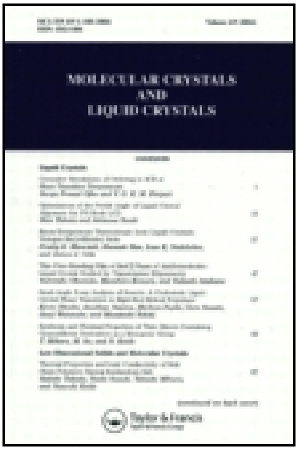

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# Convective Instabilities Under a.c. Electric Fields in a Mesogenic Azocompound Complexed with Palladium

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We report the observation of convective instabilities in a mesogenic azocompound complexed with palladium, subjected to electric fields. The analysis of the experimental data indicates that the conductive regime extends to higher frequencies with respect to that of the common nematics, even if we find that the dielectric anisotropy of the metallomesogen and of the ligand have the same order of magnitude.

## INTRODUCTION

At present, study concerning metallomesogens still represent an interesting area of research to gain new insight into liquid crystals properties and to improve their characteristics in comparison to usual organic materials.

In particular it seems that the presence of a metal atom could affect properties as birefringence, light absorption, dielectric and polarizability anisotropy and other optical effect, enabling new developments in the applicability of metallomesogens.

As concerning Azpac complex, a mononuclear palladated alkoxy azoxybenzene,[1] we already reported on optical nonlinearities,[2] optical anisotropy[3] and electrical conductivity[4] which shows significant improvement due to the complexation.

Now we are interested in the electrical characterization of Azpac complex and particularly to study its electrohydrodynamical behavior.

In this paper we present the first observation of convective instabilities in the metallorganic liquid crystals Azpac complex under electric field.

## THEORETICAL FRAME AND EXPERIMENTS

Convective instabilities under electric fields in liquid crystals have already been the subject of several studies, both theoretical and experimental ones.

Many papers dealing with nematic liquid crystals with negative dielectric anisotropy and with experimental geometry such that the external applied fields are stabilizing (contrary to the case of Freedericksz transition) have been published.

Let us briefly summarize the main features of the Carr-Helfrich mechanism[5,6] leading to instabilities in the case of materials with negative dielectric anisotropy ($\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp} < 0$) and positive conductive anisotropy ($\Delta\sigma = \sigma_{\|} - \sigma_{\perp} > 0$), where $\epsilon_{\|}$, $\epsilon_{\perp}$, $\sigma_{\|}$ and $\sigma_{\perp}$ are respectively the dielectric permittivities and the electrical conductivities parallel and perpendicular the optical axis.

We consider a homogeneous uniaxial texture with uniform director alignment along the $x$ direction (see Figure 1).

Owing to thermal orientation fluctuations of the sample alignment, we can consider a periodic fluctuation of director along the $x$-axis. When an electric field is applied on the sample along the $z$-axis, because of the conductive anisotropy, the current lines will result not parallel to the $z$-axis so that opposite sign space charges appear in the regions labelled + and − in Figure 1.

In these regions the medium moves with opposite velocity under the action of electric forces. Because of this velocity gradient a destabilizing viscous torque will appear while the electric torque due to the external applied field has a stabilizing effect. Finally, a transverse component of the electric field, rising from space charges, will lead to a destabilizing torque.

When the applied electric field reaches a critical value that makes destabilizing the total torque, the instabilities will appear. These are the well known Williams domains.

