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Model studies towards liquid crystalline dendrimers with mesogenic repeat units throughout the structure

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Abstract—Model studies towards liquid crystal dendrimers in which the mesogenic units are based on alkoxyalkylbiphenyls and repeat through the structure are described; the parent monomers show smectic mesophases demonstrating the suitability of the motifs.

The interplay between microscopic and macroscopic behaviour lies at the heart of molecular-based materials research and a superb example is provided by the field of liquid crystals. The dendrimeric molecular architecture has proved extremely fascinating, not least because the properties of dendrimers tend to be significantly different from traditional polymers based on related repeat units.[1] The dendrimeric architecture, in which branching repeat units radiate from a central core, contrasts directly with the parallel molecular ('unit') alignment in liquid crystal phases. Despite this apparent dichotomy, a number of liquid crystal dendrimers are known.[2] In most cases, these materials are prepared by substituting mesogenic units onto the termini of classical dendrimers (termed side-chain dendrimers[3] by analogy to side-chain polymers). Liquid crystal dendrimers in which the mesogenic units repeat through the structure (termed main-chain dendrimers[3]) are rare[3,4] and model studies towards such materials are described herein.

Biphenyl units, which can be considered as the archetypal liquid crystal cores,[5] were chosen as the basis for investigation. Perhaps the simplest biphenyl unit which could be used in dendrimer construction is 3,4′,5-trisubstituted biphenyl itself. This building block was briefly investigated but, as expected, model compounds of type **1** proved to be non-mesogenic. More elaborate bis-biphenyls were therefore targeted (Fig. 1). The molecular design was based on knowledge of the 'parent' biphenyl mesogens where it is known that alkoxyalkylbiphenyls are liquid crystalline[6] but bisalkoxy derivatives are not.[7]

The alkoxyalkylbiphenyl unit was therefore incorporated in the molecular design and the first targets (repeating units) were formulated as **2** and **3**. The synthesis of model monomers is shown in Scheme 1. Both syntheses follow similar routes and, in order to provide rapid access to key intermediates, rely on statistical

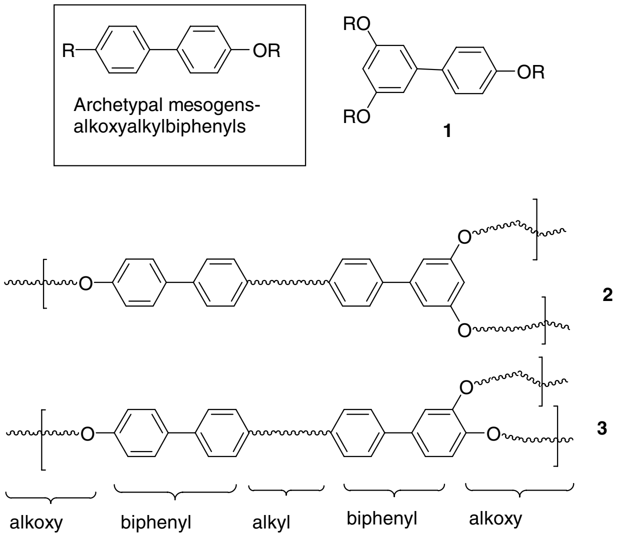

Figure 1. Dendrimer repeat units containing the alkoxyalkylbiphenyl motif.

Keywords: Dendrimers; Liquid crystals; Polycatenar.

