

Novel unsymmetrical triphenylene discotic liquid crystals: first synthesis of 1,2,3,6,7,10,11-heptaalkoxytriphenylenes

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Oxidation of 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylene yields the pentaalkoxytriphenylene-1,2-quinone; reductive acetylation of this *o*-quinone furnishes the diacetate that can be directly alkylated to 1,2,3,6,7,10,11-heptaalkoxytriphenylene derivatives showing columnar D_h phases.

Mesophases formed by discotic liquid crystals (LCs) are now well-recognised to be suitable for many device applications.^{1,2} Most of the discogens reported to date consist of a flat, or nearly flat, rigid core surrounded by a number of aliphatic side chains having binary, trigonal, tetragonal or hexagonal symmetries. Symmetrically substituted hexethers of triphenylene are the most widely synthesised and studied discotic mesogens. The potential uses of these materials as one-dimensional conductors,^{2,3} photoconductors⁴ and light emitting diodes⁵ are attracting considerable attention. Several research groups are currently working on the synthesis of symmetrical, unsymmetrical and functionalized triphenylene discotic liquid crystals.^{6–14}

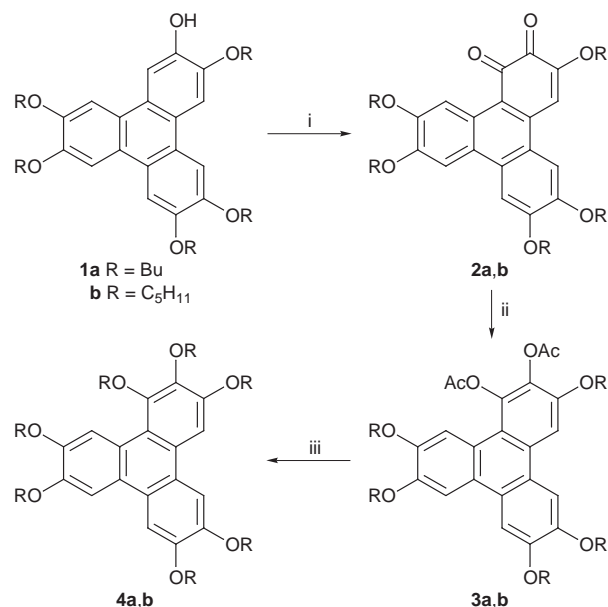
Triphenylene derivatives show mesomorphism only when the six peripheral positions are substituted with aliphatic chains. Whereas the synthesis of symmetrical hexalkoxytriphenylenes by oxidative trimerisation of 1,2-dialkoxybenzenes is quite easy, the synthesis of well-defined unsymmetrically substituted derivatives is more complicated. Breaking of symmetry in a hexaalkoxytriphenylene can be achieved by different ways, *e.g.* by changing the chain length of some of the side chains, by changing the nature of one or more side chain or by using lower or higher degrees of substitution. Tinh *et al.* reported the synthesis of several dissymmetrical hexasubstituted triphenylenes by incorporating different alkyl chains into the periphery using a statistical approach and found that introduction of dissymmetric side-chains does not affect the nature of the D_h phase but does result in the reduction of the mesophase stability.¹⁵ An easy route to unsymmetrically-substituted triphenylenes was recently reported using the so-called biphenyl route.^{6e,7e} A well-defined synthesis of unsymmetrical and low degree substituted triphenylenes has also been reported recently using organometallic chemistry.¹⁰ When one out of the six ether side chains in hexaalkoxytriphenylenes was replaced by an ester group, the stability of the mesophase was enhanced significantly.¹⁶ A plastic columnar discotic phase is reported in this type of unsymmetric triphenylene derivatives.¹⁷ In another approach to the preparation of unsymmetrical triphenylenes and to the induction of molecular dipole, colour, *etc.*, nitration and halogenation of hexaalkoxytriphenylenes has been investigated.^{6a–d,9} While the nitro or halogen group in these triphenylene derivatives could not be replaced by an alkylthio group by nucleophilic aromatic substitution,⁹ reduction of the nitro group followed by acylation with various acid chlorides yielded 'seven tail' triphenylene discotics.^{6a} However, because of the presence of the amide group, the clearing temperature of these derivatives are rather high.

We have very recently reported a highly improved synthesis of symmetrical, unsymmetrical and mono-functionalized triphenylene derivatives using MoCl_5 .^{8e} We have also reported the synthesis of various functionalized triphenylene,^{7f,8d} mixed tail

triphenylene,^{7b} low symmetry fluorescent triphenylene^{7a} and core functionalized triphenylene discotic LCs.^{8b,c}

All the triphenylene derivatives hitherto known have six or less alkoxy chains. While triphenylene derivatives with six alkoxy chains are mesomorphic, triphenylenes having less than six alkoxy chains are nonmesomorphic but can be made mesomorphic by putting other substituents onto the periphery.^{7a,b} To the best of our knowledge, there are no examples of triphenylene discotic species having more than six alkoxy chains. Here we report on a novel approach to the synthesis of triphenylene-based discotic liquid crystals containing seven alkoxy chains in the periphery. The synthesis of these novel heptaalkoxytriphenylenes is outlined in Scheme 1.

