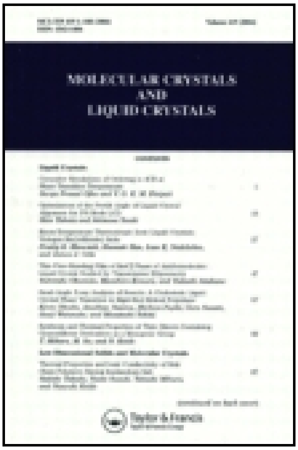

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Liquid Crystalline Organic Conductors: Studies in Crystalline and Mesomorphic Phase

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LIQUID CRYSTALLINE ORGANIC CONDUCTORS : STUDIES IN CRYSTALLINE AND MESOMORPHIC PHASE

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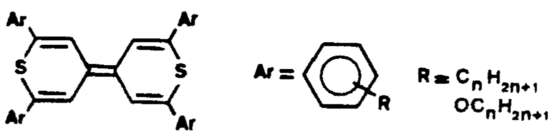
Abstract The present results concern a liquid crystalline organic conductor: DIPSAr$_4$-TCNQ. The ac conductivity was measured for the first time in the mesophase and indicates the actual possibility of obtaining organic conductors with mesomorphic behavior.

INTRODUCTION

Several attempts to prepare liquid crystals having conducting properties have been reported[1-3]. We have shown that this kind of material can be obtained starting from disk-like π-donors[1a,b,d] or π-acceptors[1c,d]. Namely, substituted dithiapyranylidenes 1, by complexation or partial oxidation, lead to mesomorphic paramagnetic species.



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The most interesting, among the prepared com-

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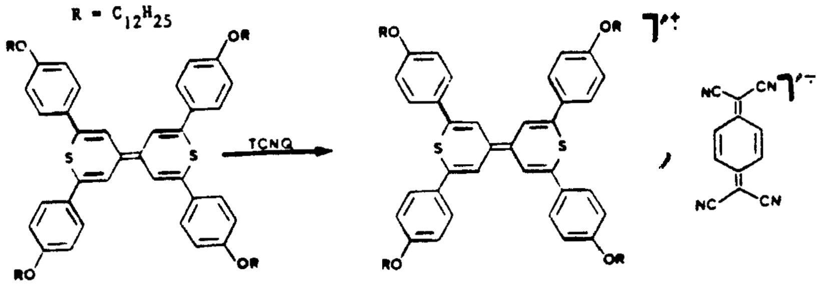
pounds, is the TCNQ complex of 1 (Ar = p-⟨O⟩-$OC_{12}H_{25}$)



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It presents liquid crystalline behavior between 120-154°C. In the crystalline phase, the conductivity has been measured[1d]. At room temperature the values are : σ_{powder} : 10^{-3} $(\Omega\ cm)^{-1}$, $\sigma_{single\ crystal}$ = 0.7 $(\Omega\ cm)^{-1}$.

In the present work, the synthesis and principal characteristics of complex 2 will be described. The results of conductivity measurements in the liquid crystalline phase of this complex are reported.

SAMPLE PREPARATION

Neutral donnors : 1a was prepared from 2,6-diarylthiopyrylium perchlorate[4] by Zn reduction[1] (Yield 77%) and purified by extraction with toluene followed by crystallization from hexane-ethanol 9:1.
Complex 2 : 0.1 mmole of 1 and 0.11 mmole of TCNQ are refluxed 15 minutes in 5 ml dichloromethane. After cooling, the complex was precipitated with

pentane. Single crystals were obtained by a diffusion technique (H-tube), solvent : CH_2Cl_2-CH_3CN, 2.10^{-3}M.

RESULTS

Mesomorphic properties

The DSC data[1d] show mesomorphic behavior, for complex 2 between 120°-154°C. The ΔH value for the first transition (Cr → M) is much greater than for the second one (M → I).

The X-ray studies[5] of this mesophase show a lamellar structure. Within the layers the donor's molecules are stacked and the intermolecular distances are 3.6 Å (figure 1). Therefore the organization in this mesophase is intermediate between those of smectic and columnar disk-like liquid crystals.

