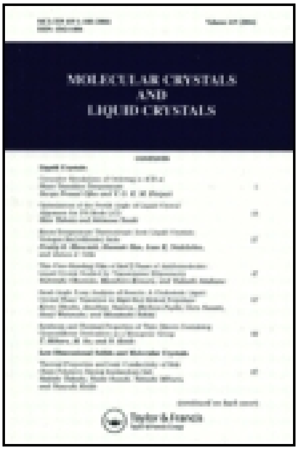

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Resistivity of a Liquid Crystalline Organic Conductor Measured Within the Mesophase from 100 to 1000 MHz

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Version of record first published: 20 Apr 2011.

To cite this article: R. Kormann, L. Zuppiroli, V. Gionis & H. Strzelecka (1986): The Resistivity of a Liquid Crystalline Organic Conductor Measured Within the Mesophase from 100 to 1000 MHz, Molecular Crystals and Liquid Crystals, 133:3-4, 283-290

To link to this article: http://dx.doi.org/10.1080/00268948608080820

Mol. Cryst. Liq. Cryst., 1986, Vol. 133, pp. 283–290
0026-8941/86/1334–0283/$15.00/0

Printed in the United States of America

The Resistivity of a Liquid Crystalline Organic Conductor Measured Within the Mesophase from 100 to 1000 MHz

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(Received July 17, 1985)

The a.c. conductivity of a liquid crystalline organic conductor is measured for the first time within the mesophase. The charge transfer complex is still conducting above the transition temperature of 120°C; but each stay in the mesophase produces an irreversible degradation of the transport properties, the consequences of which can be observed in the crystalline phase too.

Keywords: liquid crystals, organic semiconductors, electronic conduction

I. INTRODUCTION

The recent literature reports several attempts to prepare liquid crystals having the conducting properties of organic conductors. The structural analogy between the molecular stacking in conducting charge transfer complexes | 1 | and the columnar arrangement of discotic mesophases | 2 | gave the initial direction for the syntheses in this new field | 3-5 |.

This new type of materials can be prepared from disk-like π-donors | 3a | or π-acceptors | 6 |. The compound investigated in the present work is a mesomorphic TCNQ 1/1 charge transfer complex obtained from the disk-like donor molecule represented in Figure 1.

The mesophase of this complex was observed between 120 and 154°C | 7 |. The nature of the phase described by Davidson et al. | 8 | is very particular. The organisation of molecules is intermediate between those of smectic (presence of layers) and columnar phases. The donor cores remain in stack with a short core to core distance (3.6 Å). This TCNQ charge transfer complex was found to be conducting in solid state; small single crystals were obtained by a diffusion technique | 3 | and the conductivity measured by the four probes standard dc method was found to be 0.7 $(\Omega\text{cm})^{-1}$ at room temperature. But no data are available above the phase transition due to the difficulty of maintaining stable electrical contacts on the samples above this temperature.

In this communication, ac conductivity results measured in the mesophase, are presented. They have been obtained by determining the reflexion coefficient of a 0.5 mm layer of liquid crystal exposed to an electromagnetic wave in the frequency range 0.1 to 1 GHz.

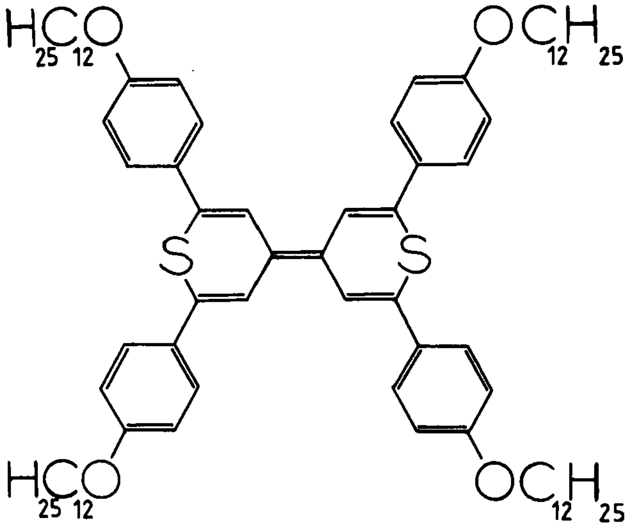

FIGURE 1 The donor disk shaped molecule of interest in the present work.

