}_0, \qquad \theta = 0 \quad \text{and} \quad \Phi x' = \Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)$$

$$\text{For } \mathbf{H} \perp \mathbf{D}_0, \qquad \Phi^H x' = \left(1 - \langle \cos^2\phi \cdot \sin^2\theta \rangle\right) \times \left[\Phi_{10}\mu_z^2 + \Phi_{11}\left(\mu_x^2 + \mu_y^2\right)\right] + \Phi_{01}\langle \cos^2\phi \cdot \sin^2\theta \rangle \left(\mu_x^2 + \mu_y^2\right)$$

With the same remarks as for the alignment $\mathbf{E} \| \mathbf{D}_0$, a first approximation can be deduced:

$$\langle \cos^2\phi \cdot \sin^2\theta \rangle = \frac{1 - \dfrac{\Delta_\perp^H}{\Delta_\perp}}{1 - \dfrac{1}{R}}$$

with $\langle P_2 \rangle = 0.65$, we obtain at 55 °C:

$$\langle \cos^2\phi \cdot \sin^2\theta \rangle = 0.49 \quad \text{and} \quad \Omega = 27°.$$

In the case of the last two determinations, the calculation is performed with some approximations and simplifying assumptions. Indeed, this relaxation domain is assumed to be of a Debye type. This is true only for frequencies lower than the apparent critical frequency of this domain. For higher frequencies, other mechanisms, such as the intramolecular motions, are involved in the relaxation, and conduce to a distributed shape to this domain.[28] Moreover, the relaxation theory used depends on a diffusion equation for the molecules submitted to a simple shape potential.[30] Finally, the calculation of Ω necessitates the knowledge of the order parameter for the compound considered. However, we verified that a variation of ± 0.03 for the value of $\langle P_2 \rangle$ only brings about a variation of $\pm 2\%$ for Ω.

Recapitulating table

All the values of Ω obtained at various temperatures are reported in table II.

Recently, A. M. Levelut has measured for this compound by means of X-ray diffraction an angle of 23 or 27° according to a direct measurement on the pattern or according to a deduction from the distance between smectic layers and molecular length. These values are reported in table II, last column.

TABLE II

Tilt angle Ω (in Degrees)

Measurement method					
Dielectric relaxation					
Domain used	M.F.		H.F.		
Alignment	$\mathbf{E}\|\|\mathbf{D}_0$	$\mathbf{E} \perp \mathbf{D}_0$	$\mathbf{E}\|\|\mathbf{D}_0$	$\mathbf{E} \perp \mathbf{D}_0$	
Determination → Temperature (°C)	1	2	3	4	X-ray diffraction
52	27	—	—	—	23
55	26	32.5	20.5	27	and
62	27.5	—	—	—	27

It must be noted that the definition of the mean direction of the molecules and hence of Ω is not unique. In fact, it depends upon the measurement method chosen.[22] However, for this compound, we see that the values obtained by the two measurement methods are rather similar. It can be seen in table II that the value of Ω obtained with determination 2 is the most different one. This point corroborates the remarks mentioned above concerning our measurements. We can also notice that the values obtained with the H.F. domain are not too different in spite of the previous remarks. It shows that when the dielectric spectra have not a M.F. domain, it is possible to use the H.F. domain to obtain the order of magnitude of Ω.

Finally, the study performed shows that Ω does not vary with the temperature. This is in accordance with other results obtained for compounds with this S_C–N transition.[8]

Acknowledgments

We wish to thank Dr. A. M. Levelut who performed the measurements of the tilting angle by the X-ray method. We also thank Drs. G. Durand, F. Hardouin and Y. Galerne for valuable discussions.

References

1. W. L. Mc Millan, *Phy. Rev. A*, **8**, 1921 (1973).
2. A. Wulf, *Phys. Rev. A*, **11**, 365 (1975).
3. D. Cabib and L. Benguigui, *J. Physique*, **38**, 419 (1977).
4. R. G. Priest, *J. Physique*, **36**, 437 (1975); *J. Chem. Phys.*, **65**, 408 (1976).
5. W. H. De Jeu, *J. Physique*, **38**, 1265 (1977).

