

Quasi-one dimensional electrical conductivity and thermoelectric power studies on a discotic liquid crystal

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Abstract. We have studied the electrical conductivity of well aligned samples of hexahexylthiotriphenylene (HHTT) in the pure as well as doped states. The dopant used was a small concentration (0.62 mole %) of the electron acceptor trinitrofluorenone (TNF). In the columnar phases, doping causes the AC(1 kHz) conductivity along the columnar axis (σ_{\parallel}) to increase by a factor of 10^7 or more relative to that in undoped samples; σ_{\parallel} attains a value of 10^{-2} S/m, which was the maximum measurable limit of our experimental set up. On the other hand, in the isotropic phase doping makes hardly any difference to the conductivity. The frequency dependence of the conductivity has been investigated. The DC conductivity of doped samples exhibits an enormous anisotropy, $\sigma_{\parallel}/\sigma_{\perp} \geq 10^{10}$, which is 7 orders higher than that reported for any liquid crystalline system, and, to our knowledge, the largest observed in an organic conductor.

We also report the first thermoelectric power studies on these ‘molecular wires’. The sign of the thermoelectric power is in conformity with the expected nature of the charge carriers, namely, holes.

Keywords. Quasi-one dimensional conductivity; thermoelectric power; discotic liquid crystals.

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1. Introduction

Liquid crystals of disc-shaped molecules, or discotic liquid crystals as they are now called, exhibit columnar phases, which consist of discs stacked one on top of the other to form columns, the different columns constituting a two-dimensional lattice (figure 1). A variety of columnar structures have been identified – upright columns, tilted columns, hexagonal lattice, rectangular lattice etc. In some cases, the discs are stacked with their molecular centres irregularly spaced to form liquid-like columns, as depicted in figure 1, whilst in others they are stacked in a regular ordered fashion [1]. An example of a compound which exhibits both types of columnar phases (disordered and ordered columns) is hexahexylthiotriphenylene (HHTT), the molecular structure and transition temperatures of which are shown in figure 2.

High resolution X-ray studies [2] have established that the *H* phase is a highly ordered hexagonal columnar phase with the discs stacked regularly within each column to form a helicoidal structure (figure 3), whilst the Col_h phase is the usual hexagonal columnar phase with a disordered stack of discs (figure 1).

The separation between the aromatic cores within a column is about 3.5 Å to 3.7 Å in the case of triphenylene and other similar compounds, so that there is considerable

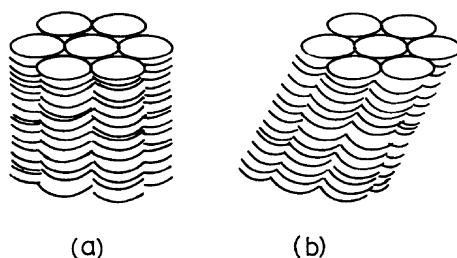


Figure 1. Columnar phases of discotic liquid crystals: (a) upright columns forming a hexagonal lattice (Col_h) and (b) tilted columns forming a rectangular lattice.

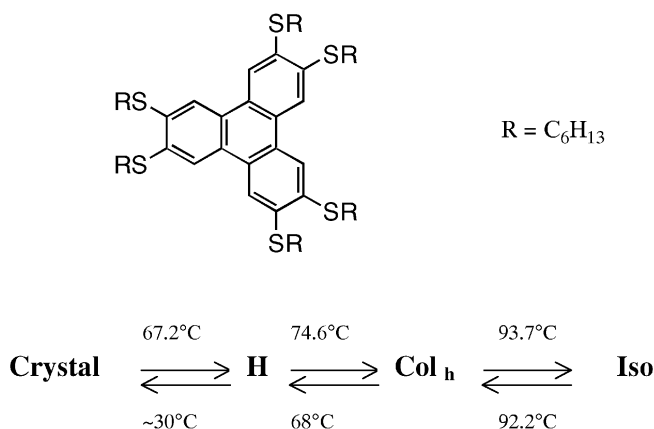


Figure 2. The structural formula of hexahexylthiotriphenylene (HHTT) and its transition temperatures.