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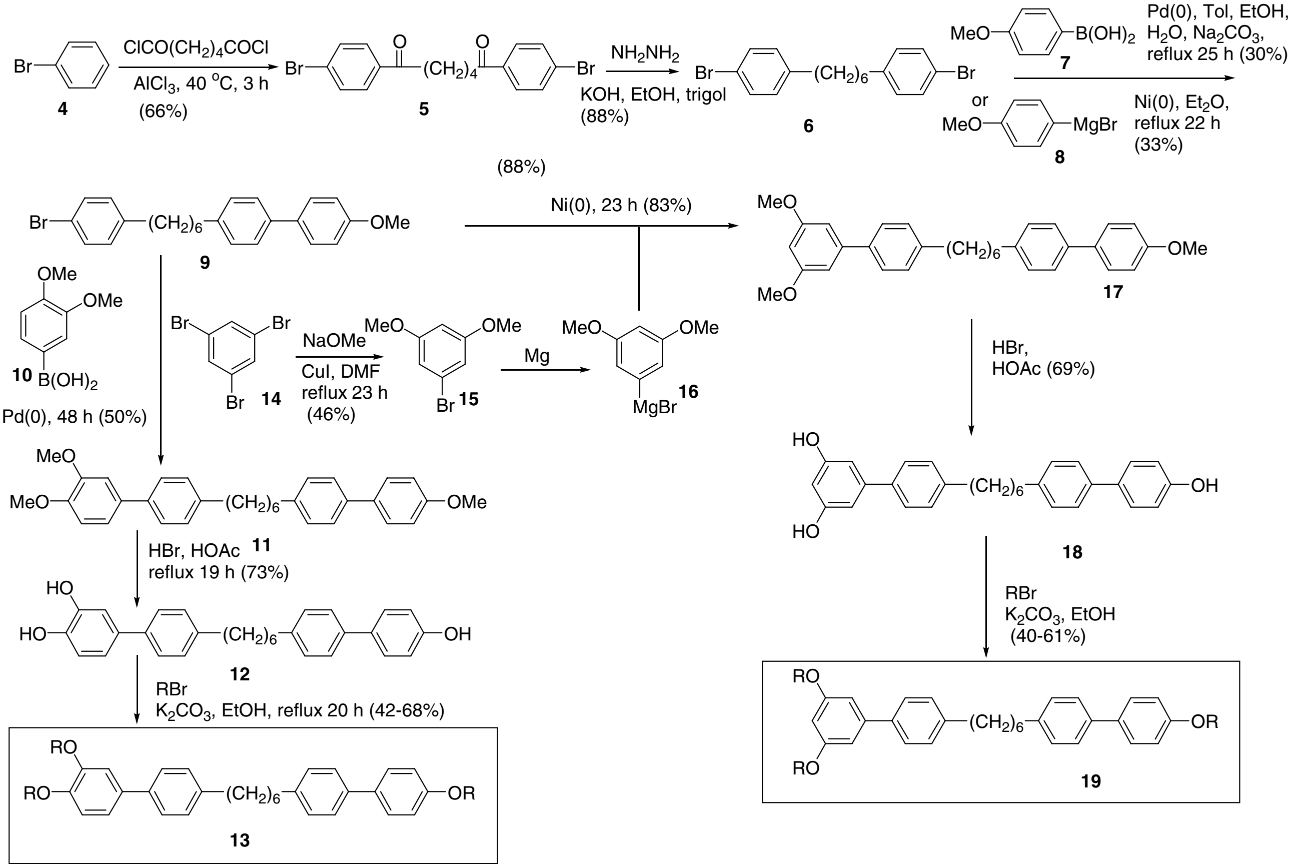


Scheme 1. Synthesis of model tricatenar monomers.

cross-coupling reactions for desymmetrisation. Friedel–Crafts reaction between bromobenzene (used as solvent) and adipoyl chloride[8,9] gave diketone **5**, which was reduced[8] using the Huang–Minlon modification of the Wolff–Kishner reaction. Suzuki coupling between dibromide **6** and 4-methoxyphenylboronic acid **7** gave an acceptable yield of singly coupled product **9** (unreacted starting material was recycled). Similar Suzuki coupling between **9** and **10** gave **11**, whereas isomer **17** was most conveniently prepared using a nickel-catalysed Kumada coupling employing the Grignard reagent formed from **15**. Trimethoxy intermediates **11** and **17** were demethylated using HBr/HOAc to give triols **12** and **18**. Realkylation gave the two series of model monomers **13** and **19**.

Liquid crystalline compounds, which present a structure which is a hybrid between rod-like and disc-like molecules, are termed 'polycatenar' liquid crystals[10] and **13** and **19** are therefore elaborated versions of tricatenar compounds. Their liquid crystalline behaviour was investigated using polarising optical microscopy (POM) and differential scanning calorimetry (DSC), and the results are summarised in Tables 1 and 2.

Both series of compounds show liquid crystal behaviour. Compounds in series **13** develop monotropic smectic phases on cooling, whereas those of series **19** show enantiotropic smectic phases. The phases were assigned as smectic A based on the textures observed under POM.