II. EXPERIMENTAL TECHNIQUE

A 30 cm long, air coaxial line was connected to a HP 4191 A rf impedance analyser, able to measure, at its input, in amplitude and in phase, the intensity reflected by anything connected there. The line was closed by a 0.5 mm thick, disk shaped, film of the charge transfer complex powder, compacted on an insulating plastic holder (Figure 2). The value of the reflexion coefficient ($+1$ for a short circuit, -1 for an open circuit, 0 for a purely resistive 50 Ω load) can be measured at the entrance of the bridge with an absolute accuracy of 2.10^{-3} for the modulous and better than 1 degree for the phase. In order to take into account the transformation of the impedances because of the presence of an air-line between the sample and the entrance of the bridge, a calibration is achieved before each experiment by connecting at the terminal part of the line, instead of the sample, three known loads. This operation allowed an accurate and experimental determination of the three different S parameters of the line as a function of the frequency. Knowing these three parameters, any reflexion coefficient ρ_E at the input of the bridge can be transformed into the reflexion coefficient ρ_S at the sample by the formula

$$\rho_S(\omega) = S_{11}(\omega) - [S_{12}(\omega)]^2/[S_{22}(\omega) - 1/\rho_E(\omega)]$$

where S is the scattering matrix of the line | 9 |. This operation multiplies by 3 the nominal error on the reflexion coefficient but the

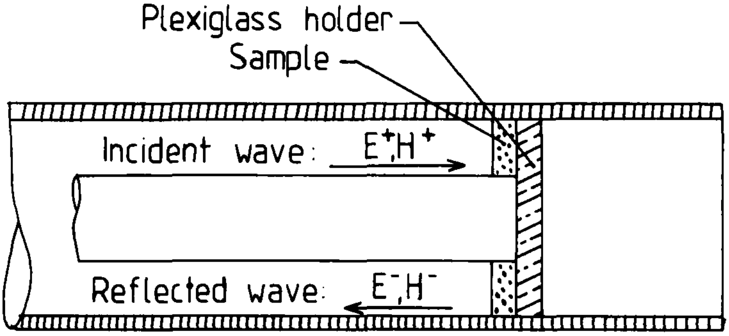

FIGURE 2 The radiofrequency coaxial line closed by the sample of interest is connected to a HP 4191 A rf impedance analyser. From the reflection coefficient measured in amplitude and in phase at the input of the analyser the computer HP 9825 calculates the conductivity of the sample. The temperature is measured by the thermocouple very close to the sample and the lower part of the line appropriately shielded is warmed in a regulated oil bath.

resolution remains lower than 10^{-3}. It is achieved on-line by a table desk HP 9825 computer connected to the bridge. Then, the computer transforms the value of the reflexion coefficient for the film of interest in a value of the ac conductivity by using a procedure analogous to the classical reading of the Smith chart | 9 |. Finally, the terminal part of the line closed by the sample and shielded by a copper socket, was introduced in a temperature stabilized oil bath. The temperature was measured close to the sample by a calibrated thermocouple.

The experimental procedure was the following: the sample was slowly warmed from 20°C to 130°C at a rate of about 10 degrees per hour. The frequency dependence of the conductivity was measured at different selected temperatures. Then it was cooled down and warmed once more for a second measurement sequence and so on.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The frequency dependence of the conductivity, measured at selected temperatures is reported on Figure 3 for the first warming cycle and Figure 4 for the second warming cycle. For an easier reading of these figures, the variations in the mesophase were separated from the variations in the crystalline phase (Figures a and b). The conductivities recorded at room temperature are about 10^{-3} $(\Omega.\mathrm{cm})^{-1}$. These values are in good agreement with the previous dc powder measurements | 3, 7 |.