overlap of the π -orbitals of adjacent molecular cores. One would, therefore, expect the electrical conductivity σ_{\parallel} along the columnar axis to be high, but, in fact, these compounds are good insulators. The reason for this is that their intrinsic charge concentration is low because of the large energy gap of about 4 eV. However, the addition of dopants, electron acceptors or donors, increases σ_{\parallel} significantly. Measurements on aligned samples of hexaalkoxytriphenylenes doped with $NOBF_4$ [3] have shown that σ_{\parallel} reaches a value of $10^{-2} S/m$. In hexakis(hexylthiotricycloquinazoline) doped with potassium a value of σ_{\parallel} of nearly $10^{-4} S/m$ has been reported [4]. Similarly, photo-induced charge carriers can give rise to high photoconductivity along the column axis [5].

We present here our experimental studies on the electrical conductivity of pure and doped HHTT [6]. Previous studies on HHTT used iodine as the dopant, which suppresses the H phase of the pure compound [7], or $AlCl_3$ which ‘failed to produce a chemically stable system whose conductivity could be studied’ [8]. We have doped HHTT with trinitrofluorenone (TNF), which is an electron acceptor [9], the concentration being 0.62 mol%. With this low concentration of TNF, the transition temperatures of the pure compound are affected only very slightly (figure 4). The doped compound may be expected to behave like a *p*-type material, i.e. the charge carriers will be holes.

Discotic liquid crystals

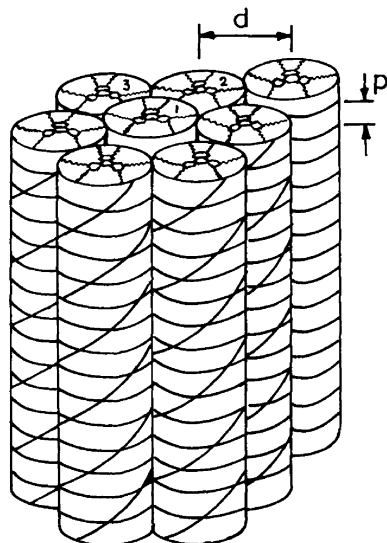


Figure 3. Schematic representation of the helicoidal structure of the ordered *H* phase of HHTT [2].

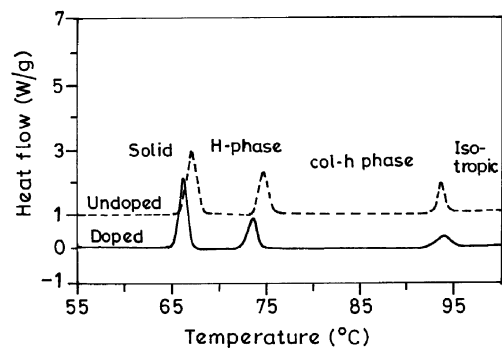


Figure 4. The differential scanning calorimetric traces for HHTT in the heating mode for (top) the pure compound and (bottom) the material doped with 0.62 mol% of TNF.

2. Experimental details

The syntheses of HHTT and TNF (by Sandeep Kumar and Manickam) are described briefly in the appendix.

The material was filled inside a sandwich-type cell formed by two gold-coated glass plates with mylar spacers. The sample thickness was about $12\ \mu\text{m}$. The interaction of the liquid crystal with the flat gold substrates produces well aligned films, with the discs parallel, or the columns perpendicular, to the walls. Using the gold coating as the electrodes, the measurement of σ_{\parallel} (parallel to the columns) is straightforward, as this

configuration corresponds to the usual “parallel plate” geometry. To measure the transverse conductivity σ_{\perp} (perpendicular to the columns) thin aluminium foils were used as electrodes adjacent to the spacers. In this case, the separation between the electrodes is some two or three orders greater than their thickness, and therefore requires a correction for the cell geometry [10]. This difficulty was overcome by measuring the conductivity in the isotropic phase and comparing it with the value measured at the same temperature using the parallel plate geometry.

AC conductivity measurements were made using an impedance analyser (HP 4194A) and DC measurements using an electrometer (Keithley 6517). The highest measurable value of σ_{\parallel} was 10^{-2}S/m , the limit being set by the sheet resistance of the gold coating. The lower (instrumental) limit was 10^{-10}S/m for the impedance analyzer and 10^{-14}S/m for the electrometer.

