Novel synthesis of calamitic and discotic liquid crystalline derivatives of tetrathiafulvalene (TTF)

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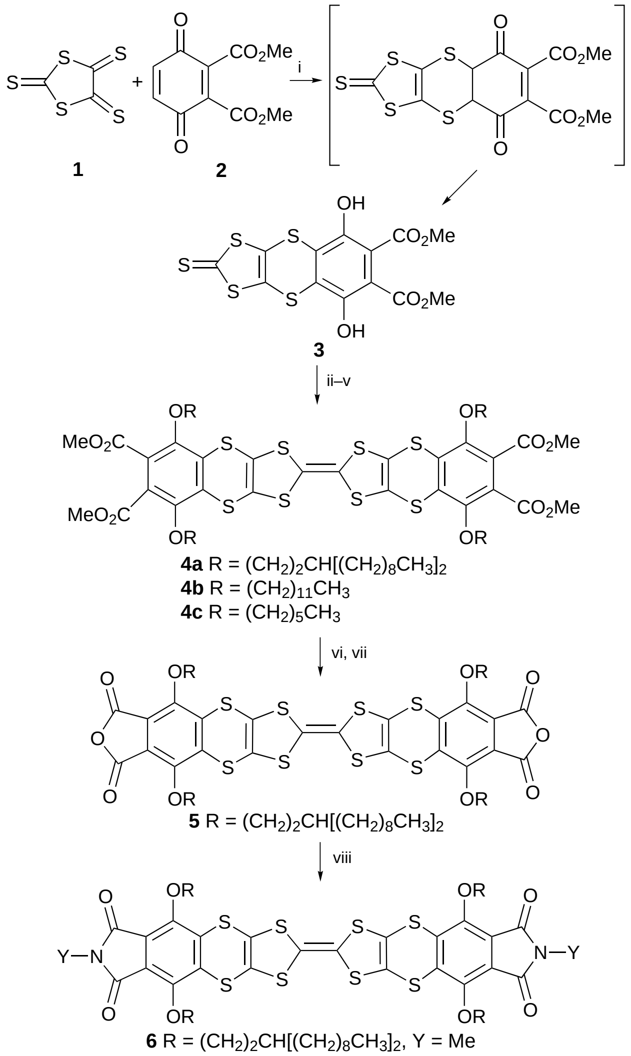
A synthesis has been developed for both calamitic and discotic mesogens based on the bis(phenylenedithio-TTF) (BPhDT-TTF) nucleus.

Only recently has attention been given to the charge transport properties of liquid crystals and the new applications that could stem from them.[1] Well defined hole transits have been obtained from the columnar phases of discotic liquid crystals[2] and it has been shown that quasi-one-dimensional electronic conduction can be induced in these systems either by n-doping[3] or by p-doping.[4] More recently it has been shown that phenylbenzothiazole-based calamitic smectic A phases (quasi-two-dimensional) give both electron and ion transits.[5] The highly efficient, anisotropic charge transport obtained suggests applications in photosensors, light-emitting diodes,[6] electrophotography and many other areas. There is, however, a need for new molecular systems. Although the success of crystalline TTF conductors[7] makes liquid crystalline derivatives of TTF an obvious synthetic target little progress has been made in this area.[8]

Our synthesis, which is shown in Scheme 1, enables us to make both calamitic and discotic mesogens based on the bis(phenylenedithio-TTF) (BPhDT-TTF) nucleus. The novel step involves a cycloaddition between 2,3-bis(methoxycarbonyl)benzoquinone **2** and 1,3-dithiole-2,4,5-trithione [depolymerised oligo(1,3-dithiole-2,4,5-trithione)] **1**.[9] Addition of simple four π electron components to 2,3-disubstituted quinones normally yields adducts of the 2,3-double bond[10] (in this case the 'wrong' regioisomer) but, fortunately, the sole product obtained was the desired hydroquinone **3**. The remainder of the synthesis, shown in Scheme 1, uses well-established reactions and procedures. Compounds **4a**, **4b** and **4c** were non-liquid crystalline (**4a**, mp 48 °C; **4b**, mp 129–130 °C and **4c**, mp 182–184 °C) but the bis(anhydride) **5** and the bis(imide) **6** both displayed enantiotropic liquid crystalline behaviour.

