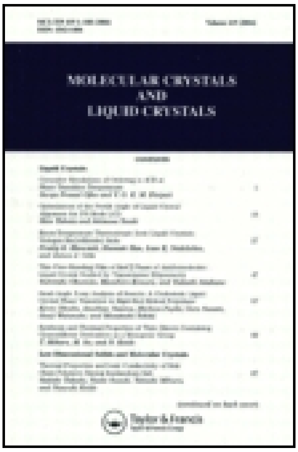

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dielectric Relaxation Investigations of New Synthetized Organo-Metallic Liquid Crystal

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Version of record first published: 24 Sep 2006.

To cite this article: T. Beica , A. L. Alexe-ionescu , A. T. Ionescu , E. Miraldi , D. Pucci & M. Rajteri (1995): Dielectric Relaxation Investigations of New Synthetized Organo-Metallic Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 270:1, 91-100

To link to this article: http://dx.doi.org/10.1080/10587259508031019

Mol. Cryst. Liq. Cryst., 1995, Vol. 270, pp. 91–100
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Dielectric Relaxation Investigations of New Synthetized Organo-Metallic Liquid Crystal

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(Received February 1, 1993; in final form May 20, 1993)

An impedance spectroscopy experimental characterization of a new synthetized Palladium complex organo-metallic liquid crystal is reported. It has been found that although organo-metallic complexes modify some of the physical properties of the liquid crystals, namely transition temperatures, values of the relaxation times and conductivity, they still have, in the nematic phase, the general behaviour of the usual liquid crystals. In particular the low frequency conductivity is very small, so one can conclude that the considered organo-metallic liquid crystal behaves like a good insulator. The temperature dependence of the static parallel and perpendicular components of the dielectric tensor are reported.

Keywords: Dielectric relaxation, organo-metallic liquid crystals.

1 INTRODUCTION

Usual nematic liquid crystals are formed by rod-like organic molecules. They behave, usually, as good insulators.[1] A few years ago, liquid crystals containing transition metals have been synthetized by different groups[2,3] in order to improve the electro-optical performances of possible devices.

The analysis of the linear and non-linear properties of a new Palladium complex[4] have been recently reported.[5,6] Their dielectric behaviour is reported here for the first time.

In this paper we present the dielectric characterization of one of these organometallic liquid crystals, performed by means of the impedance spectroscopy technique.[7-11] The real and imaginary parts of the dielectric constant have been determined versus the frequency and the temperature for two director configurations, respectively parallel and perpendicular to the applied electric field.

Our paper is organized as follows. In Sect. 2 the used experimental set-up is described. The obtained results are reported and discussed in Sect. 3. The main conclusions of our investigations are stressed in Sect. 4.

2 EXPERIMENTAL

The liquid crystal organo-metallic complex, named AZPAC, was synthetized by M. Ghedini *et al.*[4] It is one of a series of new synthetized liquid crystals,[12] which structure is reported in Figure 1.

The transition temperatures of the AZPAC are

$$T_{KN} = 82\,^{\circ}\mathrm{C} \quad T_{NI} = 102\,^{\circ}\mathrm{C}.$$

It has been obtained by complexing the liquid crystal 4-4′-bis(hexyloxy)-azoxybenzene, having a nematic phase between 80° and 126°. The used samples showed well defined transition-points when the temperature was increased, but a supercooled liquid crystal nematic phase[13] was seen, even at 18 °C, with the polarizing microscope and confirmed by the dielectric measures (see Fig. 3).

The dielectric measurements were made in the range of $1\,\mathrm{kHz} \div 5\,\mathrm{MHz}$ using a commercial impedance spectrometer controlled by a PC.

The cells are made with two parallel glass plates of $18 \times 10\,\mathrm{mm}^2$, with spacers of $50\,\mu\mathrm{m}$, coated with either ITO (Indium-Tin Oxide) or gold. The time constants of the empty cell with ITO electrodes are in the range of $10^{-6} \div 10^{-7}$ s, due to a relative high resistance of the electrodes ($\sim 800\,\Omega$). This time constants values are comparable with the expected relaxation times of the liquid crystal, so that the ITO covered cells were only used to control the liquid crystal changes versus the temperature, with a polarizing microscope. The golden electrodes cells (with electrode resistances $\sim 2\,\Omega$) have, instead, a RC time constant far beyond the instrument limits, so that the dielectric measures are performed with this type of evaporation.

