Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Transient Photoconductivity and Dark Conductivity in Discotic Liquid Crystals

Neville Boden [a], Richard J. Bushby [a], Andrew N. Cammidge [a], Jonathan Clements [a], Rong Luo [a] & Kevin J. Donovan [b]

[a] Centre for Self Organising Molecular Systems, The University of Leeds, Leeds, LS2 9JT, UK

[b] Department of Physics, Queen Mary and Westfield College, London, E1 4NS, UK

Version of record first published: 23 Sep 2006.

To cite this article: Neville Boden , Richard J. Bushby , Andrew N. Cammidge , Jonathan Clements , Rong Luo & Kevin J. Donovan (1995): Transient Photoconductivity and Dark Conductivity in Discotic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 261:1, 251-257

To link to this article: http://dx.doi.org/10.1080/10587259508033472

Mol. Cryst. Liq. Cryst. 1995, Vol. 261, pp. 251–257
Reprints available directly from the publisher
Photocopying permitted by license only

TRANSIENT PHOTOCONDUCTIVITY AND DARK CONDUCTIVITY IN DISCOTIC LIQUID CRYSTALS.

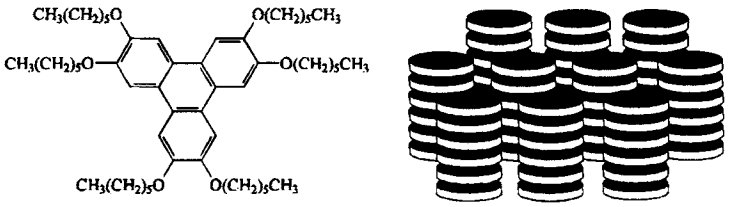
NEVILLE BODEN, RICHARD J.BUSHBY, ANDREW N. CAMMIDGE, JONATHAN CLEMENTS, AND RONG LUO,
Centre for Self Organising Molecular Systems, The University of Leeds, Leeds, LS2 9JT. UK

KEVIN J.DONOVAN,
Department of Physics, Queen Mary and Westfield College, London, E1 4NS. UK.

Abstract A comparative study of transient photoconductivity and dark conductivity in the discotic liquid crystal hexahexyloxytriphenylene (HAT6) is reported. In both experiments the transport is dispersive, and the carrier mobilities are essentially identical demonstrating that the presence of the counterions in the chemically doped conductors does not significantly perturb the mobility.

INTRODUCTION

The hexaalkoxytriphenylenes are the archetypal discotic liquid crystals.[1] They form mesophases (D_{ho}) comprised of columns of triphenylene rings arranged on a hexagonal lattice, Figure 1.



K (343K) D_{ho} (374K) I

FIGURE 1 Hexahexyloxytriphenylene (HAT6) and a schematic view of its columnar D_{ho} mesophase.

In the columns the triphenylene rings are stacked one-a-top of the other with separation of the order 3.5Å and the translational order decaying as a power law with correlation length of the order of 5 - 10 molecules.[2] We might therefore anticipate a significant degree of π-orbital overlap between adjacent triphenylene rings making these materials quasi-one-dimensional conductors. However, the gap between the valence and conduction bands is fairly large (~ 4eV), so that these materials are essentially insulating.[3] They may, however, be made to conduct by either chemical doping[4] or photochemically.[5] For example, the triphenylene ring is *electron rich*, so that when an oxidant such as $AlCl_3$ or $NOBF_4$ is dissolved into the hydrocarbon chain matrix, an electron is extracted from the triphenylene core leading to the formation of a radical cation.[6] It has been established that the positive holes are highly mobile along the columns giving rise to a quasi-one-dimensional semiconductor.[4] The level of conductivity can be varied by the degree of charge transfer (0 - 0.15), which is governed by the stoichiometry.

