Liquid Crystals
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To cite this Article Boden, N. , Bushby, R. J. and Cammidge, A. N.(1995) 'Preliminary Communications Functionalization of discotic liquid crystals by direct substitution into the discogen ring α-Nitration of triphenylene-based discogens', Liquid Crystals, 18: 4, 673 — 676

To link to this Article: DOI: 10.1080/02678299508036673

URL: http://dx.doi.org/10.1080/02678299508036673

LIQUID CRYSTALS, 1995, VOL. 18, NO. 4, 673–676

Preliminary Communications

Functionalization of discotic liquid crystals by direct substitution into the discogen ring

α-Nitration of triphenylene-based discogens

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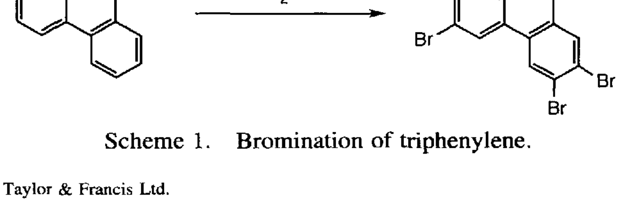
(*Received 1 August 1994; in final form 15 October 1994; accepted 18 November 1994*)

It is demonstrated for the first time that discotic liquid crystals can be functionalized by direct substitution into the central ring (core) of the discogen. It is shown that hexahexyloxytriphenylene (HAT6) can be easily nitrated to give the mono-α-nitrated product exclusively. This material, which has a discotic mesophase range between room temperature and 136°C, can be modified to give α-amino-, α-acetylamino- and α,α'-diazo-HAT6. These new materials all show enantiotropic mesophases, have permanent dipole moments and some of them are coloured. This generally applicable approach opens up a route to an enormous range of new discotic liquid crystals.

The columnar phases of discotic liquid crystals consist essentially of one-dimensional molecular stacks of 'fluids' arranged on a two-dimensional lattice. Applications of these materials will, no doubt, stem from learning how to incorporate novel functionality into this unique supramolecular architecture. The first examples of such work are now beginning to appear [1–3]. In our laboratory research is focused on developing the chemistry and applications of triphenylene-based discogens and to this end we have recently reported greatly improved syntheses of both symmetrical [4] and unsymmetrically substituted [5] derivatives. This opens up new opportunities for synthesizing a wide variety of unsymmetrically substituted triphenylenes in relatively high yield and of high purity. Such materials are important because they will give access to new kinds of phase behaviour for the triphenylenes, and also allow the preparation of structurally homogeneous polymers [6]. The triphenylene discotics studied to date are colourless materials, although Wendorff *et al.* have shown also that they can be converted into coloured derivatives through the formation of charge-transfer complexes [7]. In previous papers we have shown how triphenylene discotics can be converted into pseudo one-dimensional semiconductors [1] through doping, and more recently it has been demonstrated that the undoped systems are intrinsically photoconducting [2].

Whereas functionality can clearly be introduced by incorporation of a dopant into the pure liquid crystal, a more logical approach is to functionalize the core directly. We now describe the first synthetic route which makes this possible. In particular, we describe a new and versatile approach to functionalized triphenylene discotics and show that nitration of hexahexyloxytriphenylene (HAT6) allows substituents to be introduced into the α-position of the nucleus. The mesogens produced have enhanced liquid crystal properties and this strategy allows new functionality (colour, lateral dipole moment etc.) to be built into the structure. In particular this provides a synthetic 'tool' potentially enabling the colours of these discotics to be engineered at the molecular level.

According to most simple MO treatments of reactivity in polynuclear aromatics [8], electrophilic attack at the α-position of triphenylene should be favoured over attack at the β-position. Such treatments, however, neglect steric factors which are particularly severe in this core. As a result, attack at the α-positions is relatively rare, and predominant or exclusive β-attack is usually found to



Scheme 1. Bromination of triphenylene.

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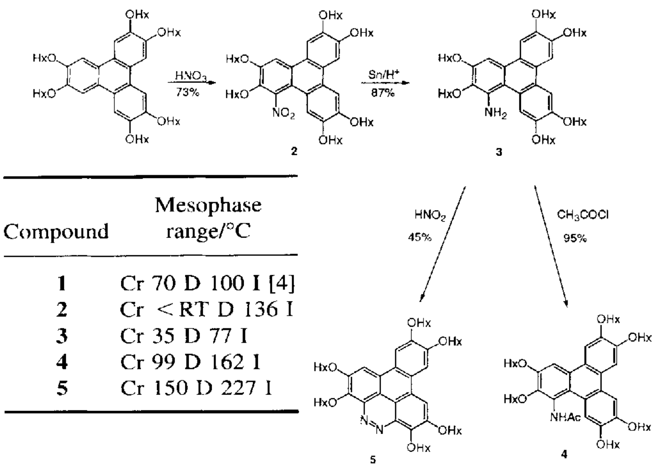


Compound	Mesophase range/°C
1	Cr 70 D 100 I [4]
2	Cr < RT D 136 I
3	Cr 35 D 77 I
4	Cr 99 D 162 I
5	Cr 150 D 227 I

Scheme 2. Functionalization of HAT6.

occur. For example bromination [9] results in substitution at the β-positions (see scheme 1).