The values of the components of the complex dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ were calculated from the complex admittance divided by ωC_0, where C_0 is the capacitance of the empty cell.

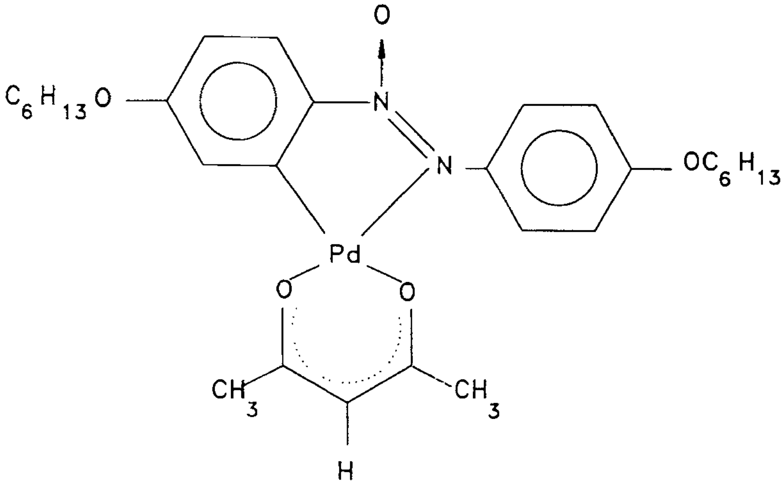

FIGURE 1 Structural formula of AZPAC.

The two useful orientations of the liquid crystal with respect to the electric field have been obtained by an orienting magnetic field of 0.9 T and rotating it with a step-motor control unit. The sample exhibits negative dielectric anisotropy and a strong tendency of a natural alignment with the long axis parallel to the walls of the cell. In order to avoid any voltage induced deformation of the director orientation, the amplitude of the electric field at the cell has been set to a value not exceeding 0.1 Volt.

In Figure 2 it is shown the block diagram of the experimental set up: the liquid crystal cell is held in a thermostat, which can be rotated, via a step motor, in a magnetic field.

3 RESULTS

In Figure 3 the dependence of the quasi-static (1 kHz) dielectric permittivity for the parallel and perpendicular director orientations versus temperature is shown. Following the arrows it is possible to see the trend of the dielectric constant with increasing and decreasing temperature, and the large supercooled nematic phase. In this phase the dielectric anisotropy is not large ($\varepsilon'_\perp \sim 4.5$, $\varepsilon'_\parallel \sim 3.8$), but marked.

The behaviour of ε' and ε'' versus frequency are given in Figure 4 and Figure 5, respectively. The labels $\parallel$ and $\perp$ refer to the nematic director parallel and perpendicular to the radiofrequency applied electric field. It is clearly shown in these figures that only the high frequency part of both the real and the imaginary part of the dielectric constant is changing with temperature. The low frequency parts ($f < 10^4$ Hz) are practically unchanging.

