**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

# Dielectric behaviour of liquid crystals with a pyramidal central unit

H. Kresse; S. Heinemann; R. Lunkwitz; C. Tschierske

**To cite this Article** Kresse, H. , Heinemann, S. , Lunkwitz, R. and Tschierske, C.(1997) 'Dielectric behaviour of liquid crystals with a pyramidal central unit', Liquid Crystals, 23: 6, 879 — 881

**To link to this Article: DOI:** 10.1080/026782997207803

**URL:** http://dx.doi.org/10.1080/026782997207803

LIQUID CRYSTALS, 1997, VOL. 23, NO. 6, 879–881

# Dielectric behaviour of liquid crystals with a pyramidal central unit

by H. KRESSE*, S. HEINEMANN
Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie,
Mühlpforte 1, 06108 Halle/S, Germany

R. LUNKWITZ† and C. TSCHIERSKE†
†Martin-Luther-Universität Halle-Wittenberg, Institut für Organische Chemie,
Kurt-Mothes-Straße 2, 06120 Halle/S, Germany

(*Received 16 May 1997; accepted 27 July 1997*)

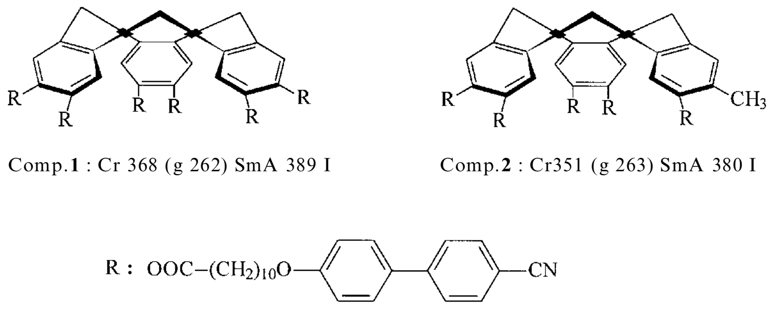
Dielectric measurements of oligomeric cyanobiphenyls connected to a pyramid-like central unit are presented. The data are interpreted in terms of the dynamics of the liquid crystalline units. There is no indication of reorientation of the central unit as whole or co-operative effects of piled up central units.

## 1. Introduction

Rod-like liquid crystalline molecules can be connected in different ways to oligomeric or polymeric aggregates [1]. One example is esterification using multifunctional alcohols or acids [2]. This gives the possibility of obtaining oligomers with a definite structure. Especially interesting are multifunctional central cores which themselves can aggregate into columns—for example, disk- and pyramid-like molecules [3–5]—and form in this way columnar liquid crystalline phases. Here one can expect a competition between two organizational principles which are dominated either by the side groups (classical nematic and smectic types) or by the cores (columns). One class of such supramolecular units contains derivatives of cyclotribenzylene synthesized for the first time by Tschierske and co-workers [6, 7]. Some of these specially designed compounds for dielectric investigations are shown below (figure 1). All temperatures are given in Kelvin. The glass transitions which could be observed by DSC measurements using a cooling rate of 10 K min$^{-1}$ have not been reported before in the literature [7]. It should be pointed out that the central core is not planar and therefore, one can expect ferroelectric behaviour if the cores are piled up [8]. Furthermore, the unsymmetrical substitution of compound **2** can result in an additional dielectric relaxation range if the coupling between the core and the strongly polar cyanobiphenyl units is strong enough [9].

## 2. Experiments

The dielectric measurements were carried out using a brass capacitor ($d$=0·2 mm). Capacity and resistance were measured by an impedance analyser HP-4192A. The whole measurement, including temperature control, was run by a computer. The sample could not be



Comp.**1** : Cr 368 (g 262) SmA 389 I

Comp.**2** : Cr351 (g 263) SmA 380 I

Figure 1. Structures of the compounds with pyramidal cores.

