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

Dynamic Dielectric Anisotropy of Nematics with Respect to Molecular Structure

J. P. Parneix [a] & A. Chapoton [a]
[a] C.H.S. L.A. C.N.R.S. n[ddot] 287, Université de Lille I, Bătiment P3, 2e étage Villeneuve D'ASCQ, 59655, Cedex, (France)
Version of record first published: 14 Oct 2011.

To cite this article: J. P. Parneix & A. Chapoton (1981): Dynamic Dielectric Anisotropy of Nematics with Respect to Molecular Structure, Molecular Crystals and Liquid Crystals, 78:1, 115-122

To link to this article: http://dx.doi.org/10.1080/00268948108082150

Mol. Cryst. Liq. Cryst., 1981, Vol. 78, pp. 115–122
0026-8941/81/7804-0115 $06.50/0

Printed in the United States of America

Dynamic Dielectric Anisotropy of Nematics with Respect to Molecular Structure

J. P. PARNEIX and A. CHAPOTON

C.H.S. L.A. C.N.R.S. n° 287, Bâtiment P3, 2e étage, Université de Lille I, 59655 Villeneuve D'ASCQ Cedex (France)

(*Received February 24, 1981; in final form June 30, 1981*)

The dielectric spectra of several nematics, such as derivatives of cyclohexane and biphenyl, azoxybenzenes, benzoate esters and tolanes are reported. In each case, the complex permittivity measurements are performed for the two main directions of the nematic sample (parallel and perpendicular to the optical axis), up to the microwave region. A comparison of the spectra has led to a partial assignment of the absorptions observed. In fact, the spectra differ significantly with molecular structure. The dielectric dispersion is analyzed and interpreted as a function of the specificity of the different molecular groups, i.e., the bridging groups, the rings, or the terminal substituent groups. The interpretations proposed (reorientation motions, molecular interaction) are discussed.

INTRODUCTION

Recently, several reviews on liquid crystal dielectric properties have been published.[1] These reviews are mainly concerned with the static or low frequency permittivities. However, most of the relaxation mechanisms take place in the gigahertz region. We report here the preliminary results on dielectric dispersion in nematics as a function of molecular structure up to 25 GHz.

Such a study allows us:

—to predict, from molecular structure, the static dielectric anisotropy of mesomorphous substances, an important factor for applications.

—to get a better understanding of the reasons for the existence of mesophases by pointing out the particular molecular interactions occurring for these compounds.

THE SUBSTANCES INVESTIGATED

In order to specify the effects of various constituent groups on molecular interactions and their involvement in dielectric anisotropy, we have carried out a systematic study, investigating the influences of bridging groups, side chains and rings for a molecule of the general formula:

GENERAL FORMULA

We investigated several nematic compounds with the above molecular structure i.e., cyclohexanes, biphenyls, azoxybenzenes, tolanes and benzoates esters.

EXPERIMENTAL

The permittivity measurements ($\epsilon^* = \epsilon' - j\epsilon''$) over the wide frequency range (1 Hz − 25 GHz) were made using only three cells:

—a parallel plate capacitor cell located at the end of a coaxial line which was used up to 1 GHz. The cell and the corresponding measuring devices were described in a previous publication.[2]

—a distributed constant cell which was used between 1 GHz and 18 GHz. It consisted of a short circuited hybrid structure with the same geometrical sizes as the standard coaxial APC 7 connector. The measuring device was a Hewlett Packard network analyzer connected to a H.P. 9825 computer. A numerical method was used to obtain, at each frequency previously chosen, the permittivity components of the sample filling the cell.[3]

—a classical short-circuited waveguide cell which was used up to 25 GHz. In this frequency range the measurements were carried out using a Hewlett Packard waveguide reflectometer.

In all cases, the measuring field strength was chosen so that nonlinear effects were negligible.

The alignment of samples was achieved by means of an external magnetic field of 10 kG. Misalignment effects due to cell walls were negligible for a magnetic induction higher than 4 kG.[4]

The temperature of various cells was maintained constant to within ±0.05°C using an electronic regulated heating stage.

Therefore, the overall accuracy is estimated to be less than 2% on ϵ' and 5% on ϵ''.

