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Improved synthesis of monohydroxytriphenylenes (MHTs)—important precursors to discotic liquid crystal families

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1. Introduction

Certain disk-like molecules ('discotics') can form liquid crystal phases. Most usually, the molecules assemble as columns to give so-called columnar mesophases (which can be compared to the smectic mesophases formed by rod-like/calamitic molecules) (Scheme 1). In some cases a less ordered nematic phase is exhibited in which the molecules retain only orientational order. Substituted triphenylene derivatives which present a flat, aromatic core surrounded by flexible chains, are the most widely studied class of discotic liquid crystals.¹ Triphenylene discotics have received particular interest because of their ability to act as one-dimensional charge transport materials, acting as photoconductors or semiconductors on doping² and, alongside other discotic frameworks, lend themselves to diverse electronic and optical applications.³

Synthetic advances^{1,4–7} have permitted triphenylene discotics to be designed and synthesized so that an extensive range of structural features can be probed. Typically, symmetrically substituted hexalkoxytriphenylenes (**HAT**s) are most conveniently prepared by oxidative cyclisation of 1,2-dialkoxybenzenes. Unsymmetrically substituted derivatives have proved more challenging, but efficient stepwise procedures have been developed to meet this demand,

ABSTRACT

Monohydroxypentaalkoxytriphenylenes are important intermediates for elaboration into complex covalently linked discotic liquid crystal assemblies. An improved, simple synthetic protocol is described that gives rapid access to these precursors in a single step.

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most conveniently employing cross-coupling strategies to synthesise bi- or terphenyl intermediates (Scheme 1).

These studies have highlighted triphenylene discotics as robust materials with a strong tendency towards columnar behaviour. Significant perturbation around the periphery can be achieved with retention of the columnar mesophase behaviour so long as conjugation to the aromatic core is preserved.⁸ However, the columnar mesophases of triphenylene, and other, discotic liquid crystals tend to resist miscibility with other organics including mesogens and other discotic systems. While such a phase separation holds advantages in certain applications in organic electronics, incorporation of additional functionality within a columnar matrix is a desirable feature, not least because the triphenylene core is itself an electron-rich component that can be further exploited in device design.

Monohydroxypentaalkoxytriphenylenes can be considered as important and versatile intermediates⁹ for the synthesis of twinned and linked structures. Retention of at least five alkoxy chains promotes liquid crystal phase formation while the single hydroxy group can be used as a conventional link point (ether or ester formation) or converted into triflate for participation in cross-coupling chemistry to introduce conjugated links (see Scheme 2). **MHT**s are of course available through refined multistep procedures as outlined above. However, these syntheses are an over-elaboration and there is demand for simplified access to material in reasonable quantities. It is known that monohydroxytriphenylenes **MHTn** can be prepared in a single step as byproducts from the cyclisation of dialkoxybenzenes.⁹ In this Letter we report



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Scheme 1. Conventional synthesis of symmetrical (HATn) and unsymmetrical hexaalkoxytriphenylenes that form columnar hexagonal mesophases.



Scheme 2. Monohydroxytriphenylenes (MHTn) are important and versatile precursors to linked and twinned structures.

an optimized protocol for their synthesis via a mixed cyclisation^{5a,10} between 1,2-dialkoxybenzene and 2-alkoxyphenol.

In the development of an improved protocol for the synthesis of monohydroxytriphenylenes a number of factors need to be considered. Although reaction yield is one important criterion, the ease of isolation of pure material (in terms of time and cost) must also be considered. Conceptually the most straightforward approach involves the use of more vigorous conditions to those traditionally employed to hydrolyse the symmetrical hexaalkoxytriphenylene (HATn) precursor.¹¹ However, it is known that such conditions lead to the formation of additional hydrolysis products that are difficult to separate from the target material.¹¹ Any useful strategy must, therefore, suppress excessive further hydrolysis to avoid any complicated purification procedures. An ideal protocol would involve the mixed cyclisation between a 1,2-dialkoxybenzene and a 2-alkoxyphenol under controlled conditions. Clearly under these conditions there are two possible origins of the target monohydroxytriphenylene MHTn. It can be formed directly through a mixed cyclisation or via hydrolysis of hexaalkoxytriphenylene and so it was important to understand the factors that promote or suppress the latter pathway under ferric chloride mediated cyclisation conditions. Hexyl chains were chosen for the study and the results from the initial experiments using 1,2-dihexyloxybenzene