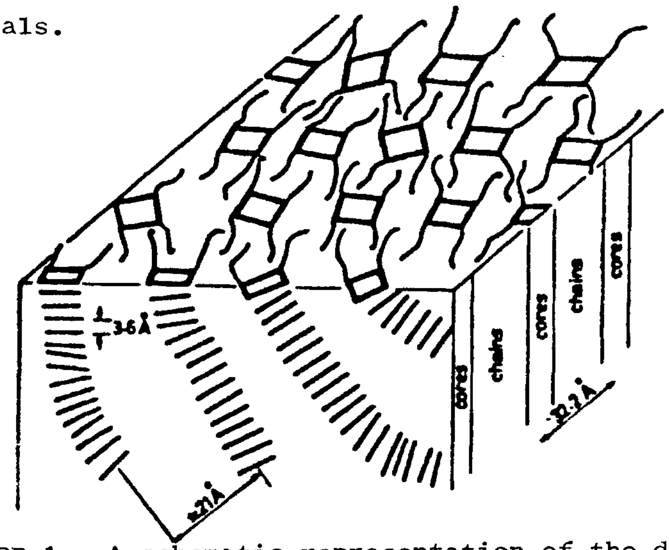

FIGURE 1 : A schematic representation of the donor organization in the mesophase of the complex 2 (the TCNQ molecules are not represented).

Electrical properties

a)Crystalline phase

DC conductivity measurements[1d] were made by a standard four probe technique in the range 250-350 K using gold wires and platinum paint. The electrical conductivity as a function of temperature curve shows a metal-like behavior with a maximum of conductivity value (0.7 $(\Omega\,cm)^{-1}$) near room temperature.

b) Mesomorphic phase

Conductivity results, presented for the first time in reference 6, were obtained by determining the reflection coefficient of a 0.5 mm layer of liquid crystal exposed to electromagnetic waves in the frequency range 0.1 to 1 GHz using the apparatus shown in figure 2.

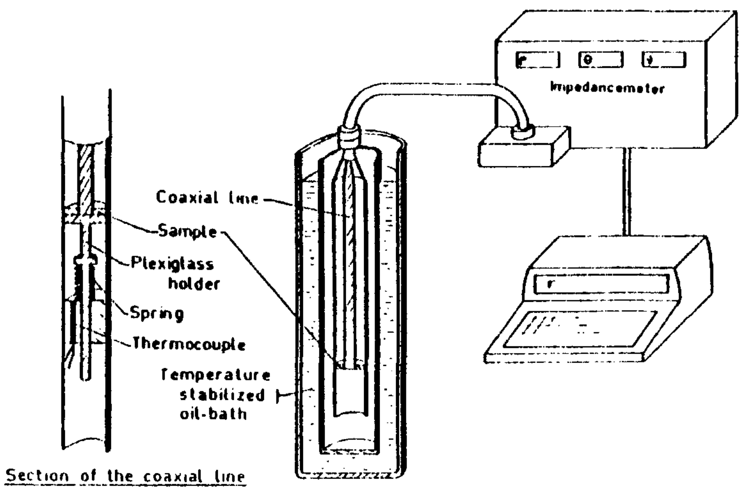

FIGURE 2 : Schematic representation of the conductivity apparatus.

The conductivity observed depends on the temperature and on the frequency (figures 3-4) of the electromagnetic waves.

