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The synthesis of triphenylene-based discotic mesogens New and improved routes

Ruth C. Borner^a; Richard J. Bushby^b; Andrew N. Cammidge^c; N. Boden^d; R. C. Borner^d; R. J. Bushby^d; A. N. Cammidge^d; M. V. Jesudason^d

^a Floraroma Ltd., UK ^b Centre for Self-Organising Molecular System (SOMS), University of Leeds, UK ^c School of Chemical Sciences & Pharmacy, University of East Anglia Norwich, UK ^d School of Chemistry, University of Leeds, Leeds LS2 9JT, England

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Ferric chloride/methanol in the preparation of triphenylene-based discotic liquid crystals

RUTH C. BORNER†, RICHARD J. BUSHBY*‡ and ANDREW N. CAMMIDGE§

†Floraroma Ltd., Teddington, Middlesex, TW11 8EE, UK

‡Centre for Self-Organising Molecular System (SOMS), University of Leeds, LS2 9JT, UK

§School of Chemical Sciences & Pharmacy, University of East Anglia Norwich, Norfolk, NR4 7TJ, UK

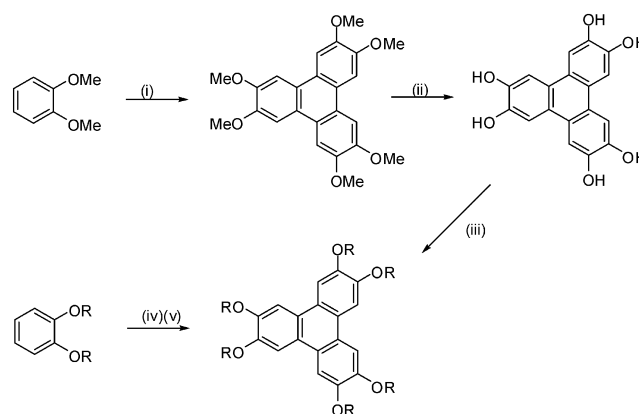
A Commentary on the paper “The synthesis of triphenylene-based discotic mesogens. New and improved routes”, by N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge and M. V. Jesudason. First published in *Liquid Crystals*, **15**, 851–858 (1993).

1. Background

In the mid 1980s we were involved with Neville Boden in two projects which required a steady supply of multi-gram quantities of triphenylene-based discotic liquid crystals, namely studies of the aggregation and phase behaviour of the discoidal amphiphile TP6E02M [1] and studies of the electronic conduction of AlCl_3 -doped hexaalkoxytriphenylenes [2]. The conductivity studies required particularly large amounts of material since the cells we were using at that time required 2–3g per measurement and the recovered material contained small amounts of dealkylation and dehydrogenation ($\text{ArOCH}=\text{CHR}$) products [3] that proved very difficult to remove. As a result the recovered discotic liquid crystal could not be recycled. None of the available syntheses really fulfilled our needs. At that time the established synthesis [4] relied on oxidative trimerisation of 1,2-dimethoxybenzene, dealkylation and realkylation as shown at the top of Scheme 1. It used 67% sulphuric acid/chloranil as the oxidising agent. Column chromatography was needed to separate and recover the reagent which, on a large scale, was very labour-intensive and time-consuming. This ‘chloranil’ route was also limited to the synthesis of hexamethoxytriphenylene necessitating the subsequent dealkylation/realkylation steps. Although an electrochemical trimerisation of longer side-chain 1,2-alkoxybenzenes could be used to prepare discogens such as HAT6 directly (avoiding the dealkylation and realkylation steps) [5–7] we found it difficult to implement this on the scale we required. Hence, in 1989 Bushby and Borner initiated a series of experiments based on the insights provided by the electrochemical studies but aimed at developing a ‘chemical’ alternative.

The particular insights from the electrochemical studies of oxidative aryl coupling that are relevant here are:

1. *The need for a full sufficiency of oxidant.* In general, the mechanism of oxidative aryl coupling involves repeated cycles of electron removal, carbon-carbon bond formation and deprotonation. Critically the product from each cycle has a more extended conjugated system than its precursor. Generally the electron removal steps become faster with each cycle whereas the radical-cation intermediates become less and less reactive and the carbon-carbon bond-forming reactions become slower. As a result, the process will continue cycle on cycle, building larger and larger oligomers until a radical cation (or sometimes dication) is formed that is stable [5]. It is important to use at least enough oxidant to convert all of the substrate through to this ultimate cation and it is usually safest to use an excess of oxidant. With kinetics of this type, a deficiency of oxidant almost always gives a complex mixture.



