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Dielectric relaxation in the smectic E phase of a liquid crystal

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Résumé. — Les auteurs présentent une étude de la relaxation diélectrique du p-phényle-benzylidène p'-butylaniline. Un domaine d'absorption, lié en particulier à la rotation des molécules autour de leur axe longitudinal est mis en évidence lorsque le champ électrique est perpendiculaire à l'axe optique. Lors de la transition $S_B \rightarrow S_E$ la fréquence critique de ce domaine diminue brutalement d'un rapport 5. De plus, l'énergie d'activation du mécanisme de rotation qui est de 0,26 eV en phase S_B passe à 0,62 eV en phase S_E . Ces résultats montrent clairement qu'en phase S_E le mouvement de rotation des molécules est fortement gêné. L'étude de ce mouvement en phase S_E est à notre connaissance la première effectuée à l'aide de la relaxation diélectrique dans ces conditions.

Abstract. — In this paper, we present a study of the dielectric relaxation of p-phenyl-benzylidene p'-butylaniline. When the electric field is perpendicular to the optical axis, an absorption domain due, in particular, to the rotation of the molecules round their longitudinal axis is observed. At the transition $S_B \rightarrow S_E$, the critical frequency of this domain sharply decreases. This frequency is about five times lower in the S_E than in the S_B phase. Moreover, the activation energy of this mechanism of rotation, which is 0.26 eV in the S_B phase, moves to 0.62 eV in the S_E phase. These results clearly show that the rotation at motion of the molecules is strongly hindered in the S_E phase. To our knowledge, the study of this notion in the S_E phase using dielectric relaxation with these conditions is the first one performed.

1. Introduction.

The smectic B and E phases show a three dimensional structure. The S_B phase is characterized by a hexagonal or pseudo-hexagonal arrangement in the plane of the smectic layers and with the molecular axes perpendicular to the layers or tilted. These phases have also been studied by X ray-diffraction. The S_E phase is characterized by a symmetry order more important than in the S_B phase and a model with a herring-bone structure has been proposed [1-3]. In this model, the rotation of the molecules about the long molecular axis is assumed to be frozen out at the transition $S_B \rightarrow S_E$. If the dipolar moment of the molecules has a component perpendicular to the longitudinal axis, the rotational motion of the molecules can be observed by dielectric relaxation.

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Fig. 1. — Static permittivity.

4. Dynamic permittivity.

The study of the dynamic permittivity allows us to obtain information concerning the molecular movements. In general, for $\mathbf{E} \parallel \mathbf{n}$, the dielectric spectrum is made of two absorption domains. The first one, at low frequencies, characterizes the reorientation of the molecules around a transversal axis [6]. The second domain, at high frequencies, is connected to the rotation around the longitudinal axis and to the libration motion (incomplete rotation around the transversal axis). For $\mathbf{E} \perp \mathbf{n}$, the absorption includes a domain located in high frequencies linked to rotational and librational motion of the molecules [6-7].

In the case of our compound, for $\mathbf{E} \parallel \mathbf{n}$, the domain due to the reorientation of the molecules is not observed. This can be explained if the dipolar moment does not have a longitudinal component or if the latter is too weak to be detected experimentally. On the other hand, for $\mathbf{E} \perp \mathbf{n}$, the magnitude of the absorption obtained is rather important. Figure 2 shows two characteristic parts :

- a linear part, at low frequencies below 1 MHz, resulting from conductivity of the material [8],
- an absorption domain in high frequencies (H.F.).

Figure 3 shows the change of ϵ'_1 versus frequency. The evolution of ϵ''_1 and ϵ'_1 in high frequencies are characteristic of relaxation mechanisms. Since the longitudinal component μ_l of the dipolar moment is very weak, the relaxation obtained is due to the transversal component μ_t . Then, the H.F. domain is mainly due to the rotation of the molecule about its longitudinal axis [9]. It can be noted that the extra absorption that appears in the high frequency part of this domain can be explained by intramolecular motions [7].

The study of the critical frequency F_c evolution of this domain H.F. versus temperature allows us to obtain information concerning the energy barrier to the rotation of the molecules. Figure 4, which shows the change of F_c as a function of $1/T$ can be described as follows. First, at the transition S_B - S_E , a very strong frequency jump can be seen. Second, if the rotation mechanism is assumed to obey an Arrhenius law :

$$F_c = F_0 \cdot e^{-w/kT}$$

the activation energy of this mechanism is found to be very different in S_B and S_E phases respectively :

$$W_B = 0.26 \text{ eV in the } S_B \text{ phase and } W_E = 0.62 \text{ eV in the } S_E \text{ phase}$$

Fig. 2. — Evolution of ϵ''_1 versus frequency at $T = 72^\circ\text{C}$.

Fig. 3. — Evolution of ϵ'_1 versus frequency at $T = 72^\circ\text{C}$.

Fig. 4. — Evolution of F_c versus $1/T$.

These results clearly show that in S_E , the characteristic time of the rotational motion is higher than in S_B , and that this mechanism requires much more energy in S_E than in S_B .

In conclusion, the dielectric relaxation shows that for this compound, the rotational motion of the molecule around its longitudinal axis exists also in the S_E phase but that this motion is considerably slowed down relative to the S_B phase.

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References

- [1] DOUCET, J., LEVELUT, A. M., LAMBERT, M., LIEBERT, L. and STRZELECKI, L., *J. Physique Colloq.* **36** (1975) C1-13.
- [2] BENATTAR, J. J., LEVELUT, A. M. and STRZELECKI, L., *J. Physique* **39** (1978) 1233.
- [3] DE VRIES, A., *Mol. Cryst. Liq. Cryst.* **63** (1981) 215.
- [4] BUKA, A., BATA, L., PINTER, K. and SZABON, J., *Mol. Cryst. Liq. Cryst. Lett.* **72** (1982) 285.
- [5] DRUON, C. and WACRENIER, J. M., *J. Phys. E.* **16** (1983) 151.
- [6] MARTIN, A. J., MEIER, G. and SAUPE, A., *Symp. Faraday Soc.* **5** (1971) 119.
- [7] DRUON, C. and WACRENIER, J. M., *Mol. Cryst. Liq. Cryst.* **88** (1982) 99.
- [8] MIRCEA-ROUSSEL, A., LEGER, L., RONDELEZ, F. and DE JEU, W. H., *J. Physique Colloq.* **36** (1975) C1-93.
- [9] NORDIO, P. L., RIGATTI, G. and SEGRE, U., *Molec. Phys.* **25** (1973) 129.