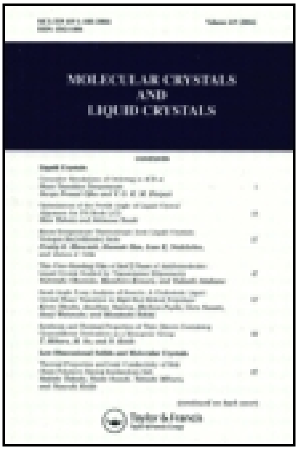

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R. A. Bissell [a], N. Boden [a], S. J. Brown [a] & R. J. Bushby [a]

[a] SOMS Centre, School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

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Electrically Conductive Calamitic and Discotic Liquid Crystals Based on Tetrathiafulvalene (TTF)

R. A. BISSELL, N. BODEN, S. J. BROWN and R. J. BUSHBY

SOMS Centre, School of Chemistry, University of Leeds, Leeds LS2 9JT, UK.

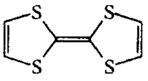
A synthesis has been developed for a discotic mesogen based on an extended tetrathiafulvalene (TTF) nucleus. Unlike previous systems, based on the TTF nucleus, this shows relatively high conductivity.

Keywords: conductivity; liquid crystal; tetrathiafulvalene

INTRODUCTION

Tetrathiafulvalene (TTF) **1** and its derivatives have generated interest over the past twenty years due to their ability to form crystalline charge transfer complexes with electron acceptors such as tetracyano-*p*-quinodimethane (TCNQ)[1]. These materials possess high one dimensional conductivities due to a stacked arrangement of partially oxidised TTF cores.

Like others, our aim has been to incorporate the TTF core into thermotropic calamitic[2] and discotic[3] liquid crystals and investigate the electrical properties of these novel materials. Consequently, the synthesis of highly functionalised rod shaped and disc shaped TTF derivatives has been necessary.



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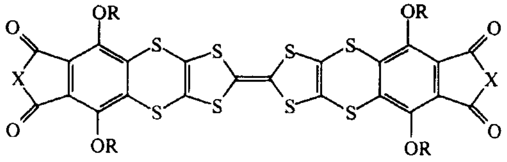
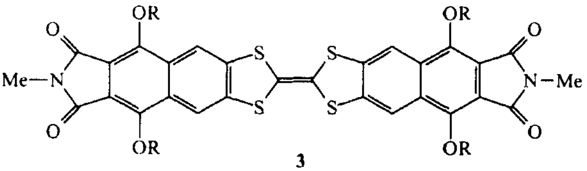


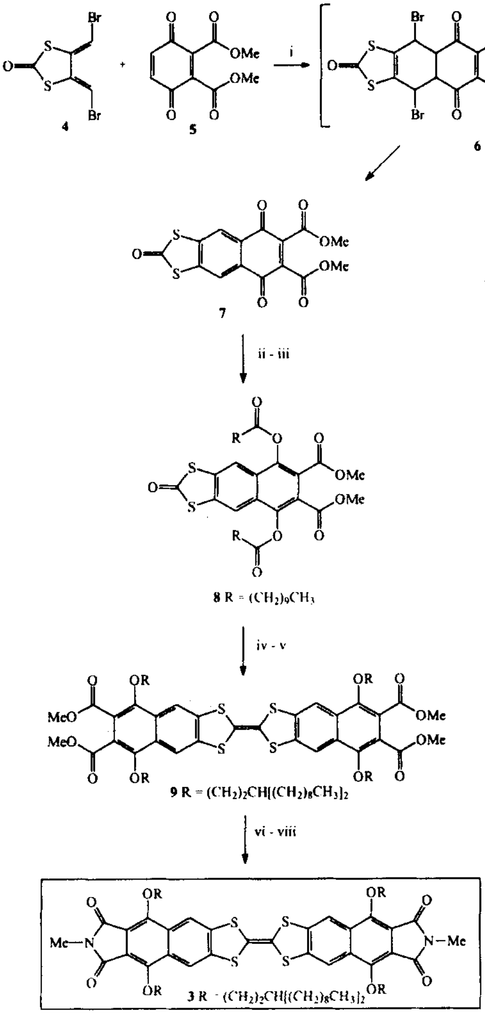
2a R = $(CH_2)_2CH[(CH_2)_8CH_3]_2$, X = O
2b R = $(CH_2)_2CH[(CH_2)_8CH_3]_2$, X = N−Me



3

In a previous paper[4] we described the synthesis of the derivatives **2a**, which gives a smectic A phase between 91.5 and 107.5°C, and **2b,** which gives a D$_r$ columnar phase between room temperature and 64.7°C. Unfortunately, compound **2b** showed very low ac conductivity (10^{1}-10^{6} Hz, 1V) 10^{-12}-10^{-7} S cm^{-1} and even when doped with 2 mol% of antimony pentachloride, giving a radical cation concentration ~10^{20} cm^{-3} (EPR), the ac conductivity (10^{1}-10^{6} Hz, 1V) only increased to 10^{-11}-10^{-6} S cm^{-1}. A possible explanation of the low conductivity (which contrasts sharply with doped triphenylene-based columnar discotic systems)[5] is that there is a major difference in geometry between the neutral molecule **2b** and its radical cation **2b**$^{\bullet+}$ giving rise to large local lattice distortions. The neutral molecule is expected to adopt a chair-like conformation whereas radical cations in related compounds are known to be planar[6].

