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Refractive index measurements of the Palladium complexed liquid crystal A'PdA2.§

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Abstract A comparative study of the birefringence of a thermotropic metallorganic complex and of its free ligand is reported for the first time. Using the method of the total reflection the ordinary and the extraordinary refractive indices of the palladium complexed liquid crystal A'PdA2 and of its free ligand 4-4'-Bis(hexyloxy)-azoxybenzene have been measured as function of temperature. Palladium complexation increases the optical density but decreases the optical anisotropy of the free ligand.

Keywords: metallomesogens, refractive index

Introduction

Since few years a great interest is growing on the synthesis and the classification of new liquid crystalline materials having one of more metal atoms as part of the molecule(1 2).

In this paper we report refractive index measurements of the nematic liquid crystal 4-4'-Bis(hexyloxy)-azoxybenzene, and its palladium complex A'PdA.

Microscope observations of this metallorganic thermotropic liquid crystal show, when the temperature in increasing, a nematic phase between 90°C and 105°C, while decreasing the temperature the optical properties of the nematic phase persist at lowest temperature in a optically anisotropic

amorphous metastable phase.

To determine the refractive indices of the two substances we measured the critical angle of the total reflection phenomenon.

We chose this method which do not require any information on the sample thickness because of the rather large temperature interval to be investigate.

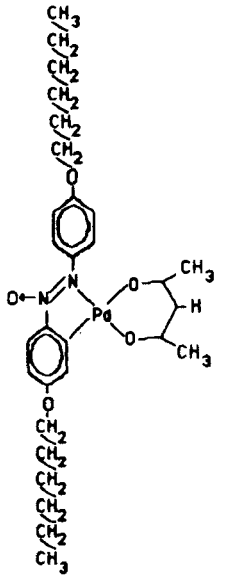

Figure 1: Structure formula of the A'PdA2 liquid crystal

Experimental and discussion

The experimental geometry is shown in Figure 1, we used a 0.9mW HeNe laser which power was weaken down to 0.1mW to reduce the thermal effect due to the absorption (3,4).

The liquid cristal cells were made by one high density prism (Schott glass SF59) and one BK7 slide. The surface of both the prism and the slide were treated by the ACM-72 polymer and rubbed by a carbon fiber brush to give an uniform planar orientation to the liquid crystal directors. The prism an the slide were spaced by four 36μm thick mylar peaces and they were sealed together.

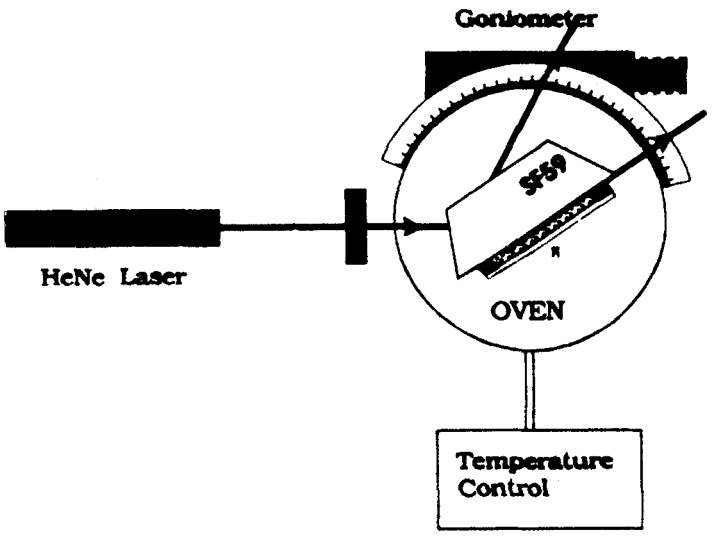

Figure 2: Experimental geometry.

The cells were warmed up to 106°C (Pd complex case) or 127°C (free ligand case) and stuffed with liquid crystal by capillarity.

The oven as well as the inside cell were placed on a rotating table whose accuracy was 0.005°deg.

We determinated the critical angle by looking at the intensive light scattering that takesplace in the sample when the laser beam propagates inside the sample almost parallel to the surfaces. To test the measuring system we measured the refractive indices of decalyne an glycerol at different temperature. The comparison of these measurements with the known values allowed us to estimate an accuracy better then 0.1% on the absolute values of the refractive indices.

The accuracy and the resolution of the temperature control system were respectively 0.2°C and 0.05°C.