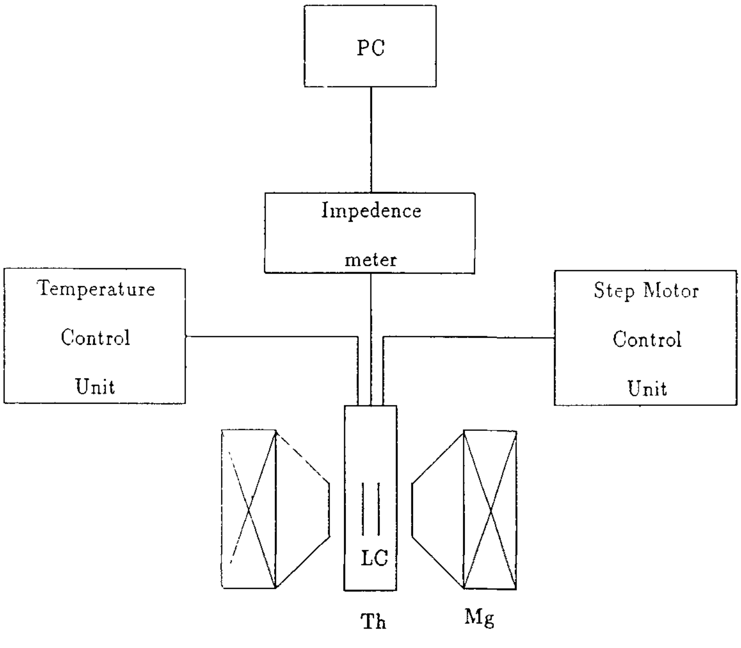

FIGURE 2 Block diagram of the experimental set up for impedance measurements: LC liquid crystal cell, Th thermostat, Mg electromagnet.

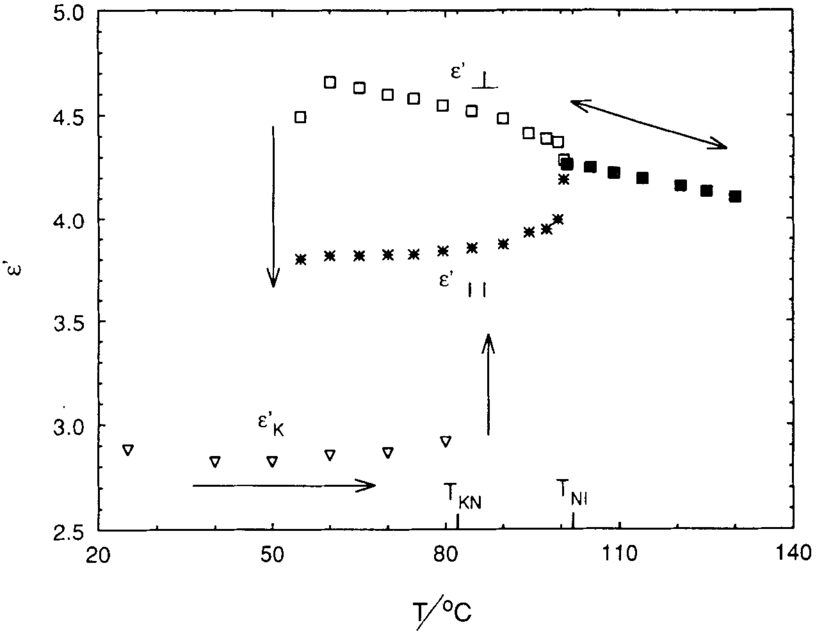

FIGURE 3 Quasi-static $\varepsilon'_{\perp}$ and $\varepsilon'_{\parallel}$ versus temperature in °C. ■ means isotropic phase. In the range 55 – 82 °C there are points measured in the supercooled liquid crystal state ($\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$) and the crystalline state ε'_{k}.