Before discussing the transport properties in the mesophase of the present organic conductor, it is useful to remind the dielectric properties of usual liquid crystalline phases | 10, 11 |. Liquid crystals are usually good insulators: at zero frequency, their room temperature conductivity is of the order of 10^{-8} to 10^{-9} $(\Omega.\mathrm{cm})^{-1}$ depending on the purity | 10 |. Most of the molecules constituting the mesophases are easily polarizable by an external dielectric field and their polarizability depends on the direction of the field with respect to the main axes of the molecules. Thus substantial dielectric losses, corresponding to an imaginary part ϵ'' of the complex dielectric constant of the order of 0.1 (conductivity of the order of the 5.10^{-5} $(\Omega.\mathrm{cm})^{-1}$) are often recorded in liquid crystals at high frequency | 11, 12 |, like in isotropic liquids, except that these losses do depend on the degree of orientation of the liquid crystalline phase by a factor of the order of two | 12 |. It is important to emphasize that the losses recorded in the present experiment and translated in terms of a frequency de-

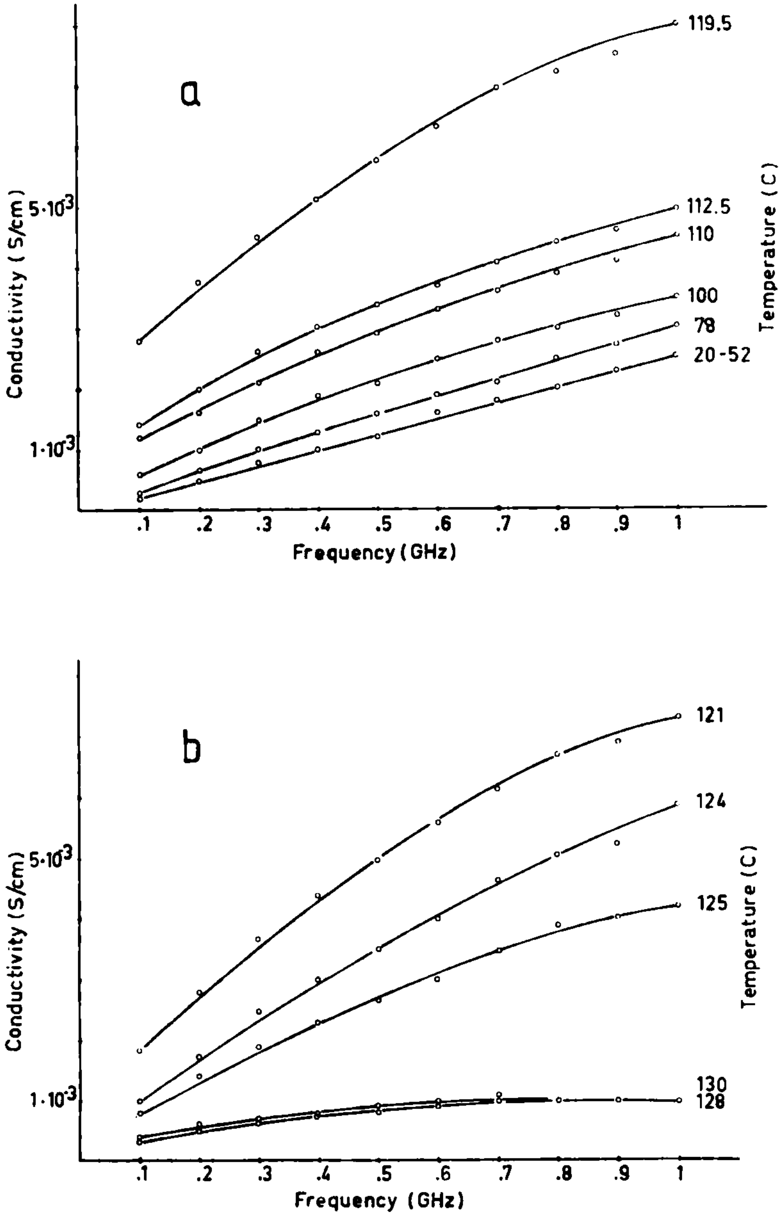

FIGURE 3 Frequency dependence of the conductivity measured at selected temperatures during the first warming cycle: a/ values in the crystalline phase where the conductivity increases with temperature, b/ values in the mesophase where the conductivity decreases with increasing temperature.