Force field (MM2) calculations on the BPhDT-TTF nucleus and crystal structures of related compounds suggest that it adopts the elongated shallow 'chair' conformation shown in Fig. 1 making it, perhaps, a more obvious choice for creating calamitic than discotic liquid crystals.

Compound **5** gives a smectic A phase between 91.5 and 107.3 °C, with a layer repeat distance of 24.3 Å, comparable to the length of the molecules. More surprisingly, compound **6** behaves as a discogen, giving a D_r columnar phase between room temperature and 64.7 °C. This is unusual, but not unprecedented, for a molecule with such a non-planar, elongated core.[11] When viewed between cross polarisers, thin films of compound **6** obtained by slow cooling from the isotropic phase showed the characteristic dendritic structures of a columnar mesophase and the X-ray analysis of this phase is detailed in Table 1. Compounds **4a**, **5** and **6** are soluble in common organic solvents and solutions display two reversible one electron oxidation waves in the anodic window showing the formation of stable radical cations. The dc and ac conductivity response of thin films (12 μm) of compounds **5** and **6** has been investigated using a variety of electrode types (indium tin oxide, gold and aluminium).[12] The liquid crystalline phase of compound **5** did not align under these conditions but compound **6** aligned homeotropically when annealed at 55 °C. Dc studies showed that both materials gave a linear (Ohmic) response up to an applied voltage of 1 V.[12] As expected, the ac conductivities (10^1–10^6 Hz, 1 V) were very low (10^{-12}–10^{-7} S cm^{-1}) and



Scheme 1 *Reagents and conditions*: i, THF, reflux, 8 h, 24%; ii, Ac$_2$O, DMAP, CH$_2$Cl$_2$, 2 h, 94%; iii, Hg(OAc)$_2$, AcOH, CH$_2$Cl$_2$, 4 h, 94%; iv, P(OMe)$_3$, C$_6$H$_6$, reflux, 5 h, 60%; v, RX, K$_2$CO$_3$, DMF, heat, 74–94%; vi, KOH, THF, MeOH, reflux, 5 h, 78%; vii, 90 °C, vacuum, 5 h, 88%; viii, MeNH$_2$·HCl, K$_2$CO$_3$, DMAP, DMF, CHCl$_3$, 3 Å molecular sieves, 80 °C, 3 days, 60%. All new compounds gave satisfactory combustion analyses and spectroscopic data.

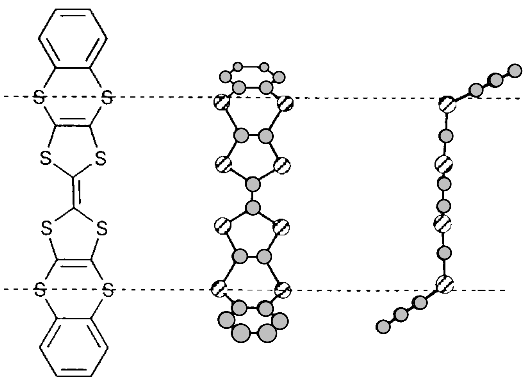


Fig. 1 Optimised geometry of BPhDT-TTF obtained using the MM2 force field method

Table 1 Powder X-ray diffraction data for the D_r phase of the diimide **6**. The calculated data is that expected for a two-dimensional cell, a = 27.3, b = 22.9 Å. Additionally there is a rather broad reflection at 4.00 Å corresponding to the separation between the rings within the stacks. It is greater than that found in crystalline TTF derivatives (ref. 13)

Reflection	Calculated/Å	Observed/Å
10	27.3	27.3
01	22.9	absent
11	17.5	17.8
20	13.7	13.7
02	11.4	11.4
21	11.7	11.4
12	10.6	10.8
30	9.1	9.7

dominated by trace ionic impurities. More surprising was the finding that, when a sample of compound **6** was p-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, 1 V) only increased to 10^{-11}–10^{-6} S cm^{-1}. This is very much lower than that normally found in doped discotics[2,3] and the reasons for this are not immediately apparent. It may imply that the radical cations formed are highly localised (small polarons) and/or pinned by the counterions. Alternatively it may be that there is a major difference in geometry between the neutral molecule and the radical cation resulting in large local lattice distortions (a structural polaron). Experiments aimed at resolving this problem and at producing related TTF derivatives with higher conductivities are in progress.

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Footnote and References

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