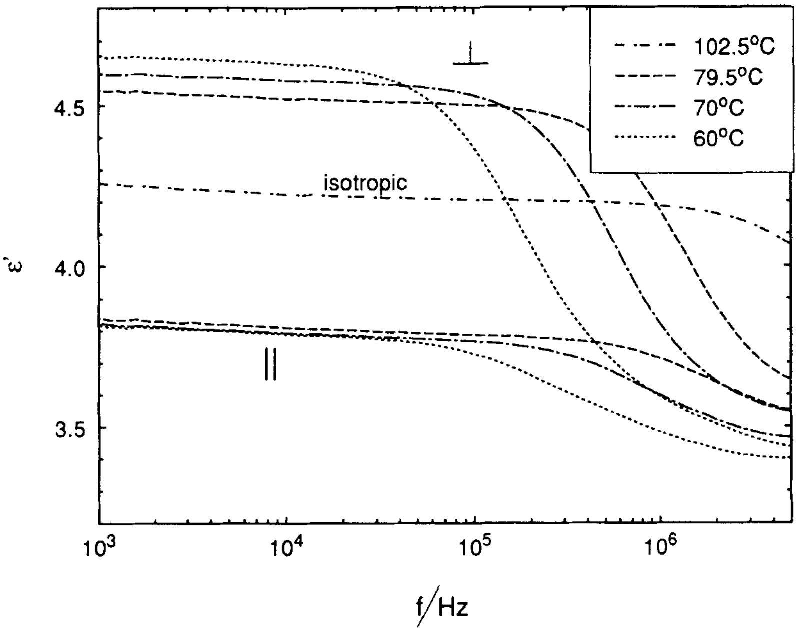

FIGURE 4 Real part ε' of the complex dielectric permittivity $\varepsilon(\omega)$. Both $\parallel$ and $\perp$ values are given for the same temperatures.

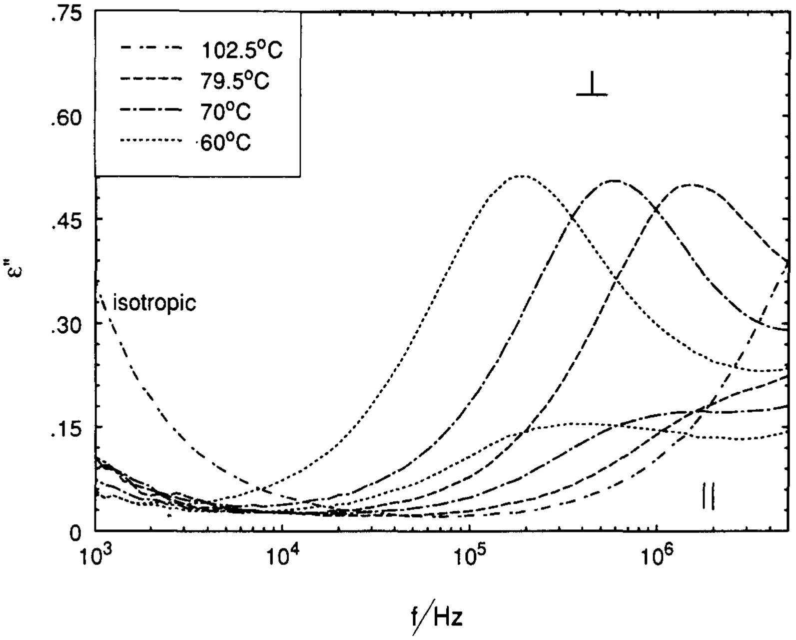

FIGURE 5 Imaginary part ε″ of the complex dielectric permittivity. Both ∥ and ⊥ values are given for the same temperatures. ⊥ absorption peaks have the same amplitude.

In Figure 5 it is noteworthy that the perpendicular loss versus temperature is higher than the parallel one, with a strong dependence on temperature.

In Figure 6 we show Cole-Cole plots for one temperature in both parallel and perpendicular alignment; a Cole-Cole plot with a zero magnetic field is also reported and it is very close to that done with magnetic field in the perpendicular orientation. This confirms that the natural orientation of the considered liquid crystal is parallel to the substrate. The values of the parallel component of the dielectric constant has been measured (for T = 60°) varying the applied magnetic field. For H = 0.9 T, $\varepsilon_\parallel$ differs of 1% from the value at H = 0.7 T; this authorizes us to suppose that with H = 0.9 T the sample is well oriented along the magnetic field.

The Cole-Cole plots were fitted by simulating the nematic cell with a suitable electric circuit. The best fits are given by the circuit of Figure 7, where CPE is a constant phase element.[7] This means that the complex dielectric permittivity is approximated by the expression.

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_0)^\beta},$$

which gives a better fit than the simple Debye's fit, where $\beta = 1$.

In this expression ε_∞, ε_s stand for the dielectric constant at very high frequencies ($\simeq n^2$) and the static dielectric constant, respectively; β is an empirical parameter which is not very far from 1.