The material is extremely sensitive to the slightest contamination by humidity, etc., and hence the greatest care had to be exercised in filling the cells. All measurements were made in dry N_2 atmosphere.

3. Results

3.1 Electrical conductivity

Measurements of σ_{\parallel} at 1 kHz were made during repeated heating and cooling of the sample over several thermal cycles. We first present the data obtained in the cooling mode (figure 5). The first point to be noted is that the highest measurable value of the conductivity with the present set up being about 10^{-2}S/m , no difference was observed between the conductivities of the Col_h and H phases. The second point is that the addition of TNF makes no observable change in the isotropic phase value relative to the undoped sample. Though there is a slight scatter in the data points, especially in the vicinity of the isotropic- Col_h transition temperature, it is clear that σ_{\parallel} increases by about 7 orders of magnitude from the isotropic to the columnar phase in the doped material, and by the same order from the undoped to the doped value in the columnar phases. It may be noted that in the alkoxytriphenylenes doped either with AlCl_3 or NOBF_4 , the observed increase in σ_{\parallel} across the isotropic-columnar transition is at most about one order of magnitude [11, 3].

Figure 6 gives the measurements in the heating mode over several thermal cycles. Again σ_{\parallel} for the columnar phases is about 7 orders greater than the isotropic value.

Figure 7 presents the dependence of the conductivity on the frequency of the measuring electric field. Data were obtained at three frequencies, 1.0, 3.162, and 10.0 kHz. No change was observed in the columnar phases (up to the measurable limit of 10^{-2}S/m), implying that the mean free path of the charge carriers, or the time between collisions, is sufficiently long. This is in agreement with the conclusions of Arikainen *et al* [3]. On the other hand, the conductivity in the isotropic phase is sensitive to frequency, which indicates a short time between collisions. Extrapolating to DC one would expect the values in the isotropic phase to be even less than those for 1 kHz, and the values in the columnar phase to be unaffected. The DC measurements for σ_{\parallel} and σ_{\perp} are given in figure 8. The curves show that the conducting molecular cores in the columns are well insulated from each other by the alkyl matrix giving rise to an extremely high conductivity anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) of $\sim 10^{10}$, which to our knowledge, is the highest anisotropy recorded

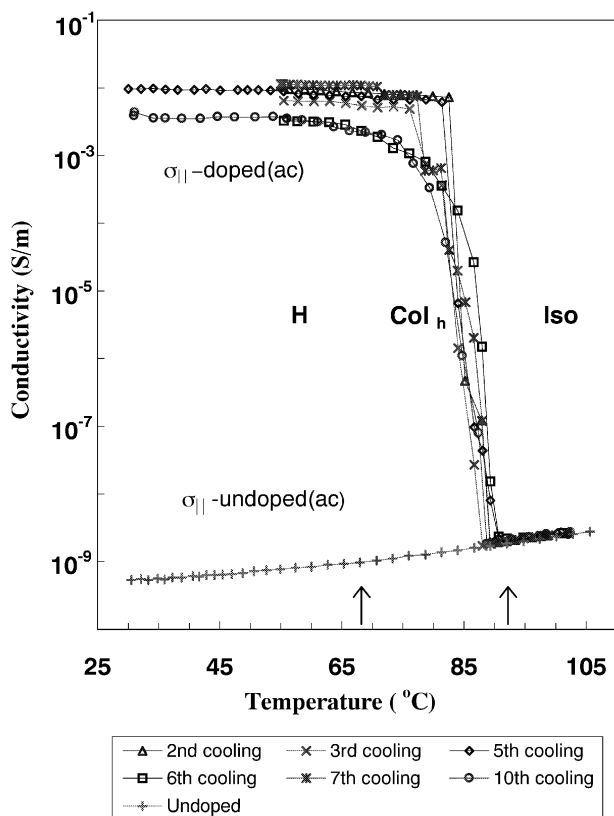
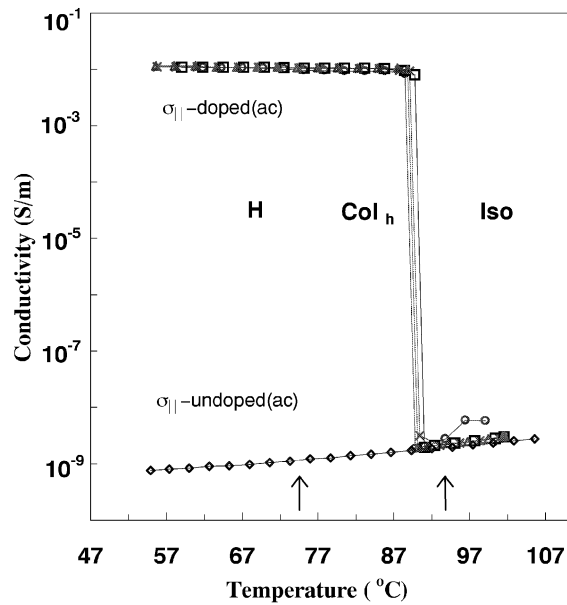