Because of the uniaxial symmetry in nematics, two permittivities can be de-

fined for the measuring electric field parallel ($\epsilon_{\parallel}^*$) or perpendicular ($\epsilon_{\perp}^*$) to the sample optical axis. The dielectric dispersion is quite different within these two directions as will be shown below. We give the experimental results in the form of Cole and Cole diagrams at constant temperature as is usual for dielectric dispersion studies.

1. Variation of the bridging group and side chains

In Figure 1, the results obtained for the principal permittivities $\epsilon_{\parallel}^*$ and $\epsilon_{\perp}^*$ are given for various substances. The chemical formulae of the constituent molecules are given for each substance on the corresponding figure.

Some remarks can be made about the different dielectric absorption observed:

—in the case of the cyanobiphenyl (Figure 1a), we note a single Debye domain at radiofrequencies for $\epsilon_{\parallel}^*$, whilst for $\epsilon_{\perp}^*$ a broadened domain at middle frequencies is evident.

—with the tolane derivative (Figure 1b), the two preceding absorptions vanish completely and new domains of relaxation are observed in the gigahertz region.

—for the azoxybenzene derivatives and the benzoate ester derivative, we obtain similar spectra, i.e., a Debye domain at radiofrequencies for $\epsilon_{\parallel}^*$ and a domain at middle frequencies for the two directions. The parallel component is clearly separated from the radiofrequency domain, while the perpendicular component is slightly broadened toward the high frequencies when an alkoxy group is substituted for an alkyl group in the side chains.

2. Variation of rings

We give, in Figure 2, the results obtained when a cyclohexane ring is substituted for a benzene ring (PCH_7) starting from the heptylcyanobiphenyl CB_7, or when the same substitution is carried out for both rings (CCH_7). The results clearly show the changes in the dielectric absorption for the two directions.

Furthermore, it should be noted that for CCH_7, $\epsilon_{\parallel}^*$ is obtained when the directing magnetic field is perpendicular to the measuring electric field and conversely for $\epsilon_{\perp}^*$. This indicates the existence of a negative anisotropy of the molecular diamagnetic susceptibility in the case of this substance.[5]

DISCUSSION

1. Radiofrequency absorption

We shall consider the radiofrequency domain, which is usually the most studied because it is quite easy to obtain experimentally. It is well-known that the

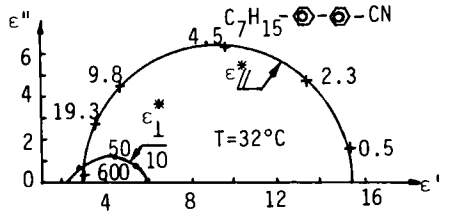

FIGURE 1a 4-heptyl 4'-cyanobiphenyl (CB7).

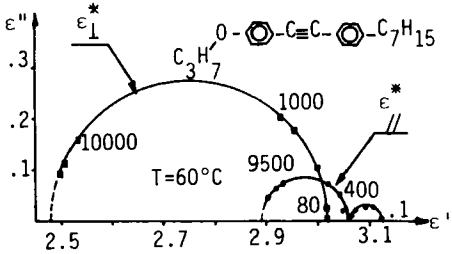

FIGURE 1b 4-propoxy 4'-heptyltolane.

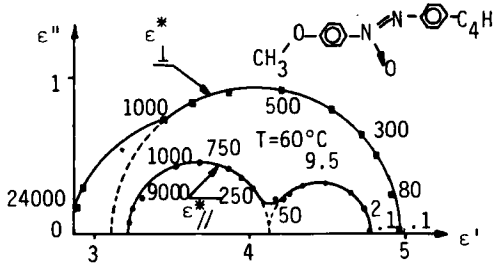

FIGURE 1c 4-methoxy-phenylazoxy-4'-butylbenzene (MPABB).

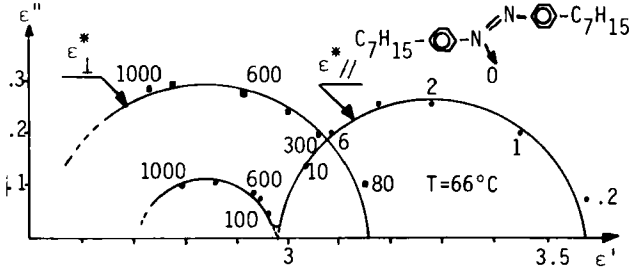

FIGURE 1d 4,4'-heptylazoxybenzène (HEPTAB).