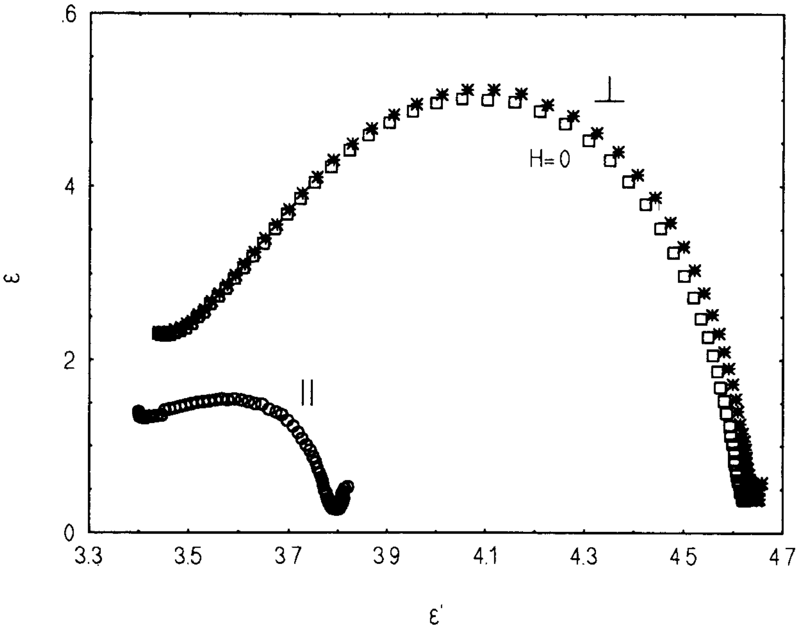

FIGURE 6 A Cole-Cole plot of experimental values of ε′ and ε″ in parallel-perpendicular orientations and without magnetic field, at $T = 60\,°C$.

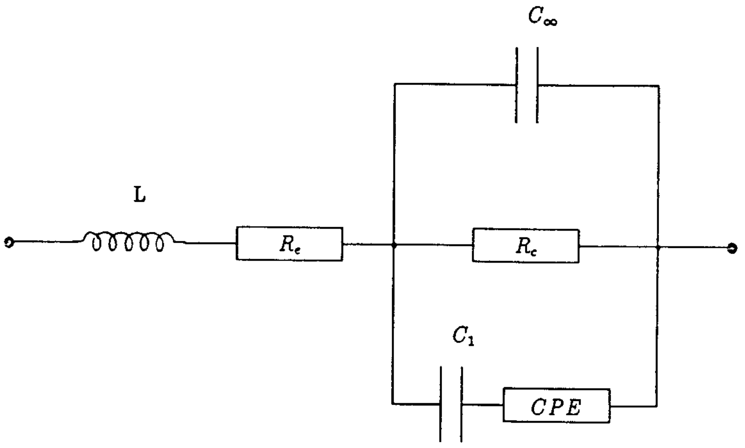

FIGURE 7 The equivalent circuit used to fit the data.

The constant phase element usually employed is an impedance function of the type $Z_{CPE} = A(i\omega)^{1-\beta}$. The relaxation time is then $\tau_0^\beta = (\varepsilon_s - \varepsilon_\infty)\varepsilon_0 A$.[7] β is mainly connected to the deformation of the loss curve $\varepsilon''(\omega)$ from the ideal one given in Debye's formula $\varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty)\omega\tau_0/(1 + \omega^2\tau_0^2)$. A plot of $\log f_c\,(f_c = 1/2\pi\tau_0)$ vs. temperature (Fig. 8)