In the case of a.c. excitation, the Carr-Helfrich mechanism keeps its validity leading a characteristic time: the relaxation time $\tau$ of space charges along the direction of the director.[7]

Depending on the value of angular frequency of applied field $\omega$, we can distinguish two different regimes:

i) $\omega\tau \leq 1$ (conductive regime). The space charges relax following the applied electric field. Williams domains, with periodicity of the same order of sample thickness, appear above an instabilities threshold.

ii) $\omega\tau > 1$ (dielectric regime). The space charges do not relax. In this case the

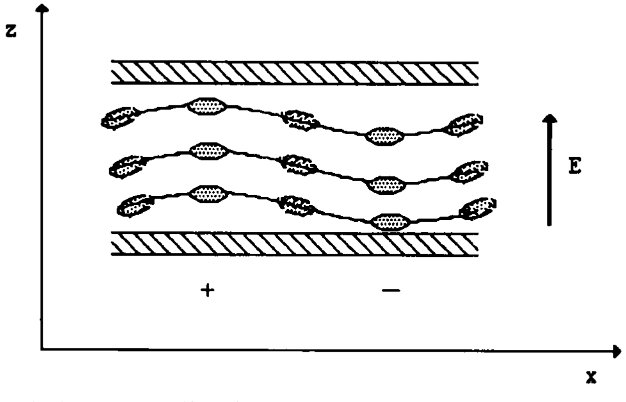

FIGURE 1 Electrohydrodynamic effects in homogeneously oriented nematic liquid crystals with negative dielectric anisotropy and positive conductance anisotropy: Carr-Helfrich mechanism.

local orientation of molecules oscillates following the applied fields. At the instabilities threshold, which is higher than the one present in the conductive regime, a periodic structure with a periodicity smaller than sample thickness appears.

The Azpac compound presents a nematic phase in the range of temperatures from 94°C to 102°C.

The experiments were performed on a homogeneous uniaxial texture obtained by sandwich type electro-optical cells. To eliminate electrode effects and obtain the homogeneous uniaxial texture, the glass plates were coated by indium oxide covered by 40 Å thick SiO layer evaporated at an angle of 60°.[8] The sample thickness was determined by Mylar spacers (20 μm).

The cell was placed in an electric oven and kept to a temperature of 100.0 ± 0.1°C. The sample was excited by an electric signal originating from an operational amplifier driven by a waveform generator.

As a first step, by means of a polarizing microscope, we performed a qualitative observation of the periodical distortion of the nematic alignment occurring at the threshold of the Williams domains.

In Figure 2 is shown a typical result of the observed Williams domains in Azpac.

In order to have a quantitative information about the critical threshold of the Williams domains, we tested the response of the sample looking at the light transmitted between crossed polarizers: a polarized He-Ne laser beam was directed into the sample and the light transmitted through an analyzer orthogonal to the incoming polarization was detected by a photomultiplier. The signal arising from the photomultiplier was sent to a digitizing oscilloscope.

To get optimum contrast, the direction of alignment of the nematic sample was at 45° with respect to the polarization of incident laser beam.

When the applied voltage reaches the threshold value, the intensity of the transmitted light changes accordingly with the applied signal.

In Figure 3 is shown the variation of the threshold $V$ (r.m.s.) vs the angular

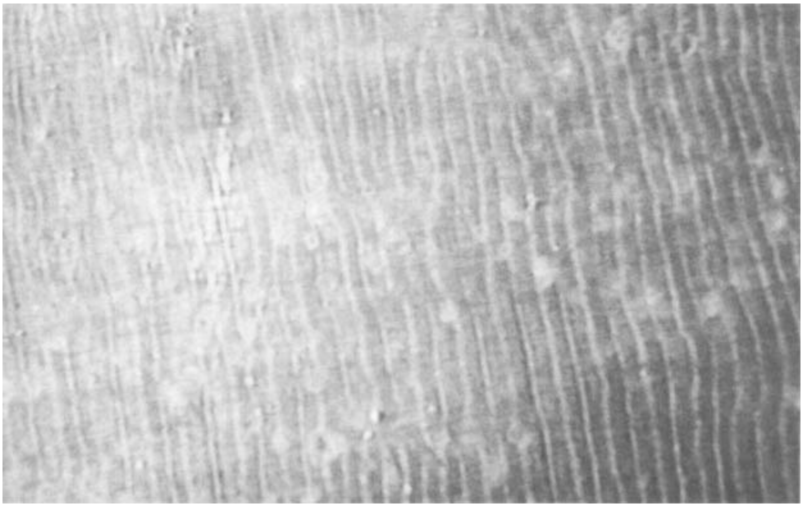

FIGURE 2 Williams domains in Azpac. See Color Plate V.

