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Discotic liquid crystals as quasi-one-dimensional electrical conductors†

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We have studied the electrical conductivity of well-aligned samples of hexa(hexylthiotriphenylene (HHTT) and hexapentyloxyanthraquinone (HPA) in the pure, as well as doped, states. The former compound was doped with 0.62 mol % by weight of the electron acceptor, trinitrofluorenone (TNF), the latter with 0.60 mol % by weight of the electron donor, anthracene. In the columnar phases, doping causes the AC (1 kHz) conductivity along the columnar axis ($\sigma_\parallel$) to increase by a factor of $10^7$ or more relative to that in undoped samples; $\sigma_\parallel$ attains a value of $10^{-2}$ S m$^{-1}$, 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 DC conductivity of doped HHTT exhibits an enormous anisotropy, $\sigma_\parallel/\sigma_\perp \geq 10^{10}$, which is seven orders of magnitude higher than that reported for any liquid crystalline system, and, to our knowledge, the largest observed in an organic conductor. Further, the perpendicular conductivity, $\sigma_\perp$, reaches the insulating regime. Thus the columnar phases behave nearly as one-dimensional conductors and may be described as ‘molecular wires’.

Thermoelectric power studies have also been carried out on the molecular wires that show a reversal of the sign on going from the p-type to the n-type system (positive for p-type and negative for n-type). This is in conformity with the expected nature of the charge carriers, namely, holes in HHTT + TNF (p-type) and electrons in HPA + anthracene (n-type). It is pointed out that since the doped systems behave nearly as one-dimensional conductors unusual physical properties might be anticipated.

Finally, we discuss very briefly some further studies that are under way. We propose to adopt the four-probe method to increase the highest measurable conductivity to the metallic range (after eliminating the lead and contact resistances) with a view to finding metallic conductivity in discotic liquid crystals. We also intend to carry out Hall-effect studies and to explore the possibility of observing superconductivity by looking for the Meissner effect in magnetic susceptibility measurements.

Keywords: discotic liquid crystals; quasi-one-dimensional electrical conductivity; thermoelectric power

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1. Introduction

Most liquid crystals of disc-shaped molecules (or discotic liquid crystals as they are now called) exhibit columnar phases with the discs stacked one on top of the other in columns, the different columns constituting a two-dimensional lattice. Since their discovery nearly 25 years ago (Chandrasekhar et al. 1977), well over 1000 discotic compounds have been synthesized and a variety of columnar structures have been identified—upright columns forming a hexagonal lattice (figure 1a), tilted columns forming a rectangular lattice (figure 1b), etc. In some cases, the columns are liquid like, i.e. the molecular centres are arranged aperiodically within each column, as depicted in figure 1, while in others they are arranged in an ordered fashion, i.e. with a much longer range of positional correlation of the molecular centres along the column axes (Chandrasekhar 1993, 1998).

X-ray studies show that the average separation between the aromatic molecular cores within a column is ca. 3.4–3.7 Å in the case of triphenylene, anthraquinone and other similar compounds, indicating an overlap of the π-orbitals between adjacent molecular cores. One would, therefore, expect the electrical conductivity $\sigma_\parallel$ along the column axis to be high but, in fact, these compounds are insulators in the pure state. This is because the intrinsic charge concentration is low, owing to the large energy band gap of 4 eV. However, the columns can be made to have electrical conductivity in the semiconducting range by the introduction of suitable electron acceptors or donors by chemical doping. Measurements on aligned samples of hexaalkoxytriphenylene doped with NOBF$_4$ (Arikainen et al. 1995) have shown that $\sigma_\parallel$ attains $10^{-2}$ S m$^{-1}$, which is in the semiconducting range. In hexakis(hexylthiotricycloquinazoline) doped with potassium, $\sigma_\parallel$ attains $10^{-4}$ S m$^{-1}$ (Boden et al. 1994b), which again is in the semiconducting range. Holes with a very short lifetime can also be created by the absorption of photons of appropriate energy (greater than or equal to the band gap), which can be made to drift under an applied electric field, enabling one to study their mobility by measuring their transit time over a known distance (the time-of-flight technique). In fact, this technique has led to valuable insights into charge transport in discotic liquid crystals by identifying the nature of the charge carriers, whether holes or electrons, by the observation of non-dispersive transport along the column axis and the temperature independence of the mobility of the charge carriers (Adam et al. 1993, 1994; Boden et al. 1995). The pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique has also been used to investigate the behaviour of charge-carrier mobility (Van de Craats et al. 1996). These stud-
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Figure 2. The structural formula of hexa(hexylthiotriphenylene (HHTT) and its transition temperatures.

