A Novel, Efficient and General Synthetic Route to Unsymmetrical Triphenylene Mesogens using Palladium-catalysed Cross-coupling Reactions

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A novel, clean and efficient route to unsymmetrical triphenylene mesogens has been developed using palladium-catalysed cross-coupling reactions involving arylboronic acids.

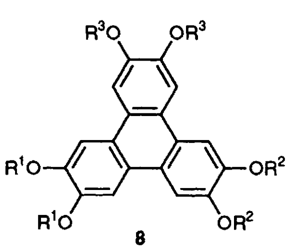
Investigations into the physical properties of discotic liquid crystal materials have been severely restricted by the relative difficulty in their synthesis, most notably in the case of the preparation of examples of unsymmetrically substituted disc-like structures. Triphenylene liquid crystals offer much scope for the investigation of asymmetrically-substituted systems because of their inherently high liquid crystal character.[1] Here we report on a novel approach to the synthesis of unsymmetrical triphenylene mesogens which involves the use of efficient palladium-catalysed cross-coupling reactions.

The principal rationale for the development of a synthetic methodology for the preparation of unsymmetrical discotic mesogens was to allow us to investigate the boundaries between traditional rod-like calamitic mesophases and the more recent disc-like discotic mesophases. Unsymmetrically-substituted discotic materials are, of course, no longer disc-shaped and depending upon the nature of the substitution pattern may well be more rod-like in nature. At this juncture between discs and rods, unsymmetrical discotic mesogens are expected to exhibit optical biaxiality. Biaxiality in liquid-crystalline systems offers tremendous scope for extremely fast-switching devices because just a slight movement of the molecules will lead to a large change in the optical response.

Traditionally, triphenylene materials have been prepared through the oxidation of 1,2-dimethoxybenzene (veratrole) or higher alkoxy-substituted homologues. Oxidants used include chloranil[2] and iron(III) chloride[3,4] but neither method offers much scope for complete generality in the preparation of unsymmetrical triphenylenes. Unsymmetrical triphenylenes have been prepared using the latter method but careful chromatographic separations of isomers are required to isolate individual isomers. A more recent method of unsymmetrical triphenylene synthesis has involved the use of an Ullman coupling to provide intermediate biphenyls.[5]

Palladium-catalysed cross-coupling reactions involving arylboronic acids have been used in the efficient synthesis of useful calamitic ferroelectric host materials.[6] This type of coupling reaction is well recognized as the best method of synthesizing unsymmetrical multiaryl systems (especially biphenyls).[7,8] Such a strategy has now been applied to the general, systematic synthesis of unsymmetrical discotic mesogens. Commercially available 4-bromoveratrole **1** was quantitatively demethylated using boron tribromide to provide the dihydroxy material **2** which was then efficiently *O*-alkylated to give good yields of materials **3** with longer alkyl chains. Compound **3a** was then treated with *n*-butyllithium to generate a lithium salt which was quenched with trimethyl borate to give the borate ester; subsequent hydrolysis *in situ* generated the arylboronic acid **4** in excellent yield. An efficient palladium-catalysed cross-coupling between boronic acid **4** and a bromide **3b** with alkoxy units different to those found in the boronic acid unit provided a high yield of the unsymmetrically substituted biphenyl **5**. At this stage it was decided to use the traditional synthesis ($FeCl_3$, H_2SO_4 and CH_2Cl_2)[5] of triphenylenes in the expectation of selectively obtaining the desired unsymmetrical triphenylene **8**. The results were extremely significant because compound **8** was cleanly produced; the slight excess of compound **7** was easily removed in the purification by column chromatography and recrystallization. Most importantly, no symmetrical triphenylene based on compound **7** was identified. This is thought to be because the biphenyl unit **5** is preformed and accordingly compound **7** is consumed quickly to give the desired product which is then worked up and isolated. The palladium-catalysed cross-coupling methodology can be extended beyond the unsymmetrical biphenyl material **5** to facilitate a general synthesis of unsymmetrical triphenylenes of identical structure to those shown in Scheme 1 (see Scheme 2). The double bromination[9] of biphenyl **5** gives only one product **9** which can be converted into a boronic acid and coupled with compound **11** to give unsymmetrical triphenylene **8**. The use of palladium-catalysed cross-coupling reactions involving arylboronic acids is very tolerant towards many functional moieties and thus enables the nature of R¹, R² and R³ to be widely varied. The latter method, shown in Scheme 2 is far superior to that shown in Scheme 1 because the oxidation method using

Table 1 Transition temperatures (°C) for a selection of unsymmetrical triphenylenes **8**