Of particular interest, the conductivity along the direction of the columns varies linearly with the concentration of dopant implying that, since $\sigma_{\|} = ne\mu_{\|}$, $\mu_{\|}$ is constant, where $\mu_{\|}$ is the charge carrier mobility along the columns, n is the density of carriers and e is the electronic charge. This is suggestive of band-like conduction. However, $\mu_{\|} \sim 10^{-4} cm^2V^{-1}s^{-1}$ is on the low side for such a process ($\mu_{\|} \geq 1 cm^2V^{-1}s^{-1}$), and significantly, impedance spectroscopy reveals a dispersive transport mechanism.[4]

These observations raise the interesting question as to whether the dispersive transport owes its origin to the presence of the counterions, or to the intrinsic disorder in the molecular packing in the columnar stacks. To resolve this issue, we have carried out comparative studies of the conductivity of hexahexyloxytriphenylene (HAT6) doped with $NOBF_4$ and the photoconductivity of the undoped material. It will be shown that charge transport is intrinsically dispersive. In this respect our photoconductivity measurements differ from recently reported ones on HAT5 which suggest a band-like transport mechanism.[5]

RESULTS

HAT6 was synthesised and purified as described previously[6] and doped by making up solutions with $NOBF_4$ in dichloromethane, of appropriate concentrations, and then attaching to a high vacuum line to remove the solvent. The doped HAT6 was transferred into the measurement cell in a dry box (O_2 < 5ppm, H_2O < 10ppm). Alternating current (5Hz to 13MHz) electrical conductivity measurements were made on samples which were aligned by slowly cooling from the isotropic phase into the columnar phase in the presence of a magnetic field (B = 2.2T).

Typical measurements of the frequency dependence of the conductivity for the aligned sample are shown in Figure 2. The conductivity anisotropy, $\sigma_\parallel/\sigma_\perp$ is approximately 10^3. For both $\sigma_\parallel$ and $\sigma_\perp$, an $\omega^{0.8}$ frequency dependence is found at higher frequencies. At lower frequencies, $\sigma \sim \omega^0$. This type of behaviour is characteristic of dispersive transport.[7,8]

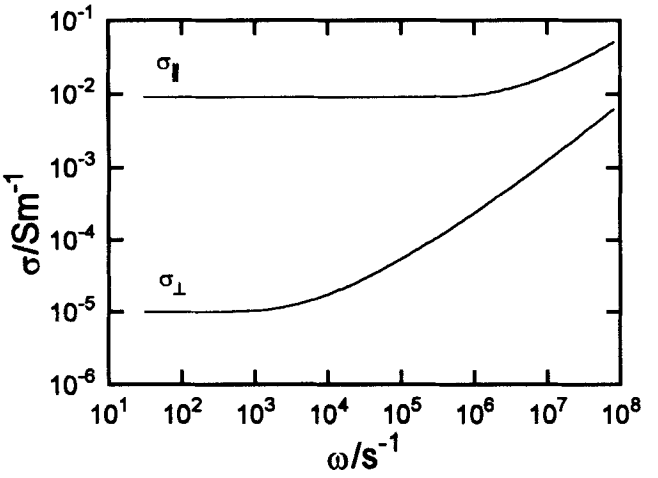


FIGURE 2 Alternating current conductivities parallel $\sigma_\parallel$ and perpendicular $\sigma_\perp$ to the axes of the columns of $HAT6/NOBF_4$ (x = 0.01) in the D_{ho} phase at 350K.

A charge carrier mobility $\mu_\parallel$ = 8.5 x $10^{-5}cm^2V^{-1}s^{-1}$ parallel to the columns is determined from the low frequency conductivity using $\sigma = ne\mu_\parallel$ where n has been

estimated from the double integration of ESR signals.[9] Similarly, the mobility in the perpendicular direction $\mu_\perp$ is estimated to be $9 \times 10^{-8} cm^2V^{-1}s^{-1}$.

For the photoconductivity experiments HAT6 was held between two quartz slides which had semitransparent electrodes evaporated upon them. A voltage V was applied to the top electrode and the other was connected via a pre-amplifier with a 1kΩ input resistance to an oscilloscope. Photocarriers were excited within a skin depth $\delta < 1\mu m$ of the top electrode with an N_2 laser of pulse duration 6ns, $\hbar\omega = 3.68eV$ (λ = 337nm). Figure 3 shows the reciprocal transit time as a function of applied electric field E. The transient photocurrents I(t), observed are shown in the inset to Figure 3.