Table 1. Thermal properties of model monomers **19** on cooling

R	Transition temperatures (isotropic liquid–smectic mesophase) °C
n-Hexyl	51
n-Heptyl	40
n-Octyl	39
n-Decyl	39
n-Dodecyl	35
n-Octanoyl	47

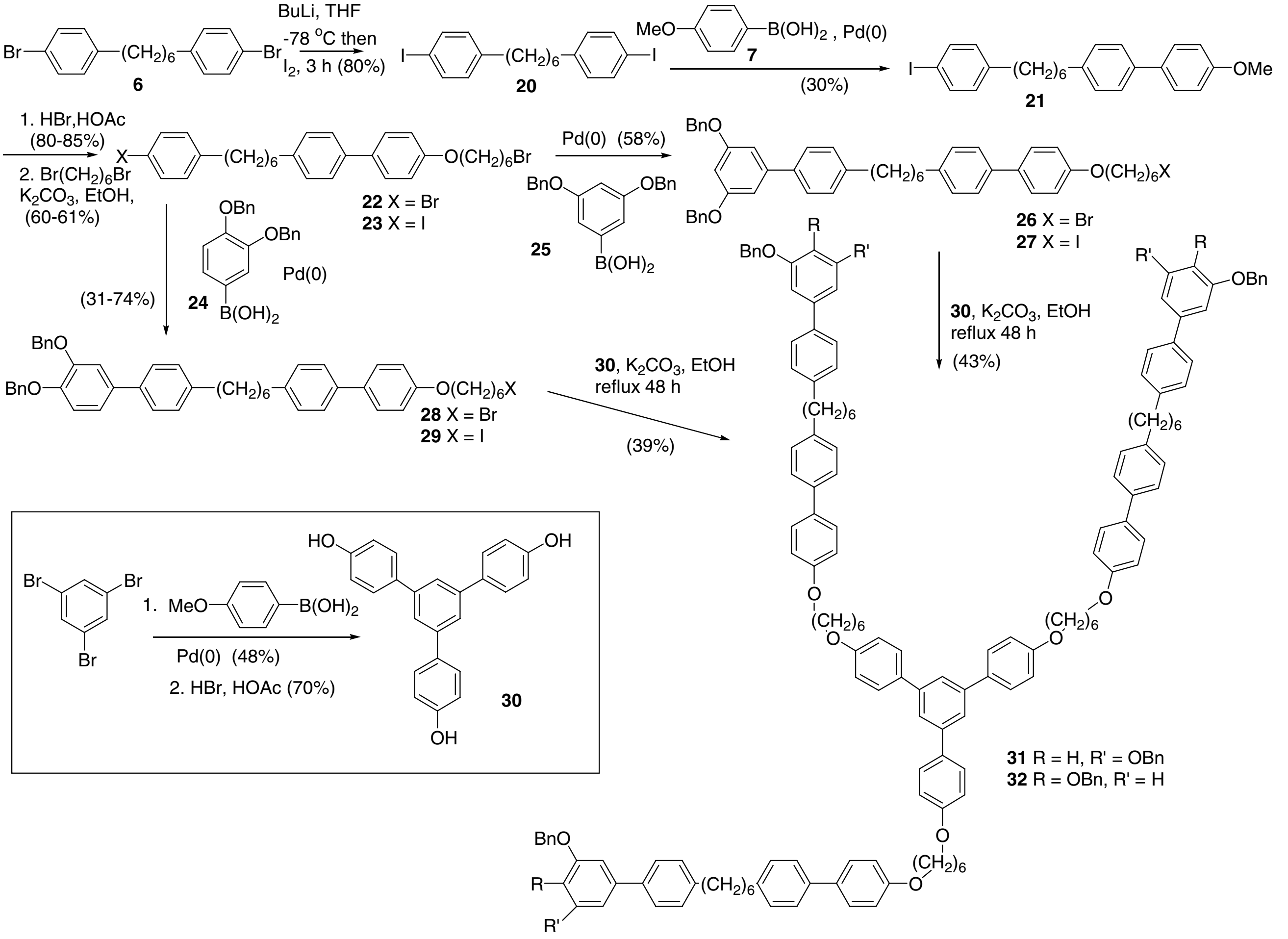
All materials show a monotropic mesophase which persists to room temperature. A more detailed table is presented in Supplementary data.

Table 2. Thermal properties of model monomers **13** on cooling

R	Transition temperatures (isotropic liquid (I)–smectic mesophase (S) – crystal (Cr)) °C
n-Hexyl	I 109 S 84 Cr
n-Heptyl	I 108 S 84 Cr
n-Octyl	I 108 S 83 Cr
n-Decyl	I 104 S 70 Cr
n-Dodecyl	I 108 S 87 Cr

All materials show an enantiotropic mesophase. A more detailed table is presented in the Supplementary data.

It is worth noting that alkoxyalkylbiphenyls typically show smectic liquid crystal behaviour also.



Scheme 2. Synthesis of first generation protected dendrimers.