Scheme 1. R = primary alkyl. Reagents: (i) chloranil/ H_2SO_4 (ii) HBr/HOAc or BBr_3 (iii) $\text{RX}/\text{K}_2\text{CO}_3$ (iv) FeCl_3/DCM (v) MeOH .

*Email: R.J.Bushby@leeds.ac.uk

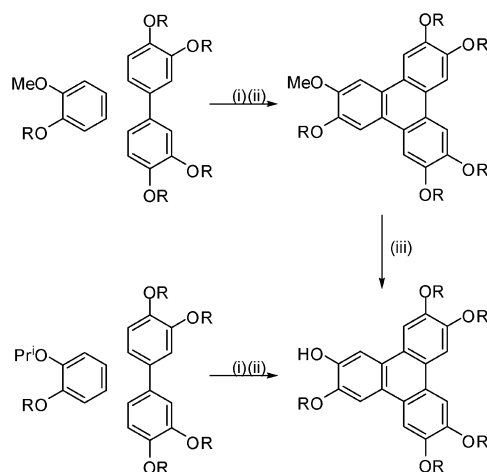
2. *The need for a non-nucleophilic/non-aqueous solvent.* Because the reaction involves radical-cation intermediates and the ultimate product is a radical cation or dication the presence of water or other nucleophiles will lead to a mixture of phenols and quinones.
3. *The need for a reductive work-up.* Addition of water to the 'ultimate' radical cation leads to a mixture of addition products. To obtain the required neutral product a one or two electron reduction is required [7].

Our studies rapidly established that ferric chloride in dichloromethane was a very satisfactory oxidant. It took longer to devise a good work-up procedure but eventually our experiments lead to the use of secondary alcohols and finally, following a suggestion from Klaus Bechgaard, to the use of methanol. Although in most ways the electrochemical literature was a good guide, in one way it deceived us. It suggested that it was necessary to add a little acid to the reaction mixture [5]. Since we had shown that the use of very aggressively acid solvents decreased the yield we tried a small amount (<1%) of acid such as sulphuric. Subsequent work showed that this was quite unnecessary. Each Ar-Ar bond formed liberates two molecules of HCl and HCl gas streams from the reaction mixture. Addition of a little sulphuric acid to the dichloromethane at the outset can hardly have a significant effect on the acidity of the medium as a whole! Hence we quickly dropped the added acid from our procedures. The only other significant changes that we have introduced through the years have been aimed at countering dealkylation. However these procedures are carried out, a small amount of dealkylation occurs. Although after 'purification' the liquid crystals may have good DSC, tlc and spectroscopic characteristics, traces of these dealkylation impurities will cause the samples to become discoloured on storage (especially if not protected from the light). On a small preparative scale (1g or less) dealkylation does not matter since the dealkylation products can be removed by careful column chromatography and recrystallisation. On a large scale this is impractical. Hence, on a large scale, we now treat the crude product with a re-alkylating mixture (RX/K₂CO₃/EtOH/reflux). The product then obtained can be purified quickly and efficiently by passage through a short silica column and recrystallization [8]. Alternatively (for hexamethoxytriphenylene) Bechgaard has suggested a procedure in which impurities are removed by treatment with dithionite and silica [9]. When these reactions are carried out on a large scale it is also important to note that the methanol workup is highly exothermic and that large amounts of formaldehyde are

liberated. Since the publication of our 1993 *Liquid Crystals* paper, other workers have suggested the use of vanadium oxychloride [10], molybdenum(V) chloride [11] ferric chloride/alumina [12], or ferric chloride in nitromethane [13] as alternative oxidants. These certainly work but we have not found any great advantages over ferric chloride/dichloromethane.

2. Subsequent developments

At about the same time as the work on the synthesis of hexaalkoxytriphenylenes we were also involved in attempts to find new routes to triphenylene-based liquid crystal polymers. These clearly had interesting properties but, at that time, the polymers that had been made involved a mixture of regiochemical linkages and/or had only been made on a tiny scale [14]. The synthesis on which we first embarked involved building an *ortho*-terphenyl through a series of Suzuki coupling reactions followed by an oxidative photocyclisation to generate the triphenylene nucleus. It was very similar to the route eventually successfully completed by the 'Hull' group [15]. It is the most general way of making discogenic triphenylene derivatives but is lengthy and difficult to execute on a multigram scale. For our work we needed to make a triphenylene monomer that was mono- or difunctionalised. Because the ferric chloride/methanol trimerisation protocol shown in Scheme 1 gives a three-fold symmetry product, at first sight it does not seem applicable. However, this trimerisation must involve a cross-coupling of a benzene derivative to a biphenyl derivative. This led Cammidge to experiment with benzene/biphenyl oxidative cross-coupling reactions. An example leading to a mono-functionalised triphenylene is shown at the top of Scheme 2.