are summarized in Scheme 3. At room temperature cyclisation using ferric chloride in CH₂Cl₂/nitromethane was accompanied by hydrolysis to the desired monohydroxytriphenylene **MHT6**. TLC analysis of the crude product clearly showed the formation of further polar compounds that presumably result from further hydrolysis. **MHT6** can be seen early in the reaction and it appears that the rate of formation of **HAT6** is comparable to the rate of its hydrolysis to MHT6. However, further hydrolysis is even more rapid so simply allowing the reaction to proceed for prolonged periods at room temperature only increases the proportion of polyhydroxylated triphenylenes at the expense of MHT6. Performing the reaction at lower temperatures was found to suppress hydrolysis. The cyclisation proceeds at a reasonable rate at 0 °C but the rate of hydrolysis is more significantly slowed so that MHT6 only appears towards the end of the reaction and is formed in trace quantities (<5%) along with products of further hydrolysis. The dominant species responsible for hydrolysis in these reactions is likely to be the HCl formed during cyclisation. This assumption was verified by performing the cyclisation reaction over solid sodium carbonate and we found that under these conditions hydrolysis was suppressed almost completely.

From the above experiments we can conclude that hydrolysis of the formed hexaalkoxytriphenylenes is slowed significantly at 0 °C and is suppressed completely by the addition of a base to neutralize the HCl formed during the reaction. These conditions were exploited in order to perform mixed cyclisations between 1,2dialkoxybenxene and alkoxyphenol, reasoning that a clean reaction (i.e., one that minimized significant further hydrolysis) would lead to simple one-step access to **MHTn**. Consequently a solution of ferric chloride in CH_2Cl_2/n itromethane was added to a 1:1 mixture of 1,2-dihexyloxybenzene and hexyloxyphenol over solid sodium carbonate at 0 °C. Surprisingly, over the course of 3 h at 0 °C the formation of **HAT6** was observed along with some baseline material,



Scheme 3. HAT6 formation and hydrolysis using ferric chloride.



Scheme 4. Controlled mixed cyclisation to give monohydroxytriphenylene MHT6.

but only trace quantities of MHT6. Variation of the reaction conditions led to the further conclusion that addition of sodium carbonate suppresses incorporation of the phenol and that, therefore, this strategy to prevent hydrolysis of formed MHTn could not be employed. Fortunately, clean and efficient mixed cyclisations to give the target **MHT** were achieved by reaction at 0 °C without sodium carbonate. In these reactions there is a balance required so that a reasonable reaction rate is achieved and the desired product (in this case MHT6) can be isolated easily and purely. Separation of MHTn from HATn can be achieved easily so long as MHTn is the dominant component. However, separation of MHTn from products of further hydrolysis can be challenging if the latter are formed in significant quantities. The most efficient protocol developed uses a statistical 2:1 mixture of 1,2-dihexyloxybenzene and hexyloxyphenol at 0 °C and gives a yield of MHT6 of 35% (Scheme 4). Increasing the ratio of dihexyloxybenzene increases the calculated yield (based on the limiting reagent) but decreases both the real yield (based on the mass of MHT6 product for equivalent scales) and the efficiency of isolation.

In conclusion, we have developed an optimized protocol for convenient preparation and isolation of monohydroxy-pentaalkoxytriphenylenes (**MHT**s) using a ferric chloride mediated mixed cyclisation strategy. Performing the reaction carefully at 0 °C provides the best balance in the reaction such that cyclisation proceeds at a reasonable rate but further hydrolysis of the **MHT** product is minimized. The protocol is reproducible and, therefore gives easy access to these important intermediates.

2. Experimental procedure

 $FeCl_3$ (3.24 g, 19.8 mmol) was dissolved in a mixed solvent of CH_2Cl_2 (20 ml) and CH_3NO_2 (2 ml). The mixture of 1,2-bis(hexyl-

oxy)benzene (1.11 g, 4 mmol) and 2-hexyloxyphenol (0.39 g, 2 mmol) was dissolved in CH_2Cl_2 (15 ml), and was then added dropwise into the FeCl₃ solution over 30 min at 0 °C. The reaction was continued for 2.5 h at 0 °C. MeOH (15 ml) was added to stop the reaction and the mixture was washed twice with HCl (5%, 20 ml) and brine (20 ml). The organic layer was dried with Na_2SO_4 , and the solvents removed under reduced pressure. The crude product was purified by column chromatography (silica gel, EtOAc/light petroleum 1:30–1:20) and afforded the two main products as colourless solids; **HAT6** (0.47 g, 42%), **MHT6** (0.52 g, 35%).

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