---

*Author for correspondence.

oriented by an external magnetic field of 0·7 T or a bias field of 35 V. The measurements were performed during cooling. Experimental data for the dielectric absorption of both samples are given in the 3D plots in figures 2 and 3. There is only one extended absorption range which is superimposed by the conductivity at low frequencies. For an ideal homeotropic orientation of such single axis systems one can expect an increase of the absorption intensity by a factor of three at the transition into the SmA phase. The decrease of the absorption intensity at the transition from the isotropic into the SmA phase indicates a spontaneous orientation of the layer normal perpendicular to the electrical measuring field.

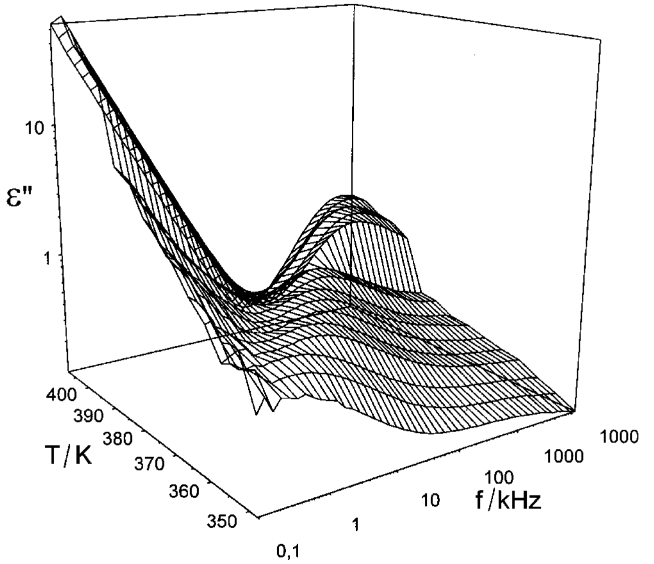


Figure 2. Dielectric loss of compound **1**.

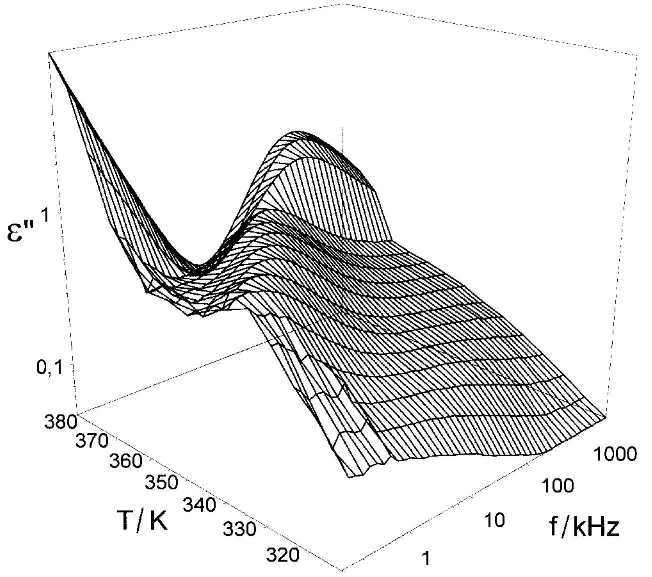


Figure 3. Dielectric loss of compound **2**.

In both cases the experimentally obtained dielectric losses were fitted to two Cole–Cole equations with consideration of the imaginary term $jA/f^N$ for the conductivity:

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{(1+j\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{(1+j\omega\tau_2)^{1-\alpha_2}} + \frac{jA}{f^N}. \quad (1)$$

For the fit, only the imaginary part of equation (1) was used. Parameters are the dielectric increments $\varepsilon_n - \varepsilon_{n+1} = \Delta_{n+1}$, the relaxation times $\tau_{n+1}$ and the distribution parameters $\alpha_{n+1}$ at different temperatures. The quantity $\omega = 2\pi f$ ($f$=frequency) was changed by variation of $f$ from 0·1 to $10^7$ Hz. From $\tau$ the relaxation frequencies $f_R$ were calculated according to $f_R = (2\pi\tau)^{-1}$.