Scheme 2. R = primary alkyl. Reagents: (i) FeCl₃/DCM (ii) MeOH (iii) HBr/HOAc or BBr₃ or Ph₂PLi/THF.

The reaction relies on some very fortunate reaction kinetics. We expected that the product would be contaminated with the trimerisation product from the dialkoxybenzene but none could be detected. Clearly the trimerisation process is much slower than the desired cross-coupling reaction. As shown in Scheme 2, the monomethoxy product can be dealkylated and the monohydroxy-triphenylene obtained can be used to make liquid crystal side-chain polymers [16]. Similarly, the corresponding dimethoxy derivatives can be elaborated into dihydroxy-triphenylenes and then into main-chain polymers [17]. A further improvement of this procedure is shown at the bottom of the Scheme [18]. It arose from studies by Zhibao Lu of the dealkylation side-reactions. He showed that the tendency to dealkylation in these ferric chloride coupling reactions followed the order methoxy < primary alkoxy << secondary alkoxy. Indeed, with excess reagent, dealkylation of isopropoxy derivatives is essentially complete. We believe that the dealkylation involves formation of an $[\text{Ar}-\text{O}=\text{CMe}_2]^+$ cation which is cleaved by the methanol on workup. Whether this explanation is true or not, the reaction does provide a very quick route to both monohydroxy- and dihydroxy-triphenylenes for making both polymers and oligomers [18, 19]. Further exploration of this benzene/biphenyl coupling reaction showed that it is possible (within certain limits) to vary the number, nature and position [20] of the substituents around the ring. This paved the way for the synthesis of discogens with five [21] and seven [22] side-chains and with side chains bearing functional groups [23]. The ferric/chloride/methanol protocol has also been used to advantage in other areas of organic synthesis [24].

It is less than thirty years since the synthesis of the first discotic liquid crystals [25]: a short history compared to that of calamitic liquid crystals. The only significant commercial development so far has been that of optical compensating films for increasing the angle of view of displays [26] but the unique properties of discotic liquid crystals will undoubtedly lead to other applications. The optical compensating films exploit triphenylene-based discotic liquid crystals and the triphenylene-based discotics are now the most widely studied of all discotic liquid crystal systems [27]. In large part this is due to the fact that they are most readily available through the development of the ferric chloride based syntheses.

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The synthesis of triphenylene-based discotic mesogens New and improved routes

N. BODEN, R. C. BORNER, R. J. BUSHBY*, A. N. CAMMIDGE and M. V. JESUDASON

School of Chemistry, University of Leeds, Leeds LS2 9JT, England

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The synthesis of discotic liquid crystal materials based on the triphenylene core normally involves the preparation of hexahydroxytriphenylene. This has traditionally been accomplished by a chloranil promoted trimerization of 1,2-dimethoxybenzene followed by demethylation of the hexamethoxytriphenylene produced. Hexahydroxytriphenylene is subsequently alkylated to give the required derivative. The overall yield of this three step procedure is low and it is difficult to perform on a large scale. It is herein shown that a modified procedure using iron III chloride instead of chloranil yields hexa-alkoxytriphenylenes in a single step. The reaction is high yielding and can be performed on a large scale. This also provides a better route than those currently available for making the unsymmetrically substituted triphenylenes required in the synthesis of polymeric discotic liquid crystals. Some related elaborations of the triphenylene nucleus are also discussed.

1. Introduction

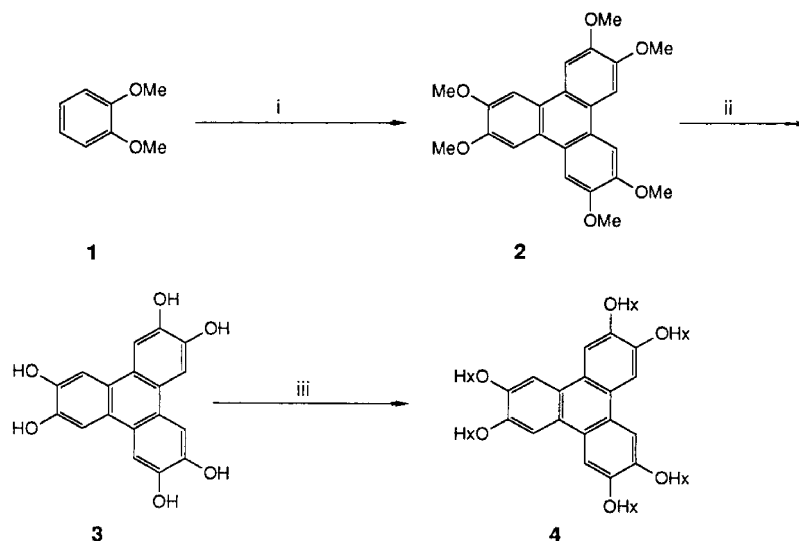
Since Chandrasekhar's paper [1] reporting the first observation of a discotic liquid crystal material there has been an ever increasing interest in the preparation of new discotic mesogens. Studies of the basic physics and research into the potential applications of discotic liquid crystals has, however, been held back by synthetic difficulties which have restricted the availability of the requisite large amounts of highly pure materials.