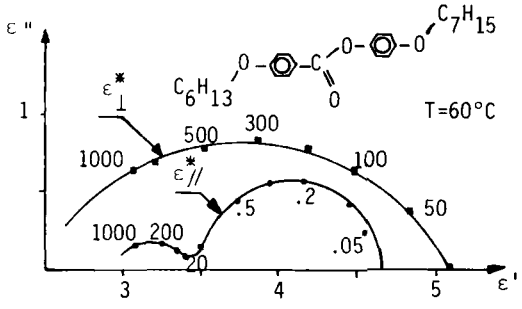

FIGURE 1e 4-hexoxy 4'-heptoxybenzoate.

FIGURE 1 Cole-Cole plots of $\epsilon_{\parallel}^{*}$ and $\epsilon_{\perp}^{*}$ in the nematic phase of various substances. The frequencies are given in MHz.

corresponding dielectric absorption is connnected with the orientation of the longitudinal component μ_l of the molecular dipole moment around the transverse axis.[6] This motion is much hindered by the nematic potential leading to large activation energies, as can be seen in Figure 3.

This figure shows the variations of the critical frequency against the inverse absolute temperature. The slope of straight lines deduced for each substance gives the activation energy W. It can be noted that the lowest value for W is obtained with the cyanobiphenyl CB_7. This can be understood as follows: the biphenyl molecules are nearly flat, and hence molecular rotations are likely to be easier than for the others. Especially, we can see the influence of rings on the activation energy: W increases from CB_7 to CCH_7. We can expect a more rigid molecular order with CCH_7.

2. Other relaxation mechanisms

Clearly two distinct mechanisms appear in unusual ranges of frequencies for liquid substances. The corresponding motions are again hindered by the nematic potential, but less than the motion investigated before. This time, they are connected with the orientation of the transverse component μ_t of dipole moments around the longitudinal axis. However, the experimental results allow us to distinguish between two motions according to the polar group position inside the molecule:

—the first motion is connected with the polar groups existing in the side chains. This can be seen in Figure 1b for tolane. The bridge —C≡C— is non polar. The only polar groups are in the side chains. The alkyl dipole is quasi-counteracted by the longitudinal component of the alkoxy group leading to a very small radiofrequency domain. Then the perpendicular component of the alkoxy group alone is responsible for the dispersion observed. Using a method

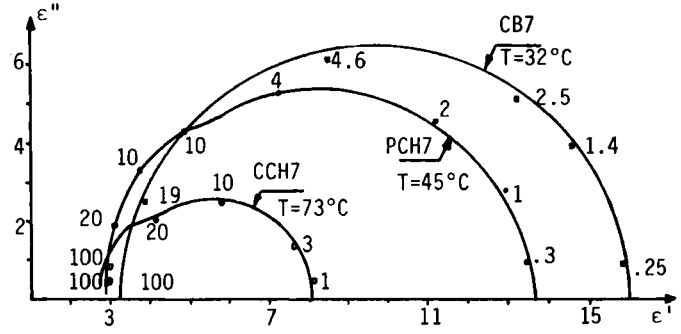

FIGURE 2a Cole-Cole plots of $\epsilon_{\parallel}^{*}$.

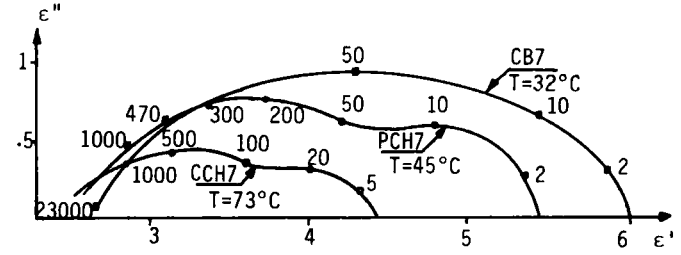

FIGURE 2b Cole-Cole plots of $\epsilon_{\perp}^{*}$.