Compounds investigated

We present our experimental studies on the electrical conductivity and thermoelectric power of two discotic compounds in the pure and doped states: hexa(hexylthiotriphenylene (HHTT) and hexapentyloxyanthraquinone (HPA).

Hexa(hexylthiotriphenylene (HHTT)

The structural formula of HHTT and its transition temperatures are given in figure 2. High-resolution X-ray studies on freely suspended strands show that the H-phase is a highly ordered hexagonal columnar phase with the discs stacked regularly within each column to form a helicoidal structure, while the Col_{h}-phase is the hexagonal columnar phase with a disordered stack of discs (Fontes et al. 1988). In previous studies on HHTT, iodine was used for saturated doping, which suppresses the H-phase of the pure compound (Vaughan et al. 1992). In another experiment, the use of AlCl_{3} as the dopant ‘failed to produce a chemically stable system whose conductivity could be studied’ (Boden et al. 1992). In the present study, we have doped HHTT with trinitrofluorenone (TNF), which is an electron acceptor (Ringsdorf & Wustefeld 1990), at a concentration of 0.62 mol % by weight (Balagurusamy et al. 1998, 1999). With such a low concentration of TNF, the transition temperatures of the pure compound are affected only very slightly (figure 3). The doped compound may be expected to behave like a p-type material, i.e. the charge carriers will be holes.

Hexapentyloxyanthraquinone (HPA)

The structural formula of HPA and its transition temperatures are shown in figure 4. Again, there is a highly ordered columnar hexagonal phase followed at a...
higher temperature by the usual hexagonal columnar phase with a disordered stack of discs. The dopant used in this case was 0.60 mol % by weight of anthracene molecule (Chandrasekhar et al. 2000). The differential scanning calorimeter traces of the pure and the doped systems confirm that the transition temperatures are affected only slightly on doping (figure 5), as is the case for HHTT doped with a small quantity of TNF.

3. Experimental details

The material was filled inside a sandwich-type cell formed by two gold-coated glass plates with mylar spacers, kept in a dry nitrogen atmosphere. The sample thickness ranged from 12 to 20 µm for different cells. On slow cooling from the isotropic phase, the interaction of the liquid crystal molecules with the flat gold-coated substrate produces well-aligned films, with the disc-like molecules parallel, or the columns
formed by them perpendicular, to the substrate walls. The gold coatings also act as electrodes, and the measurement of $\sigma_{\parallel}$ (parallel to the columns) in this configuration is straightforward, since it corresponds to the usual ‘parallel-plate’ geometry, where the probing electric field is normal to the substrates, i.e. along the column axis. In this geometry, the dimensions of the plates of the sandwich cell are very much larger than the separation between them. In order to measure the transverse conductivity $\sigma_{\perp}$ (perpendicular to the columns), thin aluminium foils kept adjacent to the mylar spacers were used as electrodes. In this case, the separation between the electrodes is several orders of magnitude larger than their thickness and hence requires a correction to be applied for the cell geometry in order to calculate the absolute conductivity from the measured conductance (see, for example, Jackson 1975). 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 (Hewlett-Packard 4194A) and DC measurements with an electrometer (Keithley 6517) in the sample cells described above. The sample cell was kept inside either a Mettler hot-stage with controller or a copper block sample heater operated with an INSETEC(USA) temperature controller. The temperature of the sample was measured with a thermistor connected to a Keithley or Hewlett-Packard digital multimeter. The highest measurable value of the conductivity along the columns was $10^{-2}$ S m$^{-1}$, which is the limit set by the sheet resistance of the gold coatings that act as electrodes. The lower limit was $10^{-10}$ S m$^{-1}$ for the impedance analyser and $10^{-14}$ S m$^{-1}$ for the electrometer. All measurements were carried out in a dry nitrogen atmosphere; some of them in such an atmosphere attained with a glove-box set-up, where the oxygen and moisture levels could be brought down to and maintained at ppm levels.