Arguably the most widely synthesized discotic mesogens are those based on a hexasubstituted triphenylene nucleus. Their synthesis traditionally involves the oxidative trimerization of 1,2-dimethoxybenzene (veratrole) **1** in 67 per cent sulphuric acid using the quinone chloranil as oxidant [2, 3]. This reaction is more or less limited to the production of hexamethoxytriphenylene **2** and if, for example, hexahydroxytriphenylene (HAT6) **4** is required, it is necessary to replace the alkoxy groups. The methyl groups can be removed either by using hydrogen bromide/acetic acid or boron tribromide. The resulting hexahydroxytriphenylene is then alkylated with hexyl bromide (scheme 1). Although the chloranil/sulphuric acid mixture can be used to trimerize 1,2-dihydroxybenzene directly, the yield of HAT6 obtained is low and purification requires repeated chromatography and repeated recrystallization. For this reason the indirect route via compounds **2** and **3**

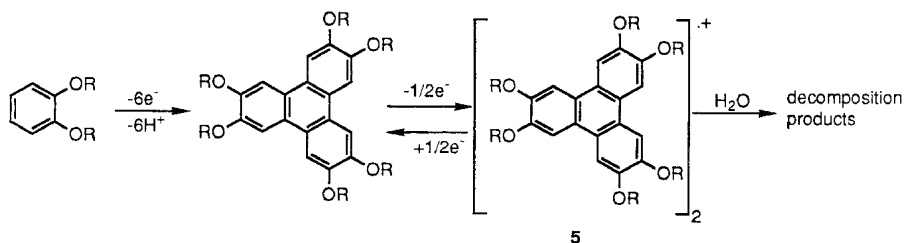
is usually more economical. The need to replace the alkoxy substituent in the 'chloranil' route is, however, a wasteful step and synthesis of hexa-alkoxytriphenylenes in this way involves two lengthy chromatographic separations (firstly to separate compound **2** from chloranil and secondly to purify the final product); this makes the whole process rather time consuming and limits the overall scale of production. In our experience it is not easy to prepare more than about 10 g of the pure mesogen in a single batch.

An alternative route (scheme 2) which has been explored is electrochemical oxidation [4–7]. For example, Bechgaard and Parker have shown that anodic oxidation of veratrole in trifluoroacetic acid/dichloromethane with tetrabutylammonium tetrafluoroborate as the supporting electrolyte gives hexamethoxytriphenylene **2**. The anode potential required to bring about the reaction is also sufficiently positive to remove an electron from the triphenylene and so the observed product from such an oxidation is not the triphenylene itself, but the radical cation salt **5** ($R=Me$). Salts of this type are decomposed by reaction with nucleophiles such as water (which is in part the reason why such reactions are carried out in acidic solvents) and so the work-up procedure is crucial to the outcome of the reaction. However, if the mixture is worked up reductively a good yield of hexamethoxytriphenylene is obtained. Such a reductive work-up can be achieved either by chemical or electrochemical methods [6]. If the reaction is carried out under carefully controlled conditions, the radical

*Corresponding author.



Scheme 1. The 'chloranil' route to hexaalkoxyxytriphenylene. Reagents: (i) 67 per cent H_2SO_4 , chloranil; (ii) HBr/HOAc or BBr_3 ; (iii) HxBr , base.



Scheme 2. The 'electrochemical' route to hexa-alkoxyxytriphenylenes.

cation salt **5** crystallizes out on the anode surface (electrocrystallization). The great advantage of the electrochemical route is that it is not limited to veratrole, but it seems that a wide range of 1,2-dialkoxybenzene derivatives can be trimerized in this way [6]. Its great disadvantage (at least in our experience) is that the reaction is slow and the work-up relatively tedious, so that we have not succeeded in making more than c. 1 g quantities in this way and in most cases we do not regard it as a serious competitor to the 'chloranil' route.