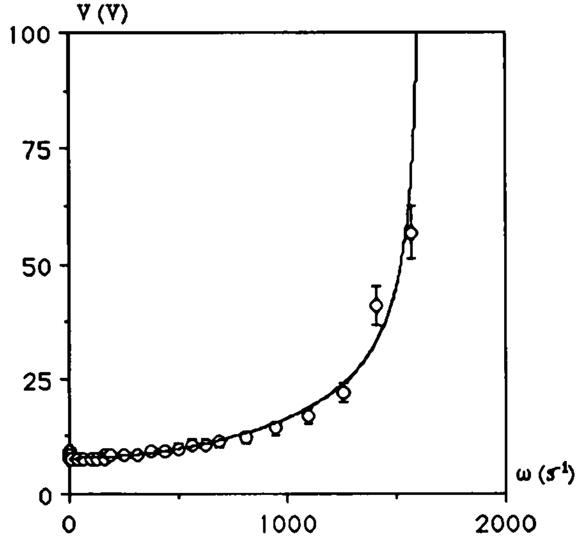

FIGURE 3 Instability threshold $V$ vs the angular frequency for a sample 20 μm thick under sinusoidal excitation. The full line represent the best-fit made using Equation (1).

frequency for sinusoidal excitation. In Figure 4 are shown the same quantities of Figure 3 in the case of square-wave excitation. In this case $V$ represents the signal amplitude.

From the above depicted figures, we can note that the behavior is similar to that found in common nematics, but the conductive regime extends to higher frequencies. Moreover, increasing the value of the frequency, for applied voltage amplitude up to 200 $V$ (r.m.s.), no instability has been seen.

## DISCUSSION

Supposing that the nematic sample is homogeneously oriented, in the conductive regime, characterized by a space charge oscillating at the frequency of the applied voltage, the threshold voltage does not depend on the thickness of the cell and its angular frequency distribution is given by[9]:

$$\langle V_c^2(\omega)\rangle = V_0^2\left[\frac{1+\omega^2\tau^2}{\xi^2-(1+\omega^2\tau^2)}\right] \qquad (1)$$

where

$$\tau = \frac{\epsilon_{\parallel}}{4\pi\sigma_{\parallel}}$$

is the relaxation time of the space charge in the direction parallel to the director, and

$$\xi^2 = \left(1 - \frac{\sigma_\perp \epsilon_\parallel}{\sigma_\parallel \epsilon_\perp}\right)\left(1 + \frac{\alpha_2}{\eta_1}\frac{\epsilon_\parallel}{\Delta\epsilon}\right)$$

is the anisotropy parameter, being $\alpha_2$ and $\eta_1$ respectively the Leslie coefficient and the coefficient of viscosity defined according to Gahwiller.[10]

In the low angular frequency approximation ($\omega \to 0$) we can write:

$$V_c^2(0) = \frac{4\pi k_3 \epsilon_\parallel}{(-\Delta\epsilon)\epsilon_\perp(\xi^2 - 1)} = \frac{V_0^2}{(\xi^2 - 1)} \tag{2}$$

$k_3$ being the bend elastic constant.

Equation (2) gives us the condition for the establishment of the instability when $\Delta\epsilon < 0$: the anisotropy parameter should be larger than unity.

The behavior of the threshold of the electrohydrodynamic instabilities is substantially different in the conductive regime with respect to one of the dielectric regime. Both regimes are separated by a critical angular frequency $\omega_c$ which is given by[9]:

$$\omega_c = \frac{(\xi^2 - 1)^{1/2}}{\tau}$$

Fitting our experimental data by means of Equation (1) (see full line in Figure 3), we obtain the following parameter values:

$$V_0 = 16.87 \text{ V}$$
$$1/\tau = 0.75\ 10^3 \text{ s}^{-1}$$
$$\xi^2 = 5.69$$

Substituting this values into Equation (2), we find:

$$V_c(0) = 7.8 \text{ V}$$

and for the critical angular frequency the value:

$$\omega_c = 1624 \text{ s}^{-1}$$

The quite large value of the anisotropy parameter, suggests that the dielectric anisotropy of the Azpac must be small and negative.

