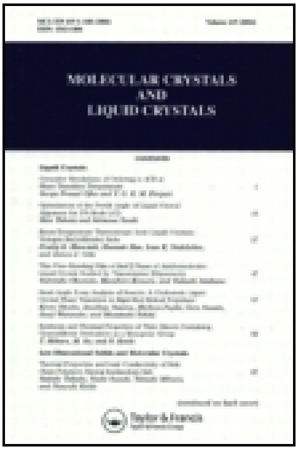

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Evidence for Flexoelectric Effects in Pallated Metallorganic Liquid Crystals

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We report the first observation of flexoelectricity in a new class of liquid crystalline materials: the metallorganic liquid crystal azocompound obtained by complexation with palladium. From our experimental data we can estimate both the values of the flexoelectric constants $|e| = |e_1 - e_3|$ and of the viscosity coefficient γ_1. The obtained value of $|e|$ for these unusual materials are found to be similar to that of usual nematics.

Keywords: flexoelectricity, metallorganic liquid crystals

The flexoelectric effect describes the coupling of an electric field with the gradient of the director field in uniaxial media.[1,2]

It's well known that owing to the rotation symmetry, in the unperturbed configuration a bulk nematic liquid crystal is non-polar. The individual molecular dipoles orientate in such a way as to have a cancellation of dipole moments on a microscopic as well as on a macroscopic scale.

However, as Meyer has shown,[1] most nematic liquid crystals when submitted to a curvature distortion exhibit a macroscopic electric polarization. The two curvature distortions active in flexoelectricity are the divergence and the bend of the director **L** with the two associated flexoelectric constant e_1 and e_3.[1,3,4]

In this work we present the first experimental evidence of flexoelectric effects in a mononuclear pallated alkoxy azoxybenzene[5] (Azpac complex). This complex derives from cyclopalladation of bis-alkyloxy-azoxybenzene with $[(PhCN)_2PdCl_2]$, followed by halo-bridge cleavage with substituted acetylacetone salts.[5]

The Azpac complex (see Figure 1) presents a nematic phase in the range of temperatures from 94°C to 102°C.[2] The dielectric anisotropy of Azpac complex was found at the temperature of 100°C to have a small negative value,[6] i.e. $\Delta \in = -0.01$.

The experiments were performed on a homogeneous uniaxial texture obtained by sandwich type electro-optical cell. To eliminate electrode effects and obtain the homogeneous uniaxial texture the glass plated were coated by indium oxide covered by thin SiO layer evaporated at an angle of 60°.[7]

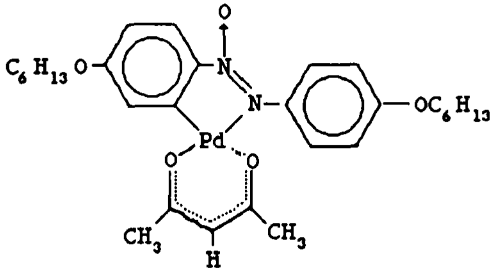

FIGURE 1 General formula of Azpac complex.

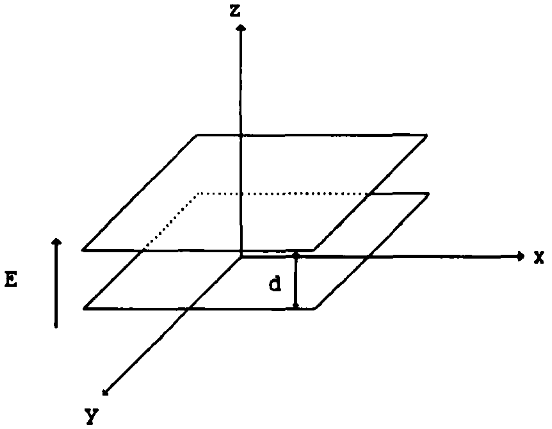

FIGURE 2 Experimental geometry.

The cell was placed in an electric oven and kept to a temperature of 100.0 ± 0.1°C. The sample thickness was determined by 36 μm thick Mylar spacers.