6. B. W. Van Der Meer and G. Vertogen, *J. Physique Colloq.*, **40**, C3-222 (1979).
7. A. S. Paranjpe, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 93 (1982).
8. A. De Vries, *J. Physique. Colloq.*, **36**, C1-1 (1975).
9. H. Hervet, F. Volino, A. J. Dianoux and R. E. Lechner, *J. Physique Lett.*, **35**, L-151 (1974); *Phys. Rev. Lett.*, **34**, 451 (1975).
10. J. Seliger, R. Osredhar, V. Zagar and R. Blinc, *Phys. Rev. Lett.*, **38**, 411 (1977).
11. F. Hardouin, G. Sigaud, M.F. Achard and H. Gasparoux, *Ann. Phys.*, **3**, 381 (1978).
12. S. L. Arora, J. L. Fergason and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **10**, 243 (1970).
13. T. R. Taylor, J. L. Fergason and S. L. Arora, *Phys. Rev. Lett.*, **24**, 359 (1970); *Phys. Rev. Lett.*, **25**, 11 (1970).
14. D. Johnson, A. Saupe, *Phys. Rev. A.*, **15**, 2079 (1977).
15. R. Bartolino, J. Doucet and G. Durand, *Ann. Phys.*, **3**, 389 (1978).
16. R. A. Wise, D. H. Smith and J. W. Doane, *Phys. Rev. A*, **7**, 1366 (1973).
17. D. J. Photinos, P. J. Bos, J. W. Doane and M. E. Neubert, *Phys. Rev. A*, **20**, 2203 (1979).
18. M. Petrov, A. M. Levelut and G. Durand, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 221 (1982).
19. V. G. Goldanskii, O. P. Keudin, N. K. Kivrina, E. F. Makorov, V. Y. Rochev and R. A. Stukan, *Soc. Phys. JETP*, **36**, 1226 (1973).
20. E. Gelerinter and G. C. Fryburg, *Appl. Phys. Lett.*, **18**, 84 (1971).
21. G. R. Luckhurst, M. Ptak and A. J. Sanson, *Chem. Soc. Far. Tr. II*, **69**, 1752 (1973).
22. Y. Galerne, *Ann. Phys.*, **3**, 397 (1978); *Phys. Rev. A*, **24**, 2284 (1981); Thèse d'Etat Orsay (1983).
23. H. Kresse, A. Wiegeleben and D. Demus, *Kristall and Technik*, **15**, 341 (1980).
24. L. Benguigui and D. Cabib, *Phys, Stat. Sol. (a)*, **47**, 71 (1978).
25. A. Buka and L. Bata, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 159 (1979); *Mol. Cryst. Liq. Cryst.*, **63**, 307 (1981).
26. A. J. Martin, G. Meier and A. Saupe, *Symp. Faraday Soc.*, **5**, 119 (1971).
27. J. P. Parneix and A. Chapoton, *Mol. Cryst. Liq. Cryst.*, **78**, 115 (1981).
28. C. Druon and J. M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **88**, 99 (1982).
29. R. M. Hornreich and S. Shtrikman, *Solid State Commun.*, **17**, 1141 (1975).
30. P. L. Nordio, G. Rigatti and U. Segre, *Molec. Phys.*, **25**, 129 (1973).
31. J. M. Wacrenier, C. Druon and D. Lippens, *Molec. Phys.*, **43**, 97 (1981); C. Druon, unpublished results.
32. M. E. Rose, Elementary theory of Angular Momentum (Wiley) (1957).
33. C. Druon and J. M. Wacrenier, *J. Phys. E.: Sci. Instrum.*, **16**, 151 (1983).
34. M. D. Benadda, J. C. Carru and C. Druon, *J. Phys. E: Sci. Instrum.*, **15**, 132 (1982).
35. C. Druon and J. M. Wacrenier, *Ann. Phys.*, **3**, 199 (1978).
36. A. M. Levelut and C. Druon, *J. Physique Lett.*, **43**, L-193 (1982).
37. G. R. Luckhurst and C. Zannoni, *Proc. R. Soc. Lond. A*, **343**, 389 (1975).
38. A. Buka and W. H. De Jeu, *J. Physique*, **43**, 361 (1982).