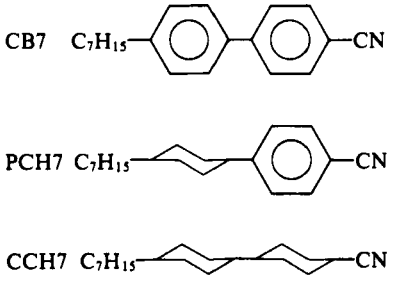

FIGURE 2 Cole-Cole plots in the nematic phase of cyano derivatives. The frequencies are given in MHz.

previously reported,[6] the dipole moment (1.3 D) and its tilting relative to the *para*-axis of the benzene ring (72°) agree quite well with the corresponding tabulated data.[7] The absorption takes place in the gigahertz range. Its amplitude ϵ''_M is about 0.3 in the perpendicular direction. This is observed again with M.P.A.B.B. (Figure 1c). For this substance the corresponding contribution in the parallel direction is too small to be observed. Finally, it can also be seen with the benzoate ester derivative (Figure 1e), where it is responsible for the broadening observed, although it is less pronounced than before because there

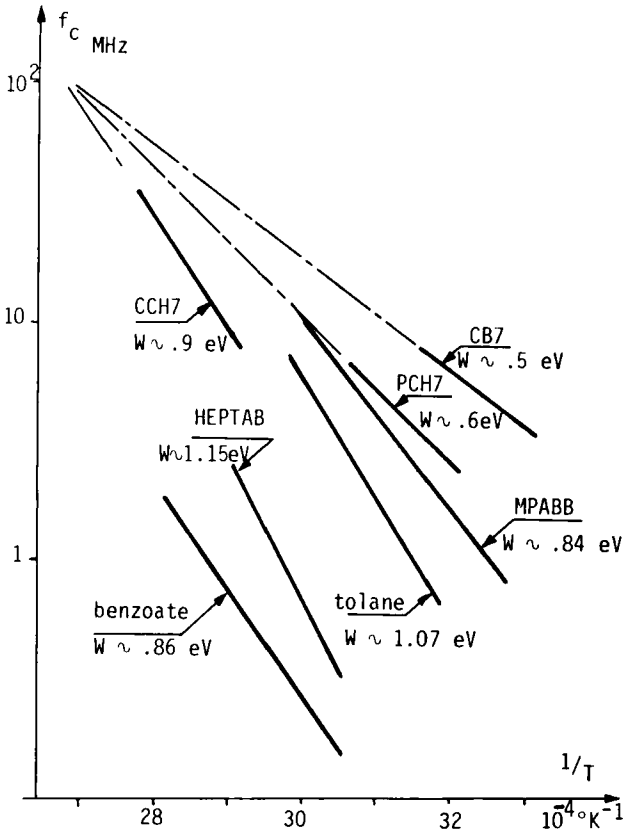

FIGURE 3 The critical frequencies as a function of 1/T for various nematic compounds (radio-frequency absorption).

is an alkoxy dipole group in each side chain leading statistically to a lower resultant perpendicular component.

—the second relaxation process involved in this section is connected with the perpendicular component of the bridge dipole moment. The existence of such a group leads in each case to a middle frequency absorption (~500 MHz) in the two directions (see Figures 1c, 1d, 1e). The lower frequency range (than for the chains) indicates that the bridging group is more rigidly fixed in the molecular body than the chains which can rotate almost freely. The corresponding dipole moment values calculated corroborated this interpretation.

Finally, in Figure 2, the molecular deformation can be seen on passing from the linear CB_7 to the chairlike molecule of CCH_7. The existence of a perpendicular component for the molecular dipole moment leads to the appearance of a middle frequency absorption in each measurement direction.

CONCLUSION

To sum up, our experimental results show the usefulness of the dielectric relaxation measurements particularly in the microwave region. They specify various motions of group moments according to their positions inside the molecular structure. Using further experimental investigation they could allow a better understanding of mechanisms responsible for the existence of mesophases.

References

1. See for example: W. H. de Jeu, *Solid State Physics,* Suppl. 14, Academic Press (1978).
2. C. Druon and J. M. Wacrenier, *J. Phys., (Paris)*, **38,** 47 (1977).
3. J. P. Parneix and S. Toutain, to be published.
4. D. Lippens, Thesis, Lille University, (1978).
5. L. Pohl, R. Eidenschink, J. Krause and G. Weber, *Phys. Lett.*, **65 A,** 2, 169 (1978).
6. D. Lippens, J. P. Parneix and A. Chapoton, *J. Phys., (Paris)*, **38,** 1465 (1977).
7. V. I. Minkin, O. A. Osipov and Y. A. Zhdanov, *Dipole Moments in Organic Chemistry,* Plenum Press, New York (1970).