In figures 3 and 4 respectively the refractive indices and the optical anisotropy of the A'PdA2 (crosses) and of its free ligand (squares) are reported versus the reduced temperature T_c-T, being Tc the nematic phase clearing point.

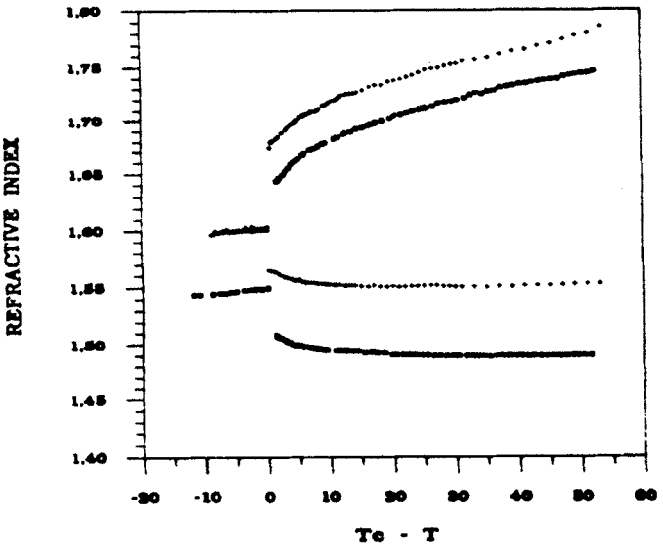

Figure 3: Ordinary and extraordinary refractive indices versus the difference Tc-T between the clearing point temperature and the measuring temperature.

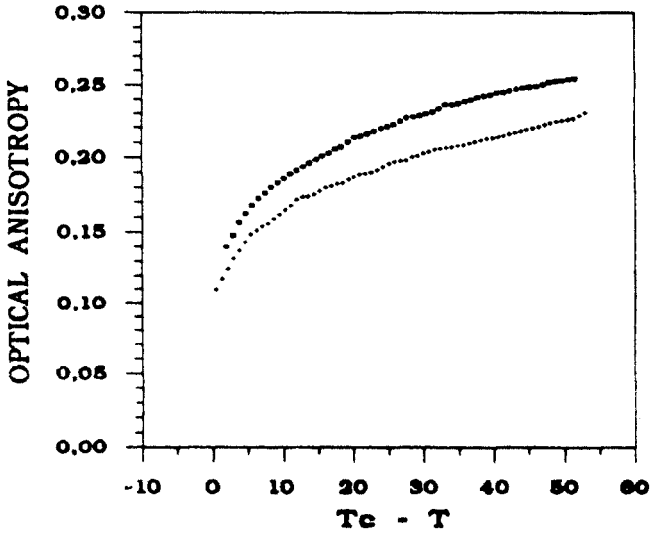

Figure 4: Free ligand (squares) and A'PdA2 (crosses) optical anisotropy as function of the reduced temperature Tc-T.

The free ligand refractive indices values are in good agreement with those reported in bibliography (5) and we attribute small differences to the fact that our technique is most sensitive to the surface induced order.

The metal complexed liquid crystal shows positive uniaxial optical behaviour as well its free ligand. In fact measures of ordinary ray refractive index made on samples aligned parallel to the incidence plane do not show significative variations when the polarization of the incoming beam is turned around the optical axis. The 4-4'-Bis(hexyloxy)-azoxybenzene optical density augments by palladium complexation , while its anisotropy reduces

Our findings differs from those of Bertram et al. (6) which found both the mean and the polarisability anisotropy of two series of liquid crystal increase by Pd and Ir complexation. We attribute the anisotropy opposite behaviour of the A'PdA2 to different location of the metal atom inside the molecule.

Conclusion

For the first time the birefringence values of a metal complex liquid crystal have been reported.We presented measurements of the refractive indices of A'PdA2 palladium complex liquid crystal and of its free ligand 4-4'-Bis(hexyloxy)-azoxybenzene.

The palladium complexation increases the value of both ordinary and extraordinary refractive indices but decreases the birefringence of the free ligand.

Taking into account that the measured values refer to the surface of the material we relate the optical density augmentation to mass density and molecular polarisability increases.

The lowest birefringence values measured for the A'PdA2 liquid cristal confirm side bounds of the free ligand molecule with the metal atom and the acetylacetonate group as suggested in figure 1.

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