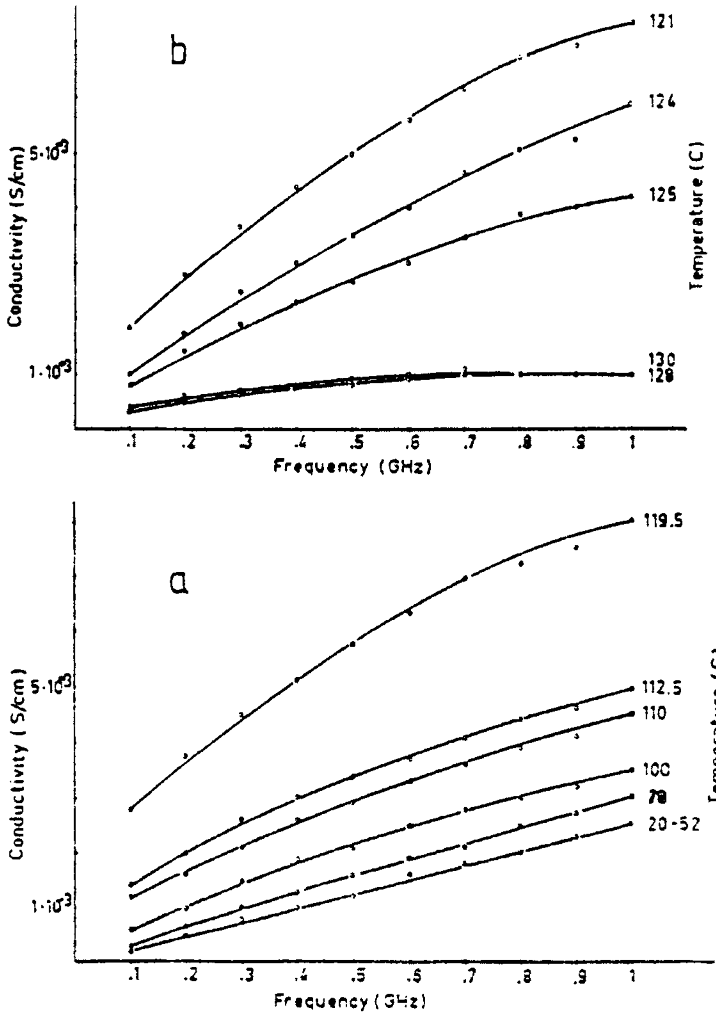

FIGURE 3 : Frequency dependence of the conductivity measured at selected temperatures during the first warming cycle : a) value in the crystalline phase, b) value in the mesophase.

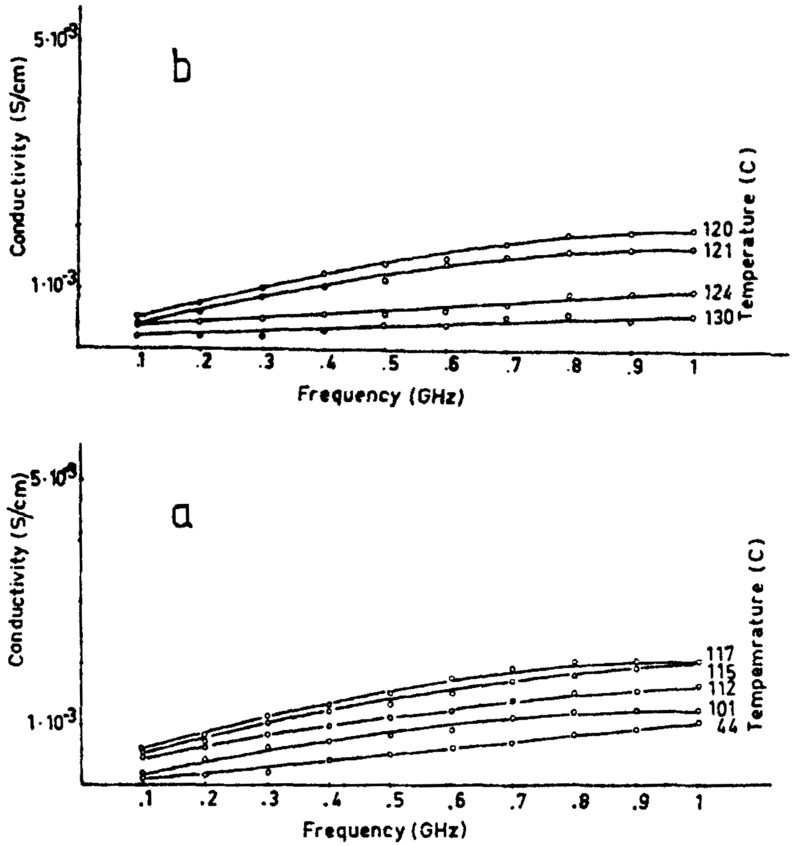

FIGURE 4 : Frequency dependence of the conductivity measured during the second warming cycle (see figure 3).

Above 120°C, after the crystal-mesophase transition, the conductivity decreases but remains at the same order of magnitude as the powder conductivity of the complex ($\sigma = 10^{-3}$ $(\Omega\ cm)^{-1}$). It is not surprising to observe a decrease of the conductivity in the mesophase. Electronic transfer is more difficult when the phase is less ordered and the thermal motion of the molecules is significantly larger. This decrease is partially irreversible.

Presumably, the crystalline phase obtained by cooling from the mesophase is not the same as the initial one. This interpretation is supported by X-ray and calorimetric studies[5].

CONCLUSION

We have demonstrated the possibility of obtaining materials exhibiting both mesomorphic and conduction properties. To the best of our knowledge, for the first time, electrical conductivity is investigated in the mesophase.

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