The experimental errors come mainly from the usual error associated with any high-resistance measurement (ca. $10^{13}$ $\Omega$) while measuring the conductivity perpendicular to the columns. The error is ca. 5% maximum in our studies, which would give a similar magnitude of the error for the conductivity anisotropy we discuss.
4. Results and discussion

(a) Electrical conductivity

The AC conductivity along the columns ($\sigma_\parallel$) were measured at three different frequencies (1.0, 3.162 and 10.0 kHz) during repeated heating and cooling of the sample over several thermal cycles for the doped and undoped HHTT. The measured data for the cooling mode are presented in figure 6. Since the sheet resistance of the gold-coating restricts the highest measurable conductivity to $10^{-2}$ S m$^{-1}$, no difference was observed between the conductivities of the $\text{Col}_h$- and H-phases. The addition of the dopant TNF hardly changes the conductivity in the isotropic phase relative to the undoped sample. On the other hand, the conductivity in the columnar phase increases by nearly seven orders of magnitude from the value in the doped isotropic phase. A similar increase is found in the doped columnar phases relative to the undoped ones. It is worth mentioning that in the alkoxytriphenylene s, doped with either AlCl$_3$ or NOBF$_4$, the conductivity anisotropy $\sigma_\parallel/\sigma_\perp$ is only about three orders of magnitude (Boden et al. 1993, 1994a; Arikainen et al. 1995).

The conductivity in the mesophase does not change with frequency in the range 1.0–10.0 kHz in the doped state (figure 6). The data points in the vicinity of the isotropic–$\text{Col}_h$ transition show this more clearly. However, the conductivity does show an increase with frequency in the isotropic phase in the doped state. In the undoped state, the frequency dependence is observed in the mesophases as well as in the isotropic phase. The frequency independence of conductivity in the mesophase in this frequency range shows that the charge carriers, namely, holes, have a much longer mean-free path or time between collisions, whereas in the undoped state and in the isotropic phase of the doped state they have a much shorter mean-free path. We show later that the thermoelectric power measurements provide confirmatory evidence that the charge carriers are holes.
The anthraquinone derivative, namely, HPA, was doped with anthracene and the electrical conductivity $\sigma_\parallel$ was measured along the columns (figure 7). It also shows an increase of nearly seven orders of magnitude in conductivity in the columnar phase relative to that in the isotropic phase, as well as that in the columnar phase in the undoped state. Further, the conductivity in the isotropic phase hardly changes on doping. These features are very similar to those found in HHTT doped with TNF. The doped HPA also shows a frequency-dependent conductivity in the isotropic phase of doped, as well as undoped, systems and in the columnar phase of the undoped state, suggesting that the charge carriers, which are expected to be n-type, namely, electrons, have a relatively short mean-free path. On the other hand, in the columnar phase of the doped state, it does not show the frequency dependence, which suggests that the electrons have a much longer mean-free path. Hence the electrons, which are expected to act as the charge carriers in this system, also behave in a similar fashion to the holes in doped HHTT, at least as far as the frequency dependence of conductivity is concerned. We show later that the sign of the thermoelectric power is opposite to that of HHTT, as is to be expected.