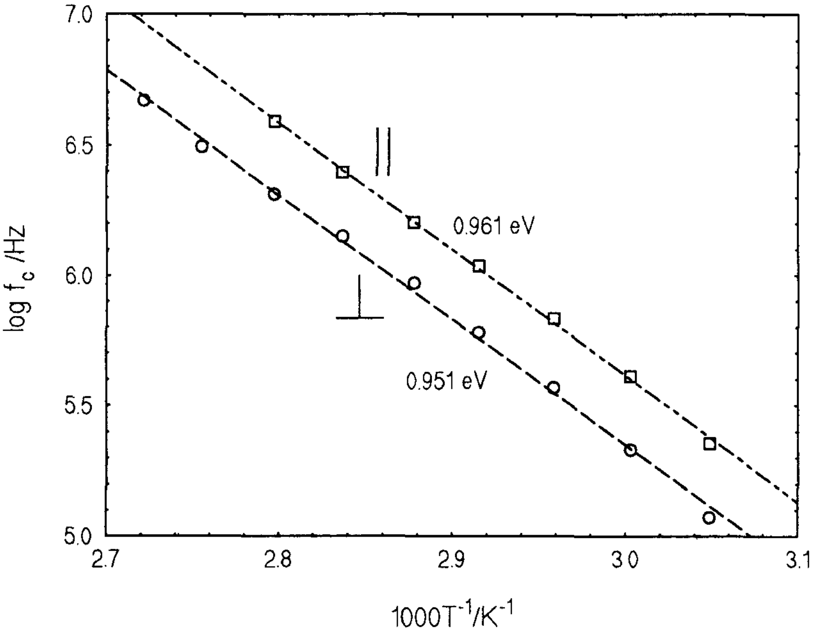

FIGURE 8 log f_c vs. 1000/T for both parallel and perpendicular orientation. In the nematic phase temperature domain the dependence is linear.

does show a fairly straight line. This allows us to consider that the Arrhenius behavior is respected and the calculated values of the activation energy were 0.951 eV for perpendicular and 0.961 eV for parallel orientation.[12]

A Cole-Cole plot and the fit are shown in Figure 9. The fit is greatly improved when a parasite inductance of about 10 nH is taken into account. The values of the fit parameters, valid for two temperatures in the supercooled range are summarized in Table 1.

R_c is the resistance of conduction, i.e. that conduction which is only present at very low frequencies or d.c., and has mainly an ionic character. From the values of R_c it is possible to compute the conductivities (Fig. 10), which show a dependence on the temperature and also a positive anisotropy. The measured values are quite low, so that the material, even in the isotropic phase, is a real insulator, and there is no overlapping of electronic orbits due to the Palladium atoms. Usually[9] the conductivity is computed with the values of another resistance which in our circuit is replaced by A. Actually A is responsible for the relaxation, not for the d.c. conductivity.

C_∞ is related to the admittance at high frequencies, and the ratio C_∞/C_0 gives the dielectric constant at very high frequencies, ε_∞.

The ratio $(C_1 + C_\infty)/C_0$ gives therefore ε_s which is the static dielectric constant, i.e. the d.c. or very low frequency one. C_∞ is quite unaffected by temperature, in the nematic phase.

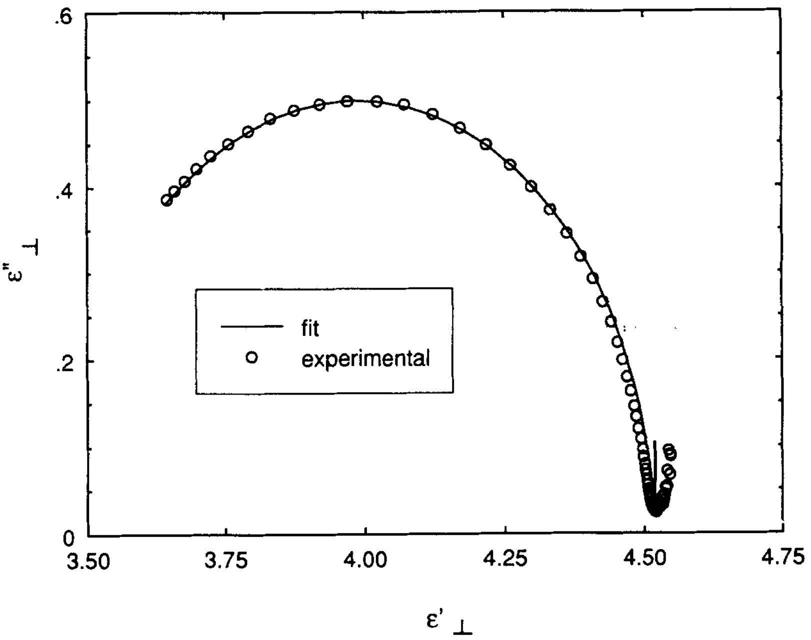

FIGURE 9 A Cole-Cole plot of experimental values of ε' and ε'' in perpendicular orientations at 79.5 °C and the fit curve.