Thus, literature precedents suggested that functionalization of, for example, HAT6 by electrophilic aromatic substitution at the β-position was an unlikely candidate for success. Nevertheless, we have found that nitration of HAT6 (**1**) using conc. nitric acid in ether/acetic acid at room temperature proceeds smoothly to produce the mono-α-nitrated product (**2**) exclusively in 73 per cent yield (see scheme 2). The yellow product is easily identified as **2** from the low-field region of its ^{1}H NMR spectrum, which clearly shows the breakdown of molecular symmetry.

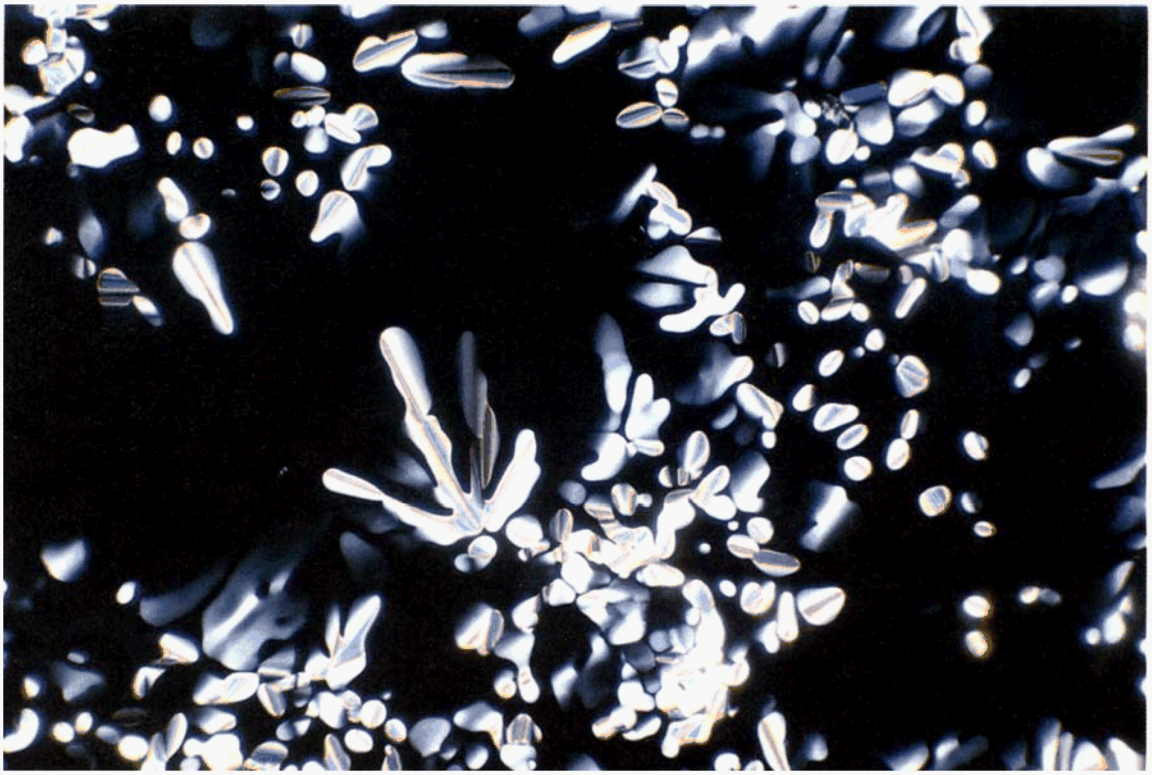
Introduction of the nitro-group permits further chemical modifications, and reduction of the nitro-group with tin in acetic acid afforded α-amino-HAT6 (**3**), which could be acylated with acetyl chloride (giving **4**). Alternatively, diazotization of α-amino-HAT6 (0°C followed by warming) gave the cyclized diazo derivative **5**. All compounds were isolated in good yields (see scheme 2). As expected in such sterically crowded compounds, steric compression leads to deshielding of the proton on the ring opposite to the α-substituent [10]. This is most marked for the α-amino substitutent where the downfield shift is 0·9 ppm.

The mesophase behaviour of the new materials was established by polarizing optical microscopy and DSC. All of the compounds exhibited a D_h-like mesophase texture, as shown in the figure for compound **4** [11]. The texture has large homeotropic domains, typical for D_h phases of hexa-alkoxytriphenylenes. Application of a small shear-force causes these regions to become brightly birefringent.