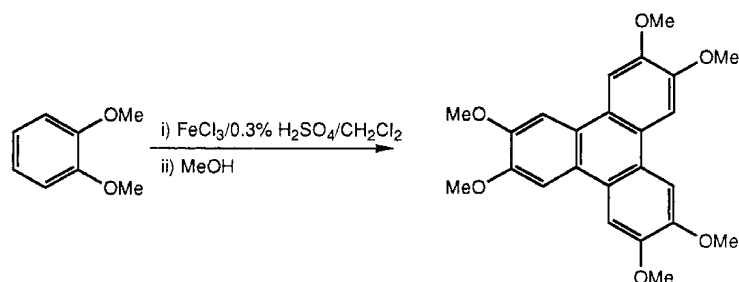
2. Results and discussion

Another alternative oxidation reagent in these reactions is ferric chloride. Bengs *et al.* have described a reaction procedure in which 1,2-bishexadecyloxybenzene was treated with ferric chloride in 70 per cent sulphuric acid at 80°C , followed by an ice/water work-up, to give a 20 per cent yield of 2,3,6,7,10,11-hexakis-hexadecyloxytriphenylene [8] and have used a similar procedure for making mixed trimers in low but unspecified yield [8].

In our experience a modified form (scheme 3) of the 'ferric chloride' route is the method of choice. The low yields reported by Bengs *et al.*, may be a result of the rather unnecessarily strong acid and high temperature employed, but more probably relate to the work-up procedure which, as in the case of the electrochemical reactions, is crucial. Oxidation of veratrole can be achieved using c. 0.3 per cent (w/v) sulphuric acid in dichloromethane at $15\text{--}25^\circ\text{C}$ for 2 h. The product is a dark green solid which is certainly an oxidized form of the triphenylene, most probably the radical cation salt **5**. This is then filtered off and reduced on the filter pad with methanol. Formaldehyde is liberated and hexamethoxyxytriphenylene obtained directly and virtually pure.

We have repeated this reaction using a range of different acids, but best yields were obtained using sulphuric (table). In truth, the HCl liberated as a byproduct in the reaction is probably the 'major' acid in all cases. A reasonable yield is obtained even if the acid is totally omitted.

This route to hexamethoxyxytriphenylene is both quicker and easier than any other route and has the



Scheme 3. The 'ferric chloride' route to hexamethoxytriphenylene.

Yield of hexamethoxytriphenylene by the ferric chloride route as a function of acid catalyst (0.3 per cent w/v) added.

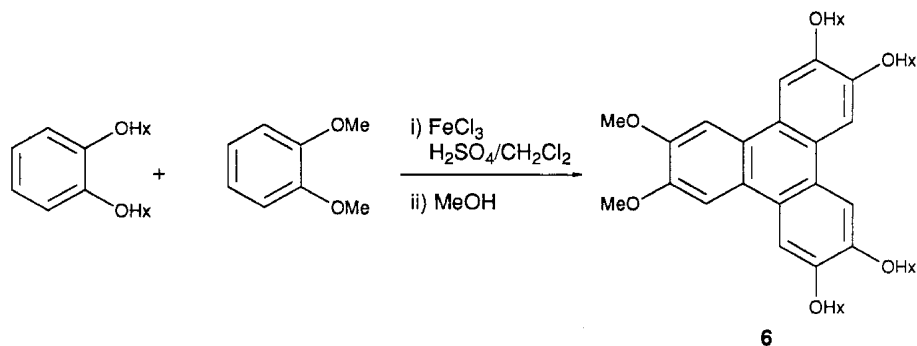
Acid	Yield per cent
Trifluoroacetic	73
Triflic	78
Chlorosulphonic	76
Concentrated sulphuric	86

advantage that it is easy to perform on a relatively large scale. It also has the advantage over the chloranil route that most 1,2-dialkoxybenzenes can be trimerized directly to give good yields (HAT3, 77 per cent, HAT4, 65 per cent, HAT6, 65 per cent, HAT8, 60 per cent, HAT9, 55 per cent). Another advantage which we have found with this route is that it can be used for mixed trimerization reactions. In the example shown in scheme 4 the yield of the tetrahexyloxy derivative is not high, but the products are easy to separate, and once again the reactions are easy to perform on a large scale providing an easier route of access to monomers for making polymeric discotic systems than those previously described in the literature [9, 10].