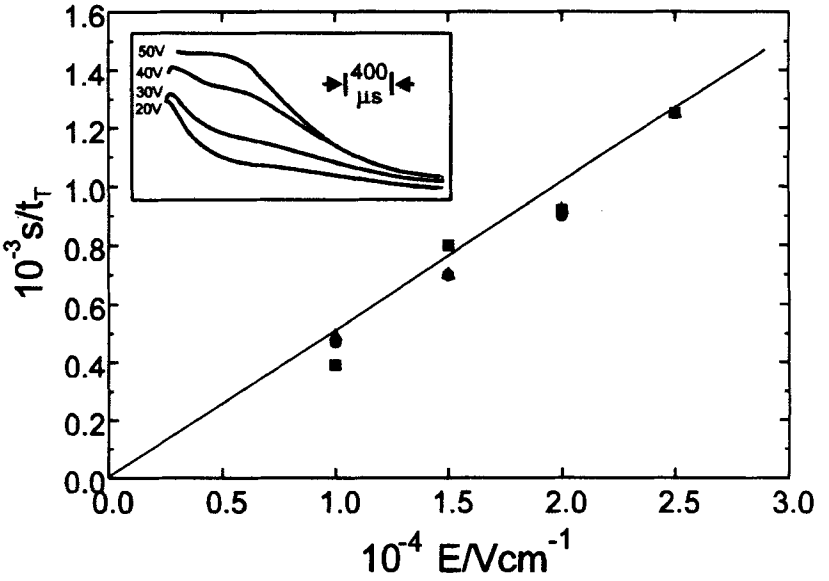


FIGURE 3 The variation of reciprocal transit time for holes, in the D_{ho} phase at 350K, with applied electric field. The transit distance is 20μm and data for three different samples is represented on the graph. The inset shows the original oscilloscope traces of hole transits, from which the data represented by the squares was taken. The slope of the graph represents a hole mobility, $\mu_h = 1.0 \times 10^{-4} cm^2V^{-1}s^{-1}$.

The shape of the current transients shown in Figure 3 are characteristic of dispersive charge transport,[7] and are at variance with the corresponding measurements recently reported for HAT5.[5]

DISCUSSION

The most notable results of this comparative study of charge carrier transport in the discotic mesophase of HAT6 are, firstly, that both experiments reveal a dispersive transport mechanism, and, secondly, the remarkable similarity between the values of charge carrier mobility measured, in the D_{ho} mesophase at 350K, by transient photoconductivity in pure HAT6, $\mu_{\|} = 1 \times 10^{-4} cm^2V^{-1}s^{-1}$, and that determined from the low frequency conductivity of HAT6/$NOBF_4$ ($x = 0.01$), $\mu_{\|} = 8.5 \times 10^{-5}\ cm^2V^{-1}s^{-1}$. Thus we may conclude that the mechanism of charge transport in both doped and pure samples of HAT6 is identical: a dispersive transport mechanism in which charge carriers hop between neighbouring molecules with a distribution of hopping rates. The presence of the counterions in the doped samples appears to have no appreciable effect on, nor play any role in, the charge transport process.

We have shown previously[9] that the charge carriers are localised entirely on the aromatic cores of the molecules: thus the charge carriers hop between the triphenylene cores of neighbouring molecules of average separation d. The mean hopping time τ is related to the measured mobility by

$$\tau = ed^2 / 2kT\mu \qquad (1)$$

leading to a value of τ of 200ps. This value of τ is many orders of magnitude longer than the timescale of either electronic motion ($\sim 10^{-15}$s) or nuclear motion ($\sim 10^{-13}$s): the charge carrier is moving relatively slowly. In these circumstances, a localised charge carrier is capable of producing lattice relaxation and/or distortion around itself, so that the effective carrier is the charge and an associated lattice distortion.[10] We have shown[3] by UV/Visible spectroscopy that in HAT6 the associated relaxation/distortion is essentially confined to the molecule on which the charge carrier resides, and therefore the most appropriate model of charge carrier transport is in terms of small polaron hopping between neighbouring donor and acceptor molecules along the stack[11,12]. The transfer

rate between donor and acceptor molecules w_{d-a} is related to their average separation d by

$$w_{d-a} = \nu_0 F \exp\left(-2\frac{(2m_e B)^{1/2} d}{\hbar}\right) \quad (2)$$

where m_e is the mass and B is the binding energy of the positive hole, ν_0 is the frequency factor, and F is a generalised Franck-Condon factor. Substituting typical values for ν_0 (10^{14} Hz), B (0.1 eV) and r (3.5Å), and the hole transfer rate ($1/\tau \sim 5 \times 10^9 s^{-1}$) leads to a value of $F \sim 10^{-4}$. Values of this magnitude are found for electron and hole transfer processes in many organic systems,[13,14] and confirm the important role that molecular reorganisation and/or vibrations play in controlling the overall electron transfer rate.