The first mechanism is related to the reorientation of the CN dipoles about the short axes of the molecules. Due to the spontaneous orientation of the layer normal perpendicular to the electrical measuring field, this part is reduced and one observes a relatively strong contribution from the reorientation about the molecular long axis at higher frequencies [10]. This cannot be neglected (figure 4) and it was considered as the second mechanism.

The fitting parameters of the low frequency mechanism 1, $\Delta_1$, $\alpha_1$ and $\tau_1$ were used to calculate the static dielectric constants $\varepsilon_0$. This was necessary because the measured $\varepsilon$ increases at low frequencies due to the formation of an electrical double layer. In order to consider this effect, the conductivity term in equation (1) was replaced by $B/f^n$ and only the real part of

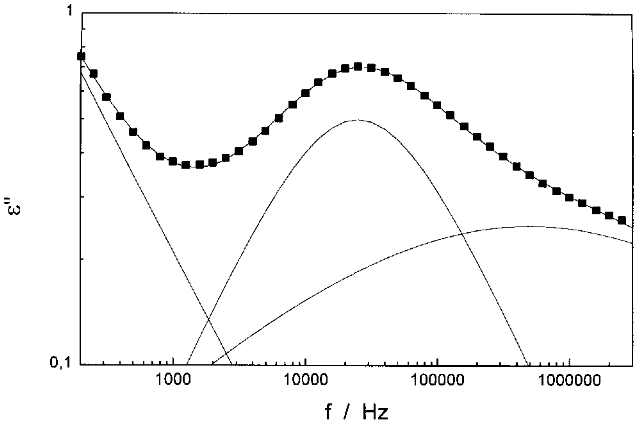


Figure 4. Measured points of $\varepsilon$ and the respective fitted curves according to equation (1) for compound **2** at $T = 371$ K. The fit parameters are: $\Delta_1 = 1{\cdot}28$, $f_1 = 25{\cdot}5$ kHz, $\alpha_1 = 0{\cdot}169$, $\Delta_2 = 1{\cdot}95$, $f_2 = 0{\cdot}506$ MHz, $\alpha_2 = 0{\cdot}683$, $A = 39{\cdot}7$ and $N = 0{\cdot}771$.

equation (1) was used. The additional term is a more general way to express the slope of $\varepsilon$ far away from the relaxation frequency [11]. The advantage of this procedure is that the static dielectric constants $\varepsilon_0$ can be better calculated in samples with a high conductivity. Due to the incomplete orientation, only the $\varepsilon_0$ data in the isotropic state can be discussed.

## 3. Discussion

The Arrhenius plot of the relaxation times for the low frequency process in figure 5 shows for both samples a step by a factor of five in the relaxation times. Such a behaviour is typical for a reorientation about the molecular short axis in lamellar systems and reflects the change in the order [10]. Furthermore, there are deviations from the straight line at lower temperatures. This and the high mean activation energies indicate the influence of the glass temperature on the dynamics. As demonstrated in figures 2 and 3, there is no indication of an additional relaxation mechanism, even at lower temperatures. Therefore, one has to assume that there is no rotation in compound **2** of the central unit like that of a disk. This should also be affected by the glass transition and therefore, it should be detected at lower temperatures. Furthermore, no anomalies in the dielectric behaviour were observed; this makes ferroelectricity improbable. There is only experimental evidence for the existence of dipole correlations in the isotropic state as demonstrated for compound **1** (figure 6). Such effects are typical for the pretransitional range and known from the literature [12].

Comprehensively one has to say that the structure in the phases under investigation is dominated by the interactions of the side groups. The central cores are decoupled from the liquid crystalline cyanobiphenyl units. Furthermore, the cores are not piled up and they show a more uncorrelated arrangement between the smectic layers.