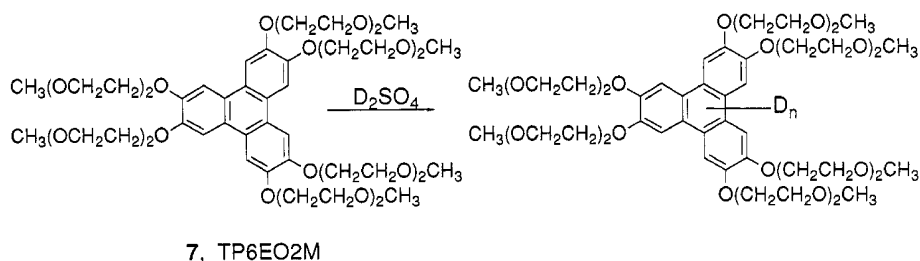
One limitation to the ferric chloride route is that it does not work for ethyleneoxy substituted triphenylenes. Hence, in the synthesis of lyotropic discotic

systems such as TP6EO2M **7**, (see scheme 5), it provides a more convenient route to making the hexamethoxytriphenylene precursor, but it does not obviate the need to substitute the alkoxy groups [3, 11]. An attempted oxidative cyclisation of 1,2-di(1,4,7-trioxaocetyl)benzene failed. In our work on this system however, a more efficient route has been developed for the synthesis of TP6EO2M from hexahydroxytriphenylene (see experimental section). It has also proved necessary to synthesize this compound deuteriated on the aromatic nucleus and in the end chains. One method for obtaining ring-deuteriated material was that described by Luz and co-workers [12]. In this the hexamethoxy compound **2** is demethylated using DBr/DOAc to give partially deuteriated **3** (scheme 1) which can be subsequently alkylated. This procedure works, but is expensive and time consuming. A much simpler method is to directly deuteriate the methoxy substituted system in strong acid [13, 14]. When TP6EO2M is dissolved in D₂SO₄, deuteration and decomposition occur at comparable rates, but with limited reaction times a good yield of partially ring-deuteriated compound is obtained (scheme 5).

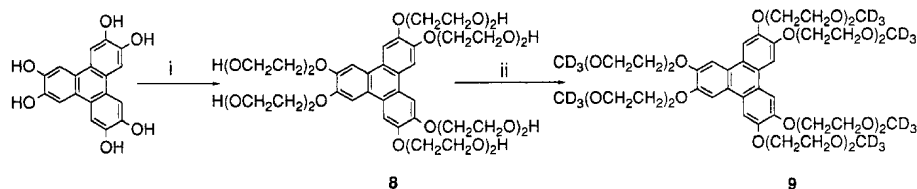
Deuteration of the end chains of TP6EO2M is more difficult, but has been achieved using the reaction sequence shown in scheme 6, details of which are discussed in the experimental section.



Scheme 4. Modification of the ferric chloride route to produce asymmetric derivatives for the synthesis of polymeric discotic liquid crystals.



Scheme 5. Ring deuteration of TP6EO2M.

Scheme 6. Synthesis of end-chain deuterated TP6EO2M. Reagents: (i) $\text{BrCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OPy}$, K_2CO_3 , EtOH; (ii) H^+ ; (iii) CD_3I , base. Py=tetrahydropyranyl.

3. Experimental

3.1. Synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene 2 (ferric chloride route)

Veratrole (23 g, 0.166 mol) was added slowly to a well stirred suspension of iron III chloride (81 g, 0.5 mol) in dichloromethane (500 ml) and concentrated sulphuric acid (1.6 g). As the veratrole was added, hydrogen chloride gas was given off and the temperature rose until the dichloromethane was boiling. The reaction mixture was stirred for a further 2 h and then filtered. Methanol was carefully added to the solid on the filter pad which changed colour from dark green to grey with copious washings. Heat and formaldehyde were liberated and it is advised that this step is performed in a well ventilated fume cupboard. The remaining solid was dried under vacuum to yield hexamethoxytriphenylene 2 as a grey solid (19.7 g, 86 per cent), mp $>300^\circ\text{C}$, δ_{H} (CDCl_3) 7.80 (6 H, s, ArH), 4.13 (18 H, s, CH_3O).

3.2. Synthesis of 1,2-dihexyloxybenzene

Bromohexane (4.92 ml, 0.0375 mol) was added to a vigorously stirred solution of catechol (1.1 g, 0.01 mol) and potassium carbonate (6.2 g) in ethanol (100 ml) under nitrogen. The reaction mixture was stirred under reflux for 16 h and filtered through Celite with copious washings of ethanol. The filtrate was concentrated *in vacuo* and subjected to column chromatography on silica, eluting with 1:1 dichloromethane: light petroleum to give the product as a pale yellow oil (2.6 g, 95 per cent), δ_{H} (CDCl_3) 6.88 (s, 4 H, ArH), 3.97 (t, 4 H,

OCH_2), 1.81 (m, 4 H, OCH_2CH_2), 1.33–1.49 (m, 12 H, CH_2), 0.97 (t, 6 H, CH_3).