Eq. (2) shows that the charge carrier transfer rate between neighbouring molecules is a very sensitive function of their separation. This is the primary cause of the dispersive transport observed. The liquid-like disorder in the columnar packing within the columns leads to a distribution of intermolecular separations, which in turn yields a very broad distribution of intermolecular transition rates. The dispersive transport observed in both the frequency dependence of the conductivity and the transient photocurrent traces is a consequence of this distribution, and is, therefore, indicative of considerable configurational disorder in the columnar packing even though it is a D_{ho} mesophase.

The similarity in the values of the mobility in the two experiments is an unexpected result, and tells us that the mobility is largely unaffected by the presence of the BF_4^- counterions in the chemically doped material. Thus the counterion does not significantly perturb the mobility distribution.

CONCLUSIONS

The charge transport along the molecular columns in the discotic liquid crystalline phase of HAT6 has been shown to be dispersive, reflecting the intrinsic, liquid-like disorder in the molecular packing. This limits the carrier mobility for HAT6 to $\approx 1 \times 10^{-4} cm^2 V^{-1} s^{-1}$ The presence of the counterion in the chemically doped conductors does not significantly affect the carrier mobility.

ACKNOWLEDGEMENTS

We wish to thank the Engineering and Physical Sciences Research Council for their financial support of this work.

REFERENCES

1. C. Destrade, M.C. Mondon, and J. Malthête, J.Phys.Colloq. 40, C3-18, (1979).
2. C.R. Safinya, N.A. Clark, K.S. Liang, W.A.Varady, and L.Y. Chiang, Mol.Cryst.Liq.Cryst., 123, 205 (1985); L.Y. Chiang, C.R. Safinya, N.A. Clark, K.S. Liany, and A.N. Bloch, J.Chem.Soc.Chem. Commun 695 (1985).
3. N. Boden, R.J. Bushby, R. Luo, and J. Clements, in preparation.
4. N. Boden, R.J. Bushby, J. Clements, M.V. Jesudason, P.F. Knowles, and G. Williams,Chem.Phys.Lett. 152, 94 (1988); N. Boden, R.J. Bushby, and J. Clements, J.Chem.Phys. 98, 5920 (1993); N. Boden, R.J. Bushby, and J. Clements, J.Mater.Sci. Mater.in Electr., 5, 83 (1994).
5. D.Adam, F.Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, Phys.Rev.Lett. 70, 457 (1993).
6. N. Boden, R.C. Borner, R.J. Bushby, A.N. Cammidge, and M.V. Jesudason, Liq.Cryst. 15, 851 (1993).
7. H. Scher, and E.W. Montroll, Phys.Rev.B., 12, 2455 (1975).
8. S. Alexander, J. Bernasconi, W.R. Schneider, and R. Orbach, Rev.Mod.Phys., 53, 175 (1981).
9. N. Boden, R.C. Borner, D.R. Brown, R.J. Bushby, and J. Clements, Liq.Cryst., 11, 325 (1992).
10. T. Holstein, Ann.Phys.(N.Y.) 8, 325 (1959); C.G. Kuper, G.D. Whitfield, Polarons and Excitons, (Plenum Press, New York, 1963).
11 R.A. Marcus, Ann.Revs.Phys.Chem. 16, 155 (1965); M.D. Newton, and N. Sutin, Ann.Rev.Phys.Chem. 35, 437(1984).
12. J. Ulstrup, and J. Jortner, J.Chem.Phys. 63, 4358 (1975).
13. J.V. Beitz, and J.R. Miller, J.Chem.Phys. 71,4579 (1979).
14. K.V. Mikkelson, and M.A. Ratner, Chem.Rev., 87, 113 (1987).