The DC conductivity measured in the doped state of HHTT, both along and perpendicular to the columns, is shown in figure 8. Along the columns, it is nearly the same as the values obtained in the AC measurements, namely, $10^{-2} \text{ S m}^{-1}$. The conductivity measured perpendicular to the columns reaches a lowest value of nearly $10^{-12} \text{ S m}^{-1}$ in the H-phase, yielding an anisotropy $(\sigma_\parallel/\sigma_\perp)$ of $10^{10}$. Furthermore, this lowest measured conductivity in the H-phase lies in the upper limit of the conductivity range exhibited by inorganic insulators (Kittel 1996a). The nearly-insulator-like behaviour observed perpendicular to the columns shows that the aliphatic matrix formed by the alkyl chains attached to the periphery of the molecular core form an insulating medium surrounding the conducting molecular cores. Thus the studied discotic liquid crystals are nearly like one-dimensional conductors and behave like ‘molecular wires’. The observed conductivity anisotropy of $10^{10}$ is, to our knowledge, the highest reported for any conducting material, and

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**Figure 7.** $\sigma_\parallel$ measured in the doped HPA in cooling mode at three different frequencies (1.0, 10.0 and 100.0 kHz).
Figure 8. Measured DC electrical conductivity, $\sigma_h$ and $\sigma_\perp$, of doped HHTT. The circle represents the value in the isotropic phase determined using the parallel-plate geometry.

about seven orders of magnitude higher than that observed previously in any liquid crystalline system.

AlCl$_3$ or NOBF$_4$ are highly non-planar structures, which prevents them from being interleaved between the aromatic cores of the columns. They tend to occupy the space between the columns and therefore assist in the hopping of the charge carriers between the columns in the transverse direction. On the other hand, TNF is a highly planar molecule, which is easily incorporated into the aromatic cores, and consequently does not assist in charge hopping from one column to the next in the lateral direction. This would account for the very high conductivity anisotropy with TNF as dopant ($\sigma_h/\sigma_\perp \gtrsim 10^7$) compared with AlCl$_3$ or NOBF$_4$, which yield much less anisotropy ($\sigma_h/\sigma_\perp \sim 10^3$) (Boden et al. 1993, 1994a; Arikainen et al. 1995).

Preliminary studies with higher TNF concentrations up to ca. 5 mol % by weight indicate a diminution of conductivity with increasing concentration of the dopant. In contrast, with AlCl$_3$ or NOBF$_4$, Boden et al. (1993) found an increase in conductivity with an increase in concentration. An explanation that suggests itself is that the AlCl$_3$ or NOBF$_4$ molecules, being non-planar, stay away from the aromatic region and thus do not interfere with the charge-carrier propagation along the columns. TNF, on the other hand, fits easily into the aromatic region of the columns and interferes with the charge-carrier propagation at high concentration. We intend to carry out further studies to establish this explanation conclusively.

(b) Thermoelectric power

The thermoelectric powers of the doped HHTT and HPA have been measured by imposing a thermal gradient along the column axis using the ‘parallel-plate’ geometry. The temperature gradient between the electrodes was established by applying a steady voltage using a high-precision power supply (HP 6654A) to a heating strip attached to the appropriate side of the sample cell. The temperature gradient was
Figure 9. Thermo-emf measured along the column axis versus $\Delta T$, 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 $\text{ca.} +3.2 \, \mu \text{VK}^{-1}$. The slight deviation from near flatness of thermo-emf arises from the stabilization time it takes for the temperature gradient to settle down to a steady value.