In a similar manner were prepared: 1,2-dipropyloxybenzene (reaction time 4.5 h, yield 89 per cent); 1,2-dibutyloxybenzene (4.5 h, 91 per cent); 1,2-dioctyloxybenzene (16 h, 79 per cent, mp 24°C , lit. [15] $23\text{--}26^\circ\text{C}$); 1,2-dinonyloxybenzene (8 h, 86 per cent, mp 37°C , lit. [15] 37°C).

3.3. Synthesis of 2,3,6,7,10,11-hexahexyloxytriphenylene [HAT6, 4] (ferric chloride route)

1,2-Dihexyloxybenzene (1.5 g, 0.0055 mol) was added to a vigorously stirred suspension of iron III chloride (2.66 g, 0.0165 mol) in dichloromethane (20 ml) with concentrated sulphuric acid (2 drops). The reaction occurred with vigorous evolution of gas and was quenched with methanol (60 ml) after 45 min. The reaction mixture was filtered and the filtrate concentrated *in vacuo* to give a black solid which was subjected to column chromatography, eluting with 1:1 dichloromethane:light petroleum to give the product as a pale yellow solid which was recrystallized from ethanol (1.09 g, 73 per cent) C–D 67°C , D–I 99.5°C . (lit. [16] 68°C , 97°C) δ_{H} (CDCl_3) 7.83 (s, 6 H, ArH), 4.23 (t, 12 H, OCH_2), 1.94 (m, 12 H, OCH_2CH_2), 1.41–1.56 (m, 36 H, CH_2), 0.93 (t, 18 H, CH_3).

In a similar manner were prepared: 2,3,6,7,10,11-hexapropyloxytriphenylene, HAT3 (77 per cent), C–I 176.5°C , (lit. [16] 177°C); 2,3,6,7,10,11-hexabutyloxytriphenylene, HAT4 (65 per cent), C–D 88°C , D–I

143.5°C, (lit. [16] 88.6°C, 145.6°C); 2,3,6,7,10,11-hexaoxyloxytriphenylene, HAT8 (60 per cent), C–D 65.8°C, D–I 84.8°C, (lit. [16] 66.8°C, 85.6°C); 2,3,6,7,10,11-hexanonyloxytriphenylene, HAT9 (55 per cent), C–D 56.5°C, D–I 78°C, (lit. [16] 57°C, 77.6°C).

3.4. Synthesis of 2,3-dimethoxy-6,7,10,11-tetrahexyloxytriphenylene 6

A solution of 1,2-dihexyloxybenzene (10 g, 0.036 mol) and veratrole (10 g, 0.074 mol) in dichloromethane (40 ml) was added to a stirred mixture of iron III chloride (70 g, 0.434 mol) and concentrated sulphuric acid (1 ml) in boiling dichloromethane (250 ml), at such a rate that gentle reflux was maintained. The mixture was stirred for a further 1 h and poured into methanol (400 ml). The dichloromethane was removed *in vacuo* and the solid filtered off and purified by column chromatography on silica, eluting with benzene. The white solid was recrystallized from dichloromethane/methanol to give the product (2.7 g, 22 per cent), mp 102°C. δ_{H} (CDCl₃) 7.84 (s, 2 H, ArH), 7.82 (s, 2 H, ArH), 7.76 (s, 2 H, ArH), 4.24 (m, 8 H, OCH₂), 4.11 (s, 6 H, OCH₃) 1.99 (m, 8 H, OCH₂CH₂), 1.40–1.60 (m, 24 H, CH₂), 0.94 (m, 12 H, CH₃). Elemental analysis: found, C (76.6 per cent), H (9.4 per cent); C₄₄H₆₄O₆ requires C (76.7 per cent), H (9.4 per cent).

3.5. Improved procedure for the synthesis of 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)triphenylene 7 (TP6EO2M)

2,3,6,7,10,11-Hexahydroxytriphenylene (1.11 g, 0.0034 mol) was added, under nitrogen, to 1-bromo-2-(2-methoxyethoxy)ethane (5.1 g, 0.028 mol) in ethanol (82 ml). Potassium carbonate (5.27 g) was added and the mixture was well stirred under reflux in an atmosphere of nitrogen for 20 h. The mixture was allowed to cool before being filtered through Celite and the filtrate evaporated *in vacuo* to give the crude product. This material was purified by column chromatography on Kieselgel, eluting first with dichloromethane followed by 2 per cent methanol in dichloromethane and finally with 4 per cent methanol in dichloromethane. Repeated recrystallization of the product from ether at 0°C gave pure TP6EO2M as white needles (1.05 g, 37 per cent) mp 53.4–53.7°C (lit. [3] 51–53°C). δ_{H} (CDCl₃) 7.88 (s, 6 H, ArH), 4.00, 4.40 (both t, 12 H, OCH₂CH₂O), 3.60, 3.80 (both m, 12 H, OCH₂CH₂), 3.40 (s, 18 H, OCH₃).