During the nitration 2-hydroxy-3,6,7,10,11-pentabutoxytriphenylene, we always found a black product in addition to the nitrated and some unreacted starting material.^{8e} If the reaction is not monitored carefully, this black material becomes the major product. We suspected that the formation of this black material was due to ring oxidation to an *o*-quinone. Oxidation of 2-hydroxy-3,6,7,10,11-pentabutoxytriphenylene **1a** with other known oxidising agents such as chromium trioxide and cerium(IV) ammonium nitrate yielded the same product. The structure of this compound was assigned as 3,6,7,10,11-pentabutoxytriphenylene-1,2-dione **2a** on the bases of its ¹H NMR and mass spectral data. Reductive acetylation of this *o*-quinone resulted in the formation of diacetate **3a**. The diacetate was directly alkylated^{8a} with alkyl halide to heptaalkoxytriphenylene **4a** in very high yield. Heptapentoxytriphenylene was prepared in the same manner. The ¹H NMR data of the products were found to be in perfect agreement with the structure.‡



Scheme 1 Reagents and conditions: i, CAN, MeCN, room temp., 2 min, 94%; ii, Ac₂O, Zn, NEt₃, reflux, 0.5 h, 92%; iii, DMSO, KOH, RBr, 60 °C, 1 h, 95%

Both heptaalkoxytriphenylenes **4a** and **4b** are mesogenic. While compound **4a** melted at 65.7 °C and clears at 70.1 °C, compound **4b** exhibited a very broad mesophase from room temperature to 65 °C. The mesophase–isotropic transition temperatures of both heptaalkoxytriphenylenes are very low compared to their hexasubstituted analogues (ca. 145 °C for hexabutoxy- and 122 °C for hexapentoxytriphenylene). This could be due to the presence of the extra alkoxy chain and the steric hindrance caused by this chain.

This methodology provides an easy, high-yielding process for the preparation of various unsymmetrical, low clearing temperature, broad mesophase triphenylene discotics. It can also be extended to other discotic cores. The potential of this new method is currently under investigation for the synthesis of various hepta-, octa-, nona- and per-alkoxytriphenylene derivatives.

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Notes and References

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‡ Selected data for **2a**: m/z (FAB) 620.2 ($M^+ + 2$ H); δ_{H} (CDCl₃) 8.91 (s, 1 H), 7.64 (s, 1 H), 7.61 (s, 1 H), 7.35 (s, 1 H), 6.98 (s, 1 H), 4.20 (m, 10 H), 1.89 (m, 10 H), 1.55 (m, 10 H) and 1.05 (m, 15 H). For **2b**: δ_{H} (CDCl₃) 8.98 (s, 1 H), 7.72 (s, 1 H), 7.68 (s, 1 H), 7.45 (s, 1 H), 7.08 (s, 1 H), 4.20 (m, 10 H), 1.95 (m, 10 H), 1.48 (m, 20 H) and 0.98 (m, 15 H). **3a**: δ_{H} (CDCl₃) 8.48 (s, 1 H), 7.84 (s, 1 H), 7.83 (s, 1 H), 7.81 (s, 1 H), 7.78 (s, 1 H), 4.19 (m, 10 H), 2.44 (s, 3 H), 2.38 (s, 3 H), 1.92 (m, 10 H), 1.60 (m, 10 H) and 1.03 (m, 15 H). For **3b**: δ_{H} (CDCl₃) 8.48 (s, 1 H), 7.84 (s, 1 H), 7.83 (s, 1 H), 7.81 (s, 1 H), 7.78 (s, 1 H), 4.18 (m, 10 H), 2.44 (s, 3 H), 2.38 (s, 3 H), 1.88 (m, 10 H), 1.47 (m, 20 H) and 0.97 (m, 15 H). For **4a**: δ_{H} (CDCl₃) 9.22 (s, 1 H), 7.83 (s, 2 H), 7.81 (s, 1 H), 7.66 (s, 1 H), 4.20 (m, 12 H), 4.01 (t, J 7.1, 2 H), 1.88 (m, 14 H), 1.56 (m, 14 H) and 0.99 (m, 21 H). For **4b**: δ_{H} (CDCl₃) 9.21 (s, 1 H), 7.83 (s, 2 H), 7.81 (s, 1 H), 7.66 (s, 1 H), 4.20 (m, 12 H), 4.01 (t, J 7.1, 2 H), 1.83 (m, 14 H), 1.49 (m, 28 H) and 1.02 (m, 21 H).

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