From the table in scheme 2 we see that introduction of an α-substitutent into the triphenylene ring has a marked effect on both the transition temperatures and range of the mesophase. In all cases, the range of the mesophase is enhanced, and in three cases the clearing temperature is higher. In the case of the α-nitro discogen the mesophase extends from at least room temperature (we have yet to investigate the low temperature phase behaviour) to 136°C. The material precipitates from solution as a liquid crystal which does not crystallize over a period of several months. The enhanced mesophase stability may arise through different effects. Introduction of the polar nitro-group is expected to increase the attraction between the cores (tending to raise the D–I transition) On the other hand, steric effects are expected to increase the core–core separation and hence the increased entropy of the side chains might stabilize the mesophase. Analogies can be drawn with the HAT*n*–TNF charge-transfer system where similar effects may be operating [7]. A more relevant comparison to the α-nitro discogen, both in terms of molecular architecture and mesophase behaviour, is with the penta-alkoxy-monoalkanoyloxytriphenylenes prepared by Werth *et al.* [12]. In these latter materials it was similarly found that the presence of the odd substituent prevented crystallization of the mesophase and raised the clearing temperature relative to the parent hexa-alkoxytriphenylene.

In conclusion, we have shown that modification of the known discogen HAT6 by substitution at the α-position provides a simple strategy for modifying mesophase behaviour. More importantly, such substituents impart additional intrinsic molecular properties (for example, local dipoles, colour, etc.) to these materials. This represents a novel step towards the preparation of potentially useful, functionalized triphenylene-based discotic mesogens. To date, the α-nitro, α-amino, α-acetylamino and α,α'-diazo derivatives have been prepared, all of which exhibit discotic mesophases. In addition to further manipulations of these materials themselves, many variations on the substitution reaction can be envisaged (in particular the use of different electrophiles and alternative triphenylene substrates). A program is underway to prepare derivatives incorporating specific functionalities and to rationalise the effects of α-substituents on mesophase behaviour.

1-Nitro-2,3,6,7,10,11-hexahexyloxytriphenylene **2**. 2,3,6,7,10,11-Hexahexyloxytriphenylene [4] (9·4 g, 11·3 mmol) was dissolved in ether (150 ml) and glacial acetic acid (30 ml). Concentrated nitric acid (3 ml) was added dropwise and the mixture stirred at room temperature for 15 min. The solution was washed with water and potassium carbonate solution and the solvent removed *in vacuo*. The residue was purified by column chromatography (silica, dichloromethane/light petroleum 1 : 1) and reprecipitated from ethanol to give 2,3,6,7,10,11-hexahexyloxy-1-nitrotriphenylene (7·2 g, 73 per cent), Cr-D < RT D–I 136°C. Elemental analysis: C, 74·15; H 9·75; N 1·65; $C_{54}H_{83}NO_8$ requires C, 74·19; H, 9·57; N, 1·60 per cent. $\lambda_{max}(\varepsilon)$ ($CHCl_3$) 350 nm (5500), 310 nm (29 200),



Texture of **4** observed following cooling from the isotropic liquid to 123°C.

280 nm (91 800). δ_H 300 MHz ($\mathrm{CDCl_3}$) 7·88 (s, 1 H, $\mathrm{Ar\underline{H}}$), 7·79 (s, 1 H, $\mathrm{Ar\underline{H}}$), 7·75 (s, 2 H, $\mathrm{Ar\underline{H}}$), 7·50 (s, 1 H, $\mathrm{Ar\underline{H}}$), 4·22–4·18 (m, 10 H, $\mathrm{OC\underline{H}_2}$), 4·05 (t, 2 H, $J = 7$ Hz, $\mathrm{OC\underline{H}_2}$) 1·98–1·90 (m, 10 H, $\mathrm{OCH_2C\underline{H}_2}$), 1·80 (t, 2 H, $J = 7$ Hz, $\mathrm{OCH_2C\underline{H}_2}$), 1·64–1·38 (m, 36 H, $\mathrm{C\underline{H}_2}$) 0·94 (t, 18 H, $J = 7$ Hz, $\mathrm{C\underline{H}_3}$).