The sample was excited by a 40 s long step-like d.c. electric signal originating from an operational amplifier driven by a waveform generator. The electric signal was applied perpendicularly to the boundary glass plates, i.e. $\mathbf{E} = (0, 0, E)$ (see Figure 2).

We tested the response of the sample looking at the transmission of monochromatic light. A polarized He-Ne laser beam was directed into the sample. The light transmitted between crossed polarizers was detected by a photomultiplier. The signal arising from the photomultiplier was sent to a digitizing oscilloscope. To ensure the best contrast, the angle between the unique axis and the polarization plane was set equal to $\pi/4$.

The applied d.c. voltage caused change of the transmitted light when a threshold was reached. The threshold of applied voltage was found to be 4.0 ± 0.1 V.

In Figure 3 is shown a picture taken at the polarizing microscope of the flexoelectric deformations appearing just above a threshold of the external applied field.

The measured times delay for the appearance of the deformation patterns vs the applied electric field are shown in Figure 4.

In order to discuss these data, let us consider a sandwich type electro-optical

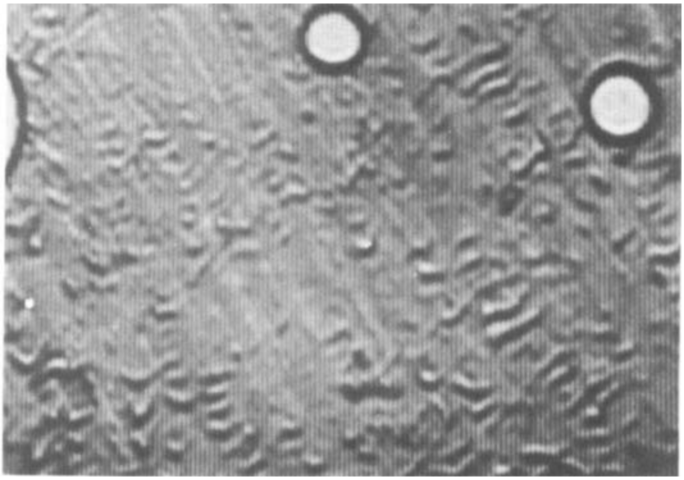

FIGURE 3 Flexoelectric deformation patterns in Azpac appearing just above the threshold for external applied field. See Color Plate VII.

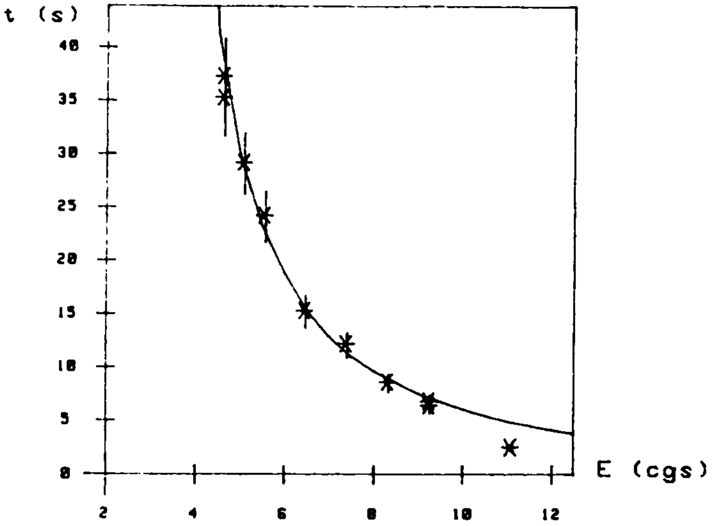

FIGURE 4 Stars are the time delay for the onset of the deformation patterns. The solid curve represents the fit made by the inverse of Equation (5).

cell containing Azpac material which in the absence of an electric field has **L** parallel to the *x*-axis (see Figure 2).