Figure 5. The measured AC electrical conductivity at 1 kHz parallel to the columns, $\sigma_{||}$, in doped HHTT in the cooling mode over several thermal cycles. The transition temperatures (DSC peak values) are indicated by the arrows.

so far for any conducting material, and about 7 orders higher than that observed previously in any liquid crystalline system. Thus the columns may well be described as ‘molecular wires’.

3.2 Thermoelectric power

The thermoelectric power of these wires were determined by imposing a thermal gradient along the column axis, using the parallel-plate geometry. The temperature gradient was increased in steps, up to about 10°C across 12 μm , the temperatures being measured by thermocouples and a digital multimeter (Keithley Model 2000). The voltage developed across the wires was measured with a nanovoltmeter (HP 34420A). The temperature gradient was then reversed and the measurements were repeated. The magnitude of the thermo-emf remains practically the same but its sign is opposite. Figure 9 gives the results. The thermoelectric power is estimated to be $\sim +2.4 \mu\text{V/K}$. The sign of the thermo-emf is in conformity with the expected *p*-type behaviour of the doped compound [12].



—○— 3rd htg. —×— 4th htg. —□— 5th htg. —△— 6th htg. —◇— undoped

Figure 6. The measured AC electrical conductivity at 1 kHz parallel to the columns, σ_{\parallel} , in doped HHTT in the heating mode over several thermal cycles. The transition temperatures are indicated by the arrows.

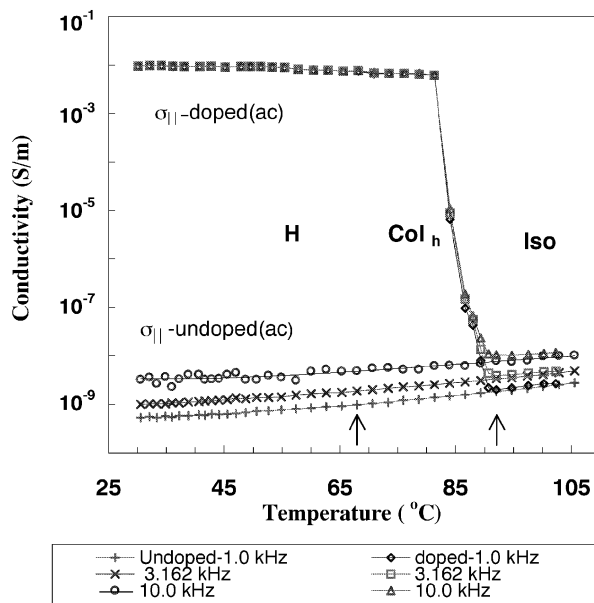


Figure 7. Experimental values of σ_{\parallel} of doped and undoped HHTT for 3 frequencies 1.0, 3.162 and 10.0 kHz in the cooling mode. The arrows indicate the transition temperatures.