3.6. Synthesis of ring deuteriated TP6EO2M

TP6EO2M (207 mg, 2.46×10^{-4} mol) was added to sulphuric acid (98 per cent, 7 ml) in deuterium oxide (4 ml) and the solution was stirred under nitrogen for

40 h. The solution was diluted with water (12 ml) and neutralized with 50 per cent sodium hydroxide solution. Chloroform (3 × 50 ml) was used to extract the product. The combined extracts were dried (magnesium sulphate) and concentrated *in vacuo* to give 208 mg of crude product which was dried *in vacuo* before purification by column-chromatography on Kieselgel, eluting with 3 per cent methanol/chloroform, giving 170 mg of the deuteriated compound as a grey solid.

This solid was recrystallized from 50 per cent ether/light petroleum (30–40°C boiling range) to give deuteriated TP6EO2M (80 mg, 39 per cent) as pale grey needles. ¹H NMR (CDCl₃) gave a spectrum that was identical to that of the undeuteriated compound, but with the intensity of the aromatic singlet much reduced. From the ratio of the integrals the compound was found to be c. 60 per cent deuteriated.

3.7. Synthesis of chain deuteriated TP6EO2M 9

Since the ¹H NMR spectra of intermediates in this sequence showed them to be essentially pure (although highly coloured) and since some of them proved difficult to purify, the sequence was carried straight through to the TP6EO2M which was then purified by column chromatography and recrystallization. *p*-Toluene sulphonic acid (100 mg) was added to a cooled (solid CO₂-acetone), stirred mixture of dihydropyran (2.3 g, 0.028 mol) and 5-chloro-3-oxapentanol (3.1 g, 0.025 mol) in dry dichloromethane (1.5 ml). After 2 h, more dichloromethane was added, the solution washed with aqueous sodium bicarbonate, dried with magnesium sulphate and concentrated *in vacuo* to give the essentially pure tetrahydropyranyl derivative as a colourless oil (5.31 g, 100 per cent) δ_{H} (CDCl₃) 4.65 (m, 1 H, OCHO), 3.4–4.0 (m, 10 H, OCH₂ and CH₂ Cl), 1.4–1.9 (m, 6 H, CH₂).

A stirred mixture of this tetrahydropyranyl derivative (3.34 g, 0.016 mol), hexahydroxytriphenylene (650 mg, 0.002 mol), potassium carbonate (1.93 g) and ethanol (25 ml) was heated under reflux in an atmosphere of nitrogen for 90 h. The mixture was filtered, the residue was washed with chloroform and the combined filtrate and washings were evaporated *in vacuo*. The oil was repeatedly extracted with light petroleum and the black residue dried *in vacuo* to give the hexakistetrahydropyranyl compound as a black semi-solid (presumably as a mixture of all possible stereoisomers), (2.04 g, 76 per cent crude). δ_{H} (CDCl₃) 7.90 (br s, 6 H, ArH), 4.75 (m, 6 H, OCHO), 4.43 (t, 12 H, ArOCH₂), 3.4–4.1 (m, 48 H, CH₂O), 1.4–1.9 (m, 36 H, CH₂).

A portion of this product (500 mg) was treated with concentrated hydrochloric acid (2 ml), water (4 ml) and tetrahydrofuran (4 ml) under an atmosphere of argon

for 18 h, the solvents were removed *in vacuo* and the residue was washed repeatedly with light petroleum and dried *in vacuo*. The alcohol **8** was then dissolved in dry dimethylformamide (10 ml). Sodium hydroxide (200 mg) was added to the stirred, cooled (solid CO₂-acetone) mixture under an atmosphere of nitrogen. It was allowed to warm to room temperature and *d*₃-methyl iodide (2.0 g) added. After a further 18 h at room temperature, tlc of the mixture showed that reaction was incomplete, and it was therefore heated at 50°C for 3 h. Water was added and the product isolated by chloroform extraction and purified by column chromatography and recrystallization to give the deuteriated TP6EO2M **9** as white needles, mp and ¹H NMR spectra identical to those previously reported (0.26 g, 74 per cent based in the crude tetrahydropyranyl derivative).

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