The syntheses of these model compounds ('monomers') therefore demonstrates their suitability as mesogenic repeat units for the construction of dendrimeric architectures. However, the syntheses and intermediates are not themselves directly suitable for use in the synthesis of dendrimers. For dendrimer synthesis, a more elaborate repeat unit is required which is selectively protected/functionalised permitting the dendrimer to be constructed generation-on-generation. The syntheses of these units and the syntheses of the first-generation, protected dendrimers are shown in Scheme 2. The syntheses again start from symmetric dibromide **6**. In some syntheses, the bromides of **6** were converted to iodides (giving **20)** via lithium–halogen exchange to improve the subsequent cross-coupling reactions. Statistical Suzuki reaction between **20** and **7** proceeded smoothly and both bromide **9** and iodide **21** were demethylated using HBr/HOAc. The resulting phenols were realkylated using excess 1,6-dibromohexane to give **22** and **23**, respectively. Separate model studies indicated that benzyl protecting groups would be suitable in the repeating units, so bisbenzyloxyphenyl boronic acids **24** and **25** were prepared (see Supplementary data) and coupled with **22**/**23**. As expected, cross coupling with the aryl iodide derivatives proceeded more readily and in higher yields. The final isolated products from these reactions were mixtures of alkyl bromides and iodides, the latter resulting from simple substitution with the iodide generated during cross coupling. Formation of such mixtures is not detrimental to the overall synthesis as both can be used in the dendrimer growth steps. Indeed, **26**/**27** and **28**/**29** have been attached to a 'core' trisphenol **30**[11] to complete the model study and produce the first generation protected dendrimers **31** and **32**[12] which, as expected, are not themselves liquid crystalline.

In conclusion, we have described the synthesis of two new series of elaborated tricatenar liquid crystals based on bisbiphenyl units. The materials were targeted as models for mesogenic dendrimer repeat units and have therefore been shown to be suitable in this respect. The syntheses have been adapted to produce differentially functionalised/protected derivatives which can be used as building blocks for dendrimer construction, and the synthesis of the first generation protected dendrimers is described.

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Supplementary data

Full experimental details, characterisation data and spectra are provided for all compounds along with more detailed tables and description of mesophase behaviour. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.05.107.

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12. Selected data: Compound **31** mp 57–62 °C; (Found: C, 84.18; H, 7.14. $C_{174}H_{174}O_{12}$. EtOH requires C, 84.37; H, 7.28); δ_H (270 MHz; $CDCl_3$) 1.40–1.86 (48H, m), 2.64 (12H, m), 4.03 (12H, m), 5.09 (12H, s), 6.61 (3H, t, *J* 2.3), 6.83 (6H, d, *J* 2.3), 6.95–7.52 (90H, m); δ_C (67.9 MHz; $CDCl_3$) 25.91, 29.16, 29.27, 31.36, 35.56, 67.88, 70.17, 100.72, 106.46, 114.71, 114.81, 123.77, 126.54, 126.99, 127.59, 127.92, 127.99, 128.31, 128.60, 128.75, 133.56, 133.69, 136.91, 138.22, 138.36, 141.24, 141.85, 142.33, 143.41, 158.43, 158.81, 160.20; *m*/*z* (FAB) 2457.6 (MH^+). Compound **32** mp 125–130 °C; (Found: C, 84.50; H, 7.07. $C_{174}H_{174}O_{12}$. EtOH requires C, 84.37; H, 7.28%); δ_H (270 MHz; $CDCl_3$) 1.20–1.50 (12H, m), 1.55–1.75 (24H, m), 1.85–1.95 (12H, m), 2.61 (12H, t, *J* 7.6,), 4.03 (12H, m), 5.18 (6H, s), 5.20 (6H, s), 6.93–7.02 (15H, m), 7.07–7.13 (6H, m), 7.18–7.23 (12H, m), 7.30–7.52 (48H, m), 7.60 (6H, d, *J* 8.6), 7.65 (3H, s); δ_C (67.9 MHz; $CDCl_3$) 25.39, 29.18, 29.27, 31.41, 35.54, 67.95, 71.40, 71.52, 114.26, 114.73, 114.82, 115.33, 120.10, 123.79, 126.55, 126.65, 127.31, 127.42, 127.81, 127.94, 128.33, 128.49, 128.77, 133.58, 133.71, 134.93, 137.37, 138.23, 141.26, 141.56, 141.87, 148.43, 149.11, 158.45, 158.83; *m*/*z* (FAB) 2457.6 (MH^+).