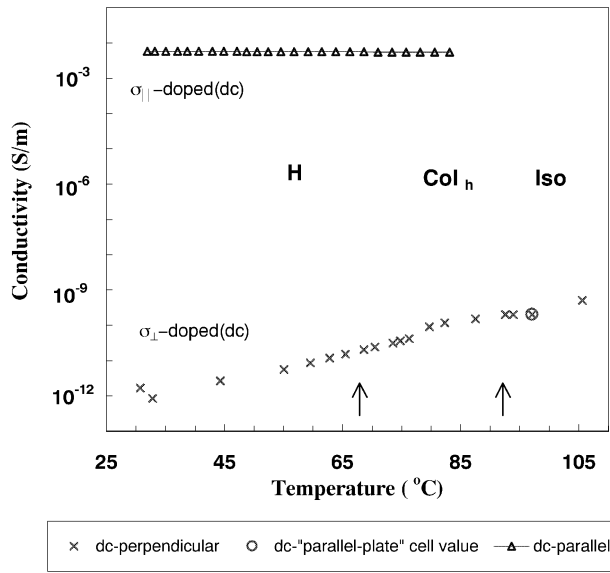


Figure 8. Experimental DC electrical conductivity σ_{\parallel} and σ_{\perp} of doped HHTT. The circle (o) represents the value in the isotropic phase determined using the parallel plate geometry.

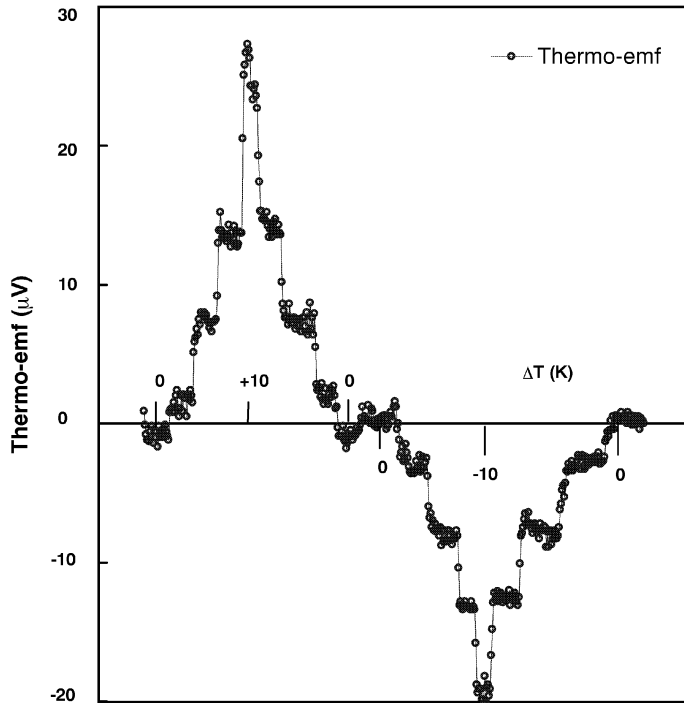


Figure 9. Thermo-emf along the column axis versus ΔT , the temperature difference between the top and bottom surfaces of the sample in the H phase of doped HHTT. The thermoelectric power is estimated to be $\sim +2.4 \mu\text{V}/\text{K}$.

4. Conclusions

We have observed extremely high anisotropic electrical conductivity in the columnar phases of HHTT doped with 0.62 mole% of the electron acceptor, TNF, the anisotropy being $\sim 10^{10}$. To our knowledge, this is the largest recorded for an organic conductor. Thermoelectric power measurements, carried out for the first time for a liquid crystalline system, show a positive sign in conformity with the expected nature of the charge carriers, namely, holes.

A hopping mechanism has been proposed to explain the conductivity [13]. Experiments are being planned with a view to studying the applicability of this model to the present case.

Appendix

Synthesis of trinitrofluorenone (TNF): 2,4,7-Trinitrofluorenone was prepared as reported in the literature [14].

Synthesis of hexahexylthiotriphenylene (HHTT): 2,3,6,7,10,11-Hexahexyl thiotriphenylene was prepared by modifying previously reported methods [15, 16]. Hexanethiol (4.0 g, 17 mmol) was added to a stirred suspension of potassium-*t*-butoxide (2.1 g, 17 mmol) in 1-methyl-2-pyrrolidinone (20 ml) and the solution was heated at 100°C for 10 min and then cooled to 70°C. Hexabromotriphenylene (1.0 g, 1.4 mmol), prepared by following the method of Breslow *et al* [17], was added and the mixture was stirred for 20 min at 70°C. After that it was poured over ice-water and the product was extracted with diethyl ether. The crude product was purified by repeated column chromatography over silica gel (230–400 mesh) eluting with 2–2.5% ethyl acetate in hexane followed by repeated crystallization (four times) in hexane–ether–acetone solution. The final product was filtered through 0.2 μm filter paper prior to crystallization.

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