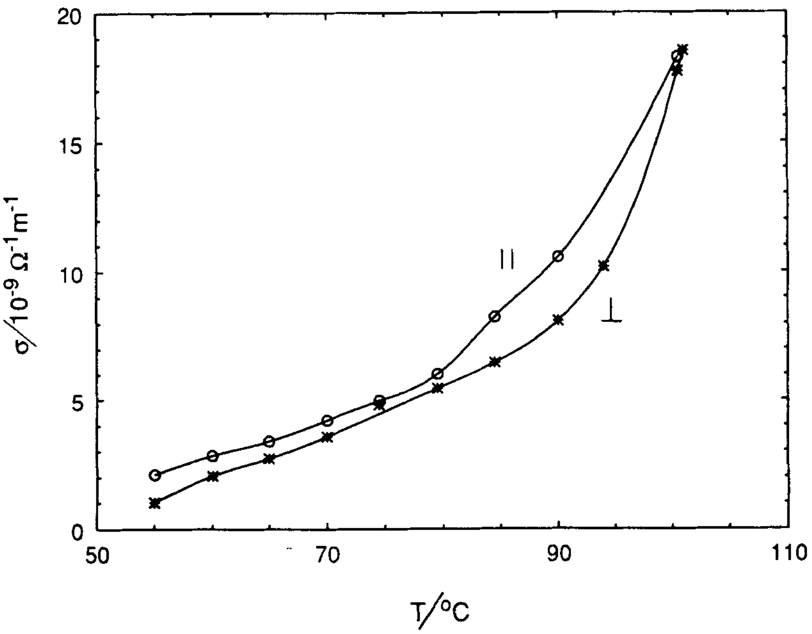

FIGURE 10 Parallel and perpendicular values of conductivity versus temperature. The overlapping of points at 72 °C is due to the experimentals errors.

TABLE 1

Parameters of the equivalent electric circuit for $\varepsilon_\perp$ at $T_1 = 74.5$ °C and $T_2 = 79.5$ °C

		T_1	T_2
C_0	*pF*	30.1 ± 0.2	30.1 ± 0.2
C_1	*pF*	30.3 ± 0.2	28.9 ± 0.3
A	10^3 *S.I. units*	11.67 ± 0.05	7.13 ± 0.03
β		0.953	0.962
R_c	$M\Omega$	55 ± 1	51 ± 1
C_∞	*pF*	106.3 ± 0.2	106.7 ± 0.3
R_e	Ω	11.2 ± 0.2	10.3 ± 0.2
L	*nH*	45 ± 10	67 ± 11

R_e is the series resistance and is mainly due to the resistance of the electrodes, but presumably it takes into account some effects of the electrodes polarization, as the small dependence on the temperature seems to indicate.

4 CONCLUSION

It has been shown that the dielectric characteristics of the organo-metallic complex AZPAC are definitely those of a normal nematic liquid crystal although the values of the physical properties as transition temperatures, relaxation times and conductivity are different from the values of the ligands.[14]

It is important to stress that the equivalent circuit fits very well the experimental data and allows an accurate and trustful interpretation of the results. It is important to notice that AZPAC is an insulator at all temperatures (when not highly decomposed) so that the overlapping of electron orbitals is not likely. The organo-metallic liquid crystal presents a supercooled state, presumably with a high viscosity.

Further studies on dielectric properties of AZPAC and its ligand are under way.

Acknowledgments

Many thanks are due to L. Bata and A. Buka (Budapest), C. Oldano, S. Bodoardo and F. Demichelis (Torino), R. Bartolino (Cosenza) for useful discussions.

This work has been partly supported by the Cassa di Risparmio di Cuneo and INFM, Istituto Nazionale Fisica della Materia (Genova).

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