From Equation (2) in the hypothesis of small dielectric anisotropy ($\epsilon_\parallel/\epsilon_\perp \sim 1$) and using the value of the bend elastic constant $K_3 = 3\ 10^{-7}$ cgs units,[11] we obtain:

$$|\Delta\epsilon| \approx 0.01 \text{ cgs units}$$

Again, for a square-wave excitation, in the conductive regime, the angular frequency distribution of threshold voltage is given by:[12]

$$V_c^2(\omega) = V_0^2 \frac{u(1 + e^u)}{[u(\xi^2 - 1) - 2\xi^2]e^u + u(\xi^2 - 1) + 2\xi^2} \tag{3}$$

where

$$u = \frac{\pi}{\omega t}$$

Also in this case the threshold voltage does not depend on the sample thickness.

Using in Equation (3) the parameter values found by the best-fit made in the sinusoidal excitation case, we find a good agreement between the predicted angular frequency distribution of threshold voltage and the experimental data (see the full line in Figure 4).

From Equation (3) we find that the critical angular frequency can be calculated by:

$$(u_c(\xi^2 - 1) - 2\xi^2)e^{u_c} + u_c(\xi^2 - 1) + 2\xi^2 = 0$$

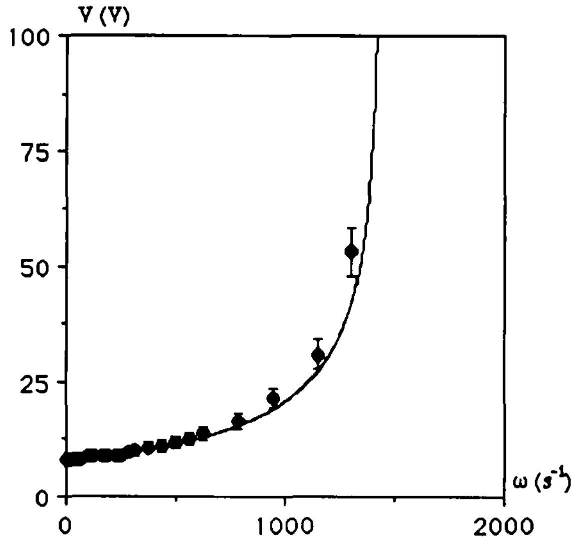

FIGURE 4 Instability threshold $V$ vs the angular frequency for a sample 20 μm thick under square-wave excitation. The full line represents the Equation (3) plotted using the parameter values found by the best-fit made in the sinusoidal excitation case.

that give us the value:

$$\omega_c = 1445 \text{ s}^{-1}$$

## CONCLUSION

In this work we have studied the dielectrical properties of a new mesogenic azocompound complexed with palladium, by looking at its electrohydrodynamic instabilities.

We have observed that the usual analysis of the Carr-Helfrich instabilities can be applied also to these compounds since it leads to a good agreement between the measured threshold voltage vs frequency and the expected theoretical behavior. Moreover from our data we see that the conductive regime extend to higher frequencies as compared to the one of common nematics. In fact, for instance, the critical frequency is about three times the one of the MBBA.[9] However, this critical frequency is about the same as the one exhibited by doped MBBA[13] (i.e. a strongly conducting nematic liquid crystal with $\Delta\epsilon < 0$). This fact indicates that due to the presence of a metal atom, the electrical conductivity of the metallomesogens increases, as expected.

Moreover, the dielectric anisotropy, found from our best fit, is of the same order of that of the free ligand,[14] in agreement with other independent experimental data we found.[15]

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