The two flexoelectric constant e_1 and e_3 associated to the two curvature distortions active in flexoelectricity are defined as:

$$\mathbf{P} = e_1\mathbf{L}(\text{div } \mathbf{L}) + e_3(\text{curl } \mathbf{L})x\mathbf{L} \tag{1}$$

When there is an external electric field the additional term **PE** must be added to the expression for the free energy.[3,4]

Let us introduce θ and ϕ, respectively the deviation of director from x-axis in the xz plane and in the xy plane. In the case of small deviation from unperturbed state, θ and $\phi << 1$, we have:

$$\mathbf{L} = (1, \phi(y, z), \theta(y, z)) \tag{2}$$

In the one constant approximation ($K_1 = K_2 = K_3 = K$), taking into account the boundary conditions $\theta = \phi = 0$ at $z = \pm d/2$ (strong anchoring of the molecules to the wall), Bobylev *et al.*[9] calculated the threshold voltage for the appearance of the flexoelectric patterns:

$$V_{\text{thr}} = E_{\text{thr}} d = \frac{2\pi K}{|e|(1 + \mu)} \tag{3}$$

being $\mu = \Delta \in K/4\pi e^2$ and $e = e_1 - e_3$.

Using the experimental value of the threshold voltage and $K = 2 \cdot 10^{-7}$ cgs units,[8] we get $|e| = 1 \cdot 10^{-4}$ cgs units.

The dynamical equations for θ and ϕ have the form:

$$\frac{\partial\theta}{\partial t} + \frac{1}{\gamma_1}\left\{K\left[q^2 + \left(\frac{\pi}{d}\right)^2\right] - \frac{\Delta \in E^2}{4\pi}\right\}\theta = \frac{eEq}{\gamma_1}\phi \tag{4a}$$

$$\frac{\partial\phi}{\partial t} + \frac{K}{\gamma_1}\left[q^2 + \left(\frac{\pi}{d}\right)^2\right]\phi = \frac{eEq}{\gamma_1}\theta \tag{4b}$$

The characteristic times corresponding to the Equations (4) are defined by:

$$\left(\frac{1}{\tau_{\text{on}}^{\pm}}\right) = \frac{1}{\gamma_1}\left\{\frac{\Delta \in E^2}{4\pi} - K\left[q^2 + \left(\frac{\pi}{d}\right)^2\right] \pm \left[\frac{\Delta \in^2 E^4}{64\pi^2} + e^2E^2q^2\right]^{1/2}\right\} \tag{5}$$

where q are the wave-vectors of the instability structures, defined by the dispersion equation:[8]

$$V^2 = \left(\frac{Kd}{e}\right)^2 \frac{\left[q^2 + \left(\frac{\pi}{d}\right)^2\right]^2}{q^2 + \mu\left[q^2 + \left(\frac{\pi}{d}\right)^2\right]} \tag{6}$$

When the field is turned off, the balance between elastic and viscous torques leads at relaxation times is given by:

$$\left(\frac{1}{\tau_{\text{off}}}\right) = \frac{K}{\gamma_1}\left[q^2 + \left(\frac{\pi}{d}\right)^2\right] \tag{7}$$

The times for the appearance and relaxation of the deformation patterns are described respectively by the inverse of Equations (5) and (7), taking in Equation (5) the positive sign of square root.

Fitting the experimental data for the onset of the deformation patterns by means of the inverse of Equation (5) [solid curve of Figure (4)], we obtain for the viscosity coefficient the value $\gamma_1 = 1.5$ cgs units, in agreement with the value found by other experimental technics.[8]

In this work we present the first observation of flexoelectricity in Azpac complex. Because of strong anchoring of the molecules to the walls obtained in our experimental configuration, the appearance of the flexoelectric domains request the reaching of a threshold voltage.

The experimental data of this threshold voltage allow the calculation of the value of the flexoelectric constant $|e|$. The obtained value of $|e| = 1 \cdot 10^4$ is of the same order as the one found in usual nematics.[4]

By fitting the measured switch-on time for the onset of the deformation patterns we were able to work out the viscosity coefficient γ_1 of Azpac, a bigger value than in usual nematics and also bigger than the one of the ligand, the mesogenic azo-compound from which it derives, but in agreement with the value found by other experimental technics.

Further experimental measurements are underway to measure both the flexoelectric coefficient e_1 and e_3.

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