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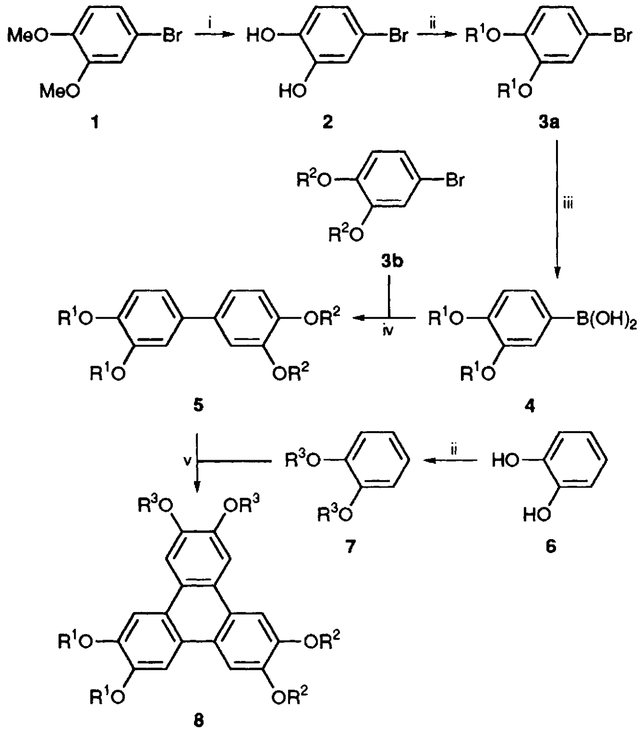
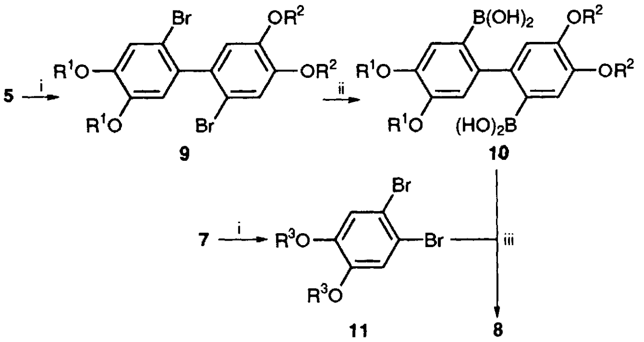
Compound				Transitions (°C)		
	R¹	R²	R³	Crys	D_{hd}	Iso
8a	Me	Me	C_6H_{13}	• 142.5	—	•
b	Me	Me	$C_{12}H_{25}$	• 125.0	—	•
c	Me	Bu	$C_{12}H_{25}$	• 87.5	—	•
d	C_8H_{17}	C_8H_{17}	$C_{12}H_{25}$	• 51.0	• 61.0	•
e	C_8H_{17}	C_8H_{17}	C_6H_{13}	• 46.0	• 84.0	•



Scheme 1 *Reagents*: i, BBr_3, CH_2Cl_2; ii, RBr, K_2CO_3, butanone; iii, a, Bu^nLi, b, $(MeO)_3B$, c, 10% HCl; iv, Pd$(PPh_3)_4$, DME, 10% Na_2CO_3; v, $FeCl_3$, H_2SO_4, CH_2Cl_2



Scheme 2 *Reagents*: i, Br_2, $CHCl_3$, $MeCO_2H$; ii, a, Bu^nLi, b, $(MeO)_3B$, c, 10% HCl; iii, Pd$(PPh_3)_4$, DME, 10% Na_2CO_3

iron(III) chloride requires activating alkoxy substituents whereas the method solely utilizing palladium-catalysed cross-coupling reactions does not.

The basic methodology offers excellent generality, however, the main strength of the strategy is that it facilitates the synthesis of a much wider range of materials than those reported here. For example, R^1, R^2, and R^3 (compound **8**) could independently represent different protecting groups which will allow the introduction of many functions other than ethers, (*e.g.* alkanoate esters, benzoate esters or directly linked aryl units). Conversion of phenolic sites to a triflate leaving group facilitates the attachment of directly linked alkyl, aryl and alkynyl moieties to triphenylene core. There is also scope to increase the number of different peripheral moieties to five where compound **5** has four different substituent groups.

Table 1 shows the melting points and mesophase transition temperatures of the initial materials **8a–e**. Where short (methyl) chains are used then melting points are very high and the materials **8c–e** are non-mesogenic. However, where the chains are longer then melting points are considerably lower and where the chain lengths are not widely different then the D_{hd} phase is exhibited to reasonably high temperature. These initial results can be considered significant and show much promise for the future.

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