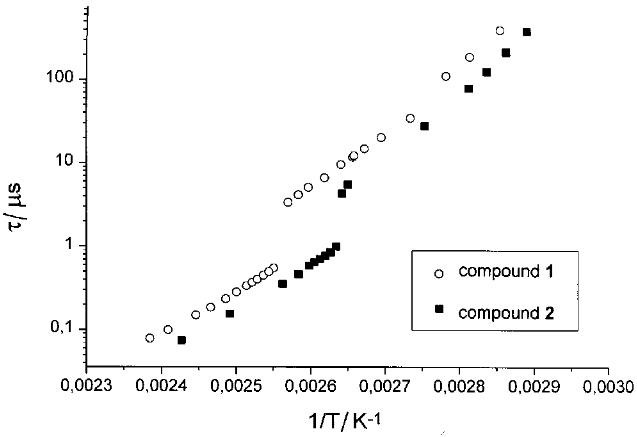


Figure 5. Arrhenius plot of the relaxation times, $E_A$/kJ mol$^{-1}$: compound **1**: 102 (I), 140 (SmA); compound **2**: 106 (I), 170 (SmA).

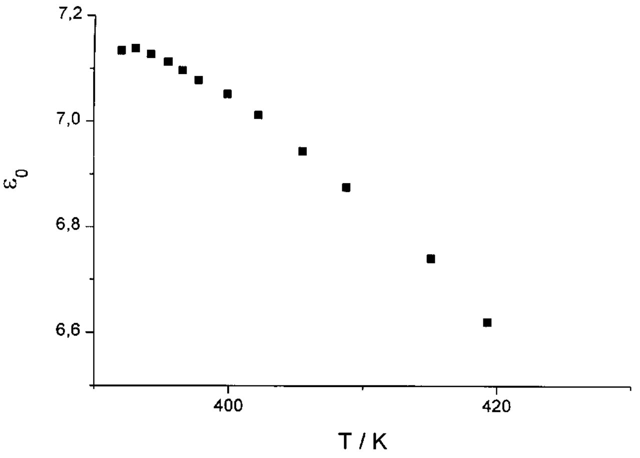


Figure 6. Static dielectric constants in the isotropic phase.

The authors gratefully appreciate the financial support from the Fonds der Chemischen Industrie.

### References

[1] Ringsdorf, H., Schlarb, B., and Venzmer, J., 1988, *Angew. Chem. intern. Ed.*, **27,** 113.

[2] Kresse, H., Novotna, E., Schiewe, B., Hohmuth, A., Delavier, P., Siemensmeyer, K., and Etzbach, K. H., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 481.

[3] Collard, D. M., and Lillya, C. P., 1989, *J. Am. chem. Soc.*, **111,** 1829.

[4] Malthete, J., and Collet, A., 1987, *J. Am. chem. Soc.*, **109,** 7544.

[5] Zimmermann, H., Poupko, R., Luz, Z., and Billard, J., 1985, *Z. Naturforsch.*, **40a,** 149.

[6] Budig, H., Diele, S., Göring, P., Paschke, R., Sauer, C., and Tschierske, C., 1994, *J. chem. Soc. chem. Commun.*, 2359; Budig, H., Diele, S., Göring, P., Paschke, R., Sauer, C., and Tschierske, C., 1995, *J. chem. Soc. Perkin Trans.*, **2,** 767.

[7] Diele, S., Lunkwitz, R., and Tschierske, C., 1997, *J. mater. Chem.* (in press).

[8] Jakli, A., Saupe, A., Scherowsky, G., and Xin Hua Chen, 1996, *Proceedings of the 16th International Liquid Crystal Conference*, Kent/Ohio, abstract C2.O03.

[9] Groothues, H., Kremer, F., Collard, D., and Lillya, C. P., 1995, *Liq. Cryst.*, **18,** 117.

[10] Kresse, H., and Shibaev, V. P., 1983, *Z. Phys. Chem.*, **264,** 161.

[11] Hill, R. M., and Johnscher, A. K., 1983, *Contemp. Phys.*, **24,** 75; Dissado, L. A., and Hill, R. M., 1987, *Chem. Phys.*, **111,** 193.

[12] Bradshaw, M. J., and Raynes, 1981, *Mol. Cryst. liq. Cryst. Lett.*, **72,** 73.