Figure 10. Thermo-emf measured along the column axis versus the temperature difference for the doped HPA in the Col$_x$-phase. The thermoelectric power is estimated to be $\text{ca.} -3.3 \, \mu \text{VK}^{-1}$.

increased in steps, up to $\text{ca.} 10^\circ \text{C}$ across 12–20 $\mu$m thick cells, by increasing the voltage applied to the heating strip in steps. The temperatures were measured by thermocouples and a digital multimeter (Keithley Model 2000). The voltage developed across the gold coatings on the two sides of the cell was measured with a nanovoltmeter (HP 34420A) at very close intervals ($\text{ca.} 10 \, \text{s}$) and recorded for 10–15 min between successive steps after increasing the heating strip voltage. During this period, a steady temperature gradient is established between the top and bottom electrodes, as shown by the temperatures measured by the thermocouples, which is also reflected in the thermo-emf attaining a steady value. After reaching the highest temperature
gradient, the heating strip voltage was reduced in steps to zero. The temperature gradient was then reversed. In this case, the magnitude of the thermo-emf remains practically the same, but its sign is reversed. The step-like change in the thermo-emf corresponds to the change in the temperature gradient soon after the heating strip voltage is changed. The thermo-emf then slowly reaches a steady value as a steady temperature gradient is established. The positive sign of the thermo-emf (figure 9) conforms with the expected p-type nature of the charge carriers in HHTT doped with TNF; the thermoelectric power is estimated to be ca. $+3.2 \mu\text{V K}^{-1}$ (Kittel 1996b). The results of the thermo-emf measurements made on HPA doped with anthracence are shown in figure 10. The sign of the thermo-emf is negative (thermoelectric power ca. $-3.3 \mu\text{V K}^{-1}$) and opposite to that determined in doped HHTT. This clearly shows that the sign of the thermo-emf reverses when the nature of the charge carrier changes from holes in HHTT to electrons in HPA.

5. Conclusion and further studies

We have studied the electrical properties of p- and n-type discotic liquid crystals, doping them with a small concentration of electron acceptor or donor. On doping, their AC electrical conductivity at 1 kHz along the columns increases by nearly seven orders of magnitude. The studied p-type system, namely, HHTT doped with TNF, shows extremely high anisotropy in DC measurements, ca. $10^{10}$ in the columnar phases, with the electrical conductivity in the perpendicular direction reaching the insulating regime. Thus the materials behave very much like one-dimensional conductors. To our knowledge, the observed anisotropy is the largest recorded for an organic conductor. The electrical conductivity of the studied n-type system, namely, HPA doped with a small concentration of anthracene, behaves similarly to doped HHTT. Due to the very similar dimensions of the column diameter, conducting molecular core and the aliphatic region surrounding the molecular cores, in HHTT and HPA, a similar anisotropy may also be expected to be seen in the doped HPA.

Thermoelectric power measurements carried out for the p- and n-type discotic liquid crystals show that the sign of the thermo-emf is in accordance with that expected from the nature of the charge carriers, namely, holes in the former, and electrons in the latter.

Since the highest conductivity, measured with two probes, along the columns in the doped systems is presently limited by the sheet resistance of the gold coatings that act as electrodes in thin-sandwich cells, we are planning four-probe measurements in suitably aligned samples that would allow measurements of the true conductivity in these, as well as other, systems. The four-probe measurements, which eliminate the lead and contact resistances (Roth 1995), would also allow measurements of extremely high conductivities reaching well above the metallic range in the liquid crystalline phases. The possibility of realizing discotic liquid crystals showing metallic conductivities will be explored. Hall-effect studies along with four-probe measurements of the conductivity are also being planned, which would throw light on the behaviour of the charge carriers in the doped state. Magnetic susceptibility measurements of the systems studied here, as well as newer systems, would be performed, which would probe the magnetic interactions of the charge carriers with spin, either among themselves alone or in combination with those of magnetic atoms embedded.
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in the molecular core. As these systems can behave as nearly one-dimensional electronic systems, unusual behaviour in their physical properties can be anticipated. Furthermore, the possibility of observing superconductivity in doped discotic liquid crystals will be explored by looking for the Meissner effect in magnetic susceptibility measurements.

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