1-Amino-2,3,6,7,10,11-hexahexyloxytriphenylene ***3***. 2,3,6,7,10,11-Hexahexyloxy-1-nitrotriphenylene (5 g, 5·72 mmol) and tin powder (5 g) were stirred in boiling glacial acetic acid for 4 h and the hot solution decanted into water. The mixture was shaken with dichloromethane (3 × 200 ml) and the solvents removed *in vacuo*. The residue was recrystallized from ethanol to afford 1-amino-2,3,6,7,10,11-hexahexyloxytriphenylene (4·2 g, 87 per cent), Cr–D 35°C D–I 77°C. δ_H, 300 MHz ($\mathrm{CDCl_3}$) 8·82 (s, 1 H, $\mathrm{Ar\underline{H}}$), 7·83 (s, 1 H, $\mathrm{Ar\underline{H}}$), 7·80 (s, 1 H, $\mathrm{Ar\underline{H}}$), 7·77 (s, 1 H, $\mathrm{Ar\underline{H}}$), 7·37 (s, 1 H, $\mathrm{Ar\underline{H}}$), 4·57 (brs, 2 H, $\mathrm{N\underline{H}_2}$) 4·24–4·15 (m, 12 H, $\mathrm{OC\underline{H}_2}$), 1·95–1·90 (m, 12 H, $\mathrm{OCH_2C\underline{H}_2}$), 1·57–1·38 (m, 36 H, $\mathrm{C\underline{H}_2}$) 0·93 (t, 18 H, $J = 7$Hz, $\mathrm{C\underline{H}_3}$).

1-Acetylamino-2,3,6,7,10,11-hexahexyloxytriphenylene ***4***. 1-Amino-2,3,6,7,10,11-Hexahexyloxytriphenylene (1·6 g, 1·9 mmol) was stirred in dichloromethane (40 ml) with potassium carbonate (2 g) and acetyl chloride (0·5 g, 6·4 mmol) overnight. The solids were filtered off and the solvents removed *in vacuo*. The residue was purified by column chromatography (silica, benzene/dichloromethane 1 : 1) to give 1-acetylamino-2,3,6,7,10,11-hexahexyloxytriphenylene (1·59 g, 95 per cent), Cr–D 99°C D–I 162°C. Elemental Analysis: C, 75·6; H, 10·0; N, 1·6; $\mathrm{C_{56}H_{87}NO_7}$ requires C, 75·89; H, 9·90; N, 1·58 per cent. δ_H, 300 MHz ($\mathrm{CDCl_3}$) 8·67 and 8·53 (both s, 1 H, $\mathrm{N\underline{H}}$), 7·83–7·62 (m, 5 H, $\mathrm{Ar\underline{H}}$), 4·22–4·18 (m, 10 H, $\mathrm{OC\underline{H}_2}$), 4·02 (t, 2 H, $J = 7$ Hz, $\mathrm{OC\underline{H}_2}$), 2·32 and 1·75 (both s, 3 H, $\mathrm{COC\underline{H}_3}$), 1·98–1·78 (m, 12 H, $\mathrm{OCH_2C\underline{H}_2}$), 1·60–1·35 (m, 36 H, $\mathrm{C\underline{H}_2}$), 0·94 (t, 18 H, $J = 7$ Hz, $\mathrm{C\underline{H}_3}$).

α,α′-Diazo derivative of HAT6 ***5***. 1-Amino-2,3,6,7,10,11-Hexahexyloxytriphenylene (0·5 g, 0·59 mmol) was stirred in dichloromethane (10 ml) and glacial acetic acid (5 ml) at 5°C. Sodium nitrite (0·2 g, 2·9 mmol) in water (2 ml) was added and the mixture was stirred at room temperature for 2 h and at 40°C for 30 min. The solution was washed with water (2 × 20 ml) and the solvents removed *in vacuo*. The residue was separated by column chromatography (silica, dichloromethane then dichloromethane/ethyl acetate 9 : 1) and recrystallized from dichloromethane/ethanol to give α,α′-diazo-HAT6 as an orange solid (225 mg, 45 per cent), Cr–D 150°C D–I 227°C. Elemental Analysis: C, 75·7; H, 9·7; N, 3·1; $\mathrm{C_{54}H_{82}N_2O_6}$ requires C, 75·83; H, 9·67; N, 3·28 per cent). λ_{max} (ε) ($\mathrm{CHCl_3}$) 440 nm (7500), 350 nm (11 700), 270 nm (73 300). δ_H, 300 MHz ($\mathrm{CDCl_3}$) 8·40 (s, 2 H, $\mathrm{Ar\underline{H}}$), 7·98 (s, 2 H, Ar$\underline{H}$), 4·75 (t, 4 H, OC$\underline{H}_2$), 4·39 (t, 4 H, $J = 7$ Hz, OC$\underline{H}_2$), 4·29 (t, 4 H, $J = 7$ Hz, OC$\underline{H}_2$), 2·10–1·98 (m, 12 H, $OCH_2C\underline{H}_2$), 1·70–1·36 (m, 36 H, C$\underline{H}_2$), 0·94 (t, 18 H, $J = 7$ Hz, C$\underline{H}_3$).

We wish to thank the Engineering and Physical Sciences Research Council for financial support.

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