In this paper we describe the synthesis of an analogous system where the planar geometry of the neutral molecule is retained after doping.



Scheme 1 *Reagents and conditions*: i, CH_3CN, reflux, 12 h, 65%; ii, 5% Pd (C), EtOAc, 40°C, 12 h, 82%; iii, RCOCl, DCM, C_6H_5N, reflux, 2 h, 80%; iv, $P(OMe)_3$ C_6H_6, reflux, 6h, (53%); v, RX, K_2CO_3, DMF, reflux, 4 days, 16%; vi, KOH, THF, MeOH, reflux, 5h, 95%; vii, Ac_2O, DCM, reflux, 2h, 83%; viii, $MeNH_2.HCl$, K_2CO_3, DMAP, DMF, $CHCl_3$, 3 Å molecular sieves, 80°C, 3days, 68%.

DISCUSSION

The bisimide-dinaphtho-TTF **3** was synthesised as outlined in Scheme 1.

Initially, 4,5-bis(bromomethylene)-1,3-dithiole-2-one **4** was reacted with 2,3-dimethoxycarbonyl quinone[7] **5** in a Diels-Alder reaction to produce adduct **6** which formed the quinone **7** by elimination of 2 moles of hydrogen bromide. This was reduced to the hydroquinone which was protected by reaction with decanoyl chloride. The product **8** was converted to the tetrathiafulvalene in good yield using trimethyl phosphite. Removal of the decanoyl protecting groups and subsequent alkylation of the phenolic sites was performed in one pot under mild basic conditions in the presence of 1-bromo-3-nonyl-dodecane[8].

Hydrolysis of the ester **9** was carried out using potassium hydroxide and the tetraacid was obtained on acidic work. This was converted to the bis-anhydride using acetic anhydride before condensation with methylamine to produce the bisimide-dinaphtho-TTF **3**.

RESULTS

The bisimide-dinaphtho-TTF **3** gives a D_r columnar liquid crystal phase between 30 and 106 °C. The K to D_r transition readily supercools. A typical polarising microscopy image is shown in figure 1.

Preliminary powder X-ray diffraction of the D_r phase has revealed that the molecules pack on a rectangular 2-d lattice.

Compound **3** displays two reversible one electron oxidation waves, $E_1 = +0.48$ V and $E_2 = +0.95$ V *vs* Ag/AgCl, in the anodic window showing the formation of stable radical cations.

The dc and ac conductivity measurements on thin films (6 μm) of **3** have been carried out using an indium tin oxide electrode[9]. Dc studies showed

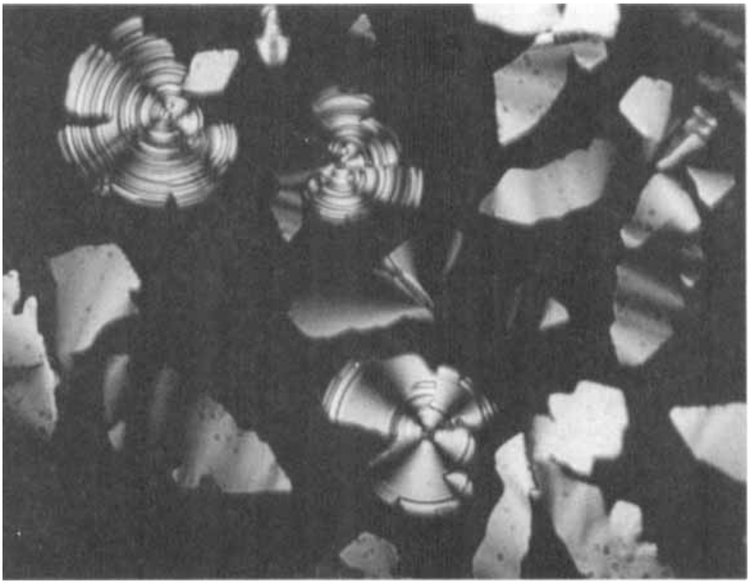


FIGURE 1 Dendritic texture of the D_r columnar phase of bisimide-dinaphtho-TTF **3**, 90°C, crossed polars, x 200
(See Color Plate V at the back of this issue)

that the material gives a linear (Ohmic) response up to an applied voltage of 1 V[7]. The sample was cooled down from the isotropic liquid into the mesophase where it was found that in the isotropic phase, the ac conductivity (10^1-10^7 Hz, 1V) was very low (10^{-10}-10^{-6} Scm^{-1}) as expected. However on cooling into the mesophase, the ac conductivity increases to 10^{-6} Scm^{-1} (10^1-10^7 Hz, 1V).

CONCLUSIONS

The bisimide-dinaphtho-TTF **3** exhibits a D_r mesophase. Preliminary measurements show that the undoped material, when cooled into the D_r phase, has a conductivity 10^6 times greater than that of derivative **2b**.

Normally, these systems require to be doped or converted to charge-transfer complexes to generate a high concentration of charge carriers. In this case, however, it seems that the system is self-doped or that the charge carriers are generated by air-oxidation[10]. The origin of these charge carriers and the effect of doping and charge-transfer complex formation are currently under investigation.

Acknowledgements
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