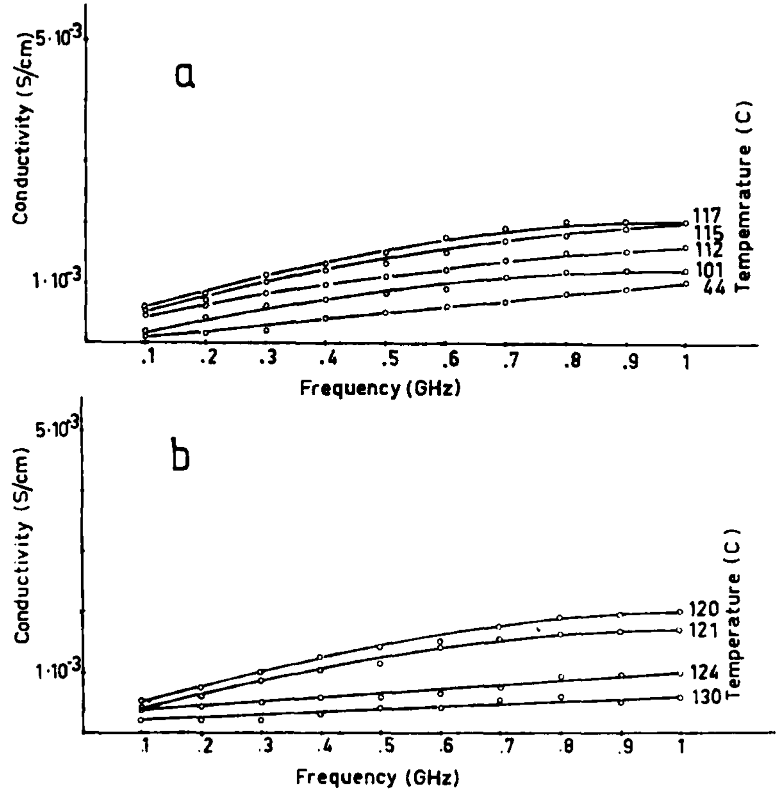

FIGURE 4 Frequency dependence of the conductivity measured during the second warming cycle (see Figure 3).

pendent conductivity are of a completely different nature, because the conductivity of the present compound is, at zero frequency, at least 5 to 6 orders of magnitude higher than those of insulating usual liquid crystals. Even at frequencies in the range 10 MHz to 1 GHz where a Debye absorption peak is recorded in insulating liquid crystals due to dipole or quadrupole friction, the losses are, in the latter, at least one order of magnitude lower than in the former conducting compound. In the present work, we are not dealing with dipole friction but with charge propagation in a disordered medium.

Coming back to the results in the crystalline phase, it is clear that the frequency dependence of the conductivity is quite large (a factor of 2 to 5 depending on the temperature between 100 and 1000 MHz). The fact is not surprising because of the granular character of the powder: conductivity is dominated by intergranular barriers and increases with increasing temperature or increasing frequency. Because of that, it is neither surprising to see a much lower frequency dependence at 130°C after the "melting" of the powder into the liquid crystalline mesophase. But, above this transformation, while the sample is becoming less granular and its transport properties closer to the intrinsic ones, the absolute value of the conductivity of the melt decreases with increasing temperature as in Figure (3.b). This effect, visible at any frequency, can only be due to a decrease of the intrinsic conductivity (microscopic electron transport) when entering the mesophase. What is important to notice is that this decrease is partly irreversible as shown in Figure 4 corresponding to a second warming cycle. There the effects are qualitatively the same as already described for the first cycle but at a lower scale. The degradation of the conductivity achieved in the mesophase is reflected in irreversible consequences in the solid state too.

These results are in good agreement with X-ray and calorimetric observations during warming and cooling cycles |(8.b)|. After heating several hours at 130°C, the characteristic structure of the mesophase is maintained down to room temperature. Even a shorter heating of a few minutes at 130°C leads to visible structural and transport changes in the crystalline phase.

IV. CONCLUSION

The original ac technique described in the present paper is based on a measurement of the electromagnetic wave absorption in a layer of about 1 mm of conducting liquid crystal. It gives a reliable value of the conductivity within the mesophase and allows to follow the electrical properties of the sample when it crosses the crystal to liquid crystal phase transition. It is not surprising to observe a decrease of the conductivity in the mesophase: electronic transfer is more difficult when less ordered is the phase and significantly larger is the thermal motion of molecules. But this decrease is partly irreversible. Presumably, the crystalline state obtained by cooling from the mesophase is not the same as the initial one. This interpretation is supported by the X-ray and calorimetric studies of Davidson. Anyway, the conductivity of a liquid crystalline charge transfer complex, measured within the mesophase is of the same order of magnitude $\sigma \sim 10^{-3}$ $(\Omega.\text{cm})^{-1}$ as the powder conductivity of this complex.

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