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Synthesis of a hexaalkoxybenzo[*b*]triphenylene mesogen†

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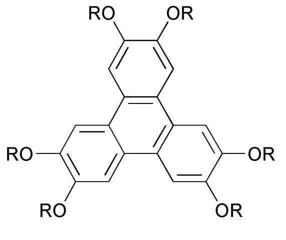
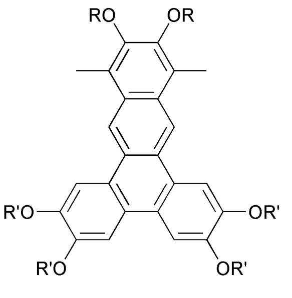
The synthesis of the first mesogenic hexaalkoxybenzo[*b*-]triphenylene derivative is reported; this compound exhibits a broad columnar liquid crystal phase at temperatures only slightly above room temperature.

Hexaalkoxytriphenylenes (**HAT**s) constitute one of the largest and most important classes of molecules that exhibit columnar liquid crystal phases. Research over the past several years has amply demonstrated the potential that these and related materials have as components in semiconductor devices such as LEDs, chemical sensors and field effect transistors.[1] Recently, there has been considerable interest in the design of "macrodiscotic" mesogens, *i.e.* disc-shaped molecules that possess aromatic cores much larger than triphenylene. These more extended structures are commonly liquid crystalline over very broad temperature ranges and exhibit high charge carrier mobilities.[2–8]

Comparatively little work has been carried out on discotic mesogens with core sizes intermediate between that of triphenylene and the macrodiscotic mesogens. Since it would be useful to know what impact, if any, small increases in core size have on phase behavior, we decided to synthesize the hexaalkoxybenzo[*b*]triphenylene derivatives **1a** and **1b**. Despite the marked similarity between these molecules and **HAT** derivatives, there have been no reports of mesogenic molecules based upon the benzo[*b*]triphenylene core.[9]



HAT



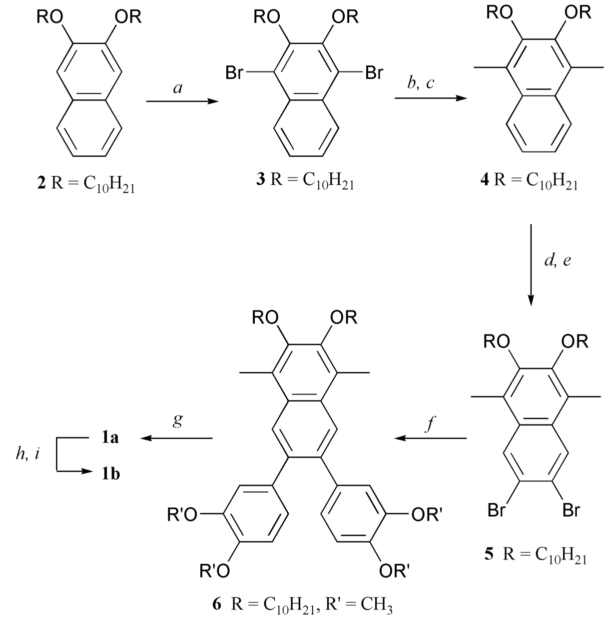
1a R = $C_{10}H_{21}$, R' = CH_3
1b R = R' = $C_{10}H_{21}$

Our synthetic strategy (Scheme 1) focused on constructing these structures starting from 2,3-didecyloxynaphthalene, **2**, which was obtained from 2,3-dihydroxynaphthalene in 93% yield using Williamson etherification conditions. The selective installation of reactive functional groups at the 6- and 7-positions of this naphthalene derivative proved to be our major synthetic challenge, since electrophilic substitution tends to occur instead at the 1- and 4-sites. In order to circumvent this problem, it was necessary to block these positions prior to further elaboration. To this end, compound **2** was converted in near quantitative yields to the 1,4-dibrominated product, **3**, by treatment with bromine in acetic acid. These halogens were then replaced by treating **3** with *n*-butyllithium followed by methyl iodide to afford 1,4-dimethyl-2,3-didecyloxynaphthalene, **4**.

With these methyl groups in place, bromination occurs preferentially at the 6- and 7-positions to yield the dibrominated product, **5**. A large excess of bromine had to be employed to ensure that substitution took place at both sites; if only two equivalents of bromine were used, the monobrominated product, **7**, was formed as a major impurity. Unfortunately, when a large excess of brominating agent was employed, ring substitution was invariably accompanied by some reaction at the benzylic positions to give compounds **8** and **9** as side products. This problem could be dealt with by treating the crude mixture of the di-, tri- and tetrabrominated products **5**, **8** and **9** with $NaBH_4$ in order to selectively remove the bromines at the benzylic positions. Using this 2-step procedure, we were able to obtain **5** in good yields.

Coupling of the dibromo intermediate **5** with 3,4-dimethoxyphenyleboronic acid under standard Suzuki conditions affords the diphenylnaphthalene derivative **6**. We then coverted this compound to the benzo[*b*]triphenylene product **1a** with $FeCl_3$, using a similar procedure as that reported for the synthesis of triphenylene derivatives from *o*-terphenyls.[10] The success of this oxidatiive cyclization step highlights another advantage conferred by the methyl groups at the 1- and 4-positions. While 2,3-dihydroxy or 2,3-dialkoxy naphthalene derivatives are prone to intermolecular coupling reactions at the 1- and 4-positions in the presence of oxidants such as $FeCl_3$,[11] the presence of the methyl groups effectively precludes the possibility of these side reactions from taking place.

Not surprisingly, compound **1a** exhibits no liquid crystal phase, but instead melts directly from a crystalline solid to an



Scheme 1 *Reagents and conditions:* a) Br_2, AcOH, 85%; b) *n*-BuLi, Et_2O, −78 °C; c) CH_3I, 93%; d) Br_2, CH_2Cl_2; e) $NaBH_4$, DMSO, 50 °C, 3 days, 75%; f) 3,4-dimethoxyphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O, 70 °C, 40%; g) $FeCl_3$, CH_2Cl_2, 44%; h) BBr_3, CH_2Cl_2; i) 1-bromodecane, K_2CO_3, DMF, 110 °C, 5 days, 42%.

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† Electronic supplementary information (ESI) available: full synthetic and analytical details. See http://www.rsc.org/suppdata/cc/b3/b305462d/

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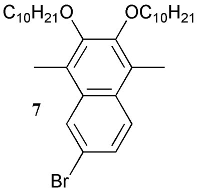

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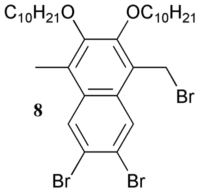

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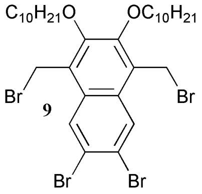

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isotropic liquid at 144 °C. For this reason, we decided to prepare an analogue in which the methoxy groups were replaced by longer chains that would be more conducive to liquid crystallinity. To this end, **1a** was dealkylated using BBr_3 and the resulting hexahydroxy intermediate was converted to the hexakis(dececyloxy)benzotriphenylene product, **1b**.

The thermal properties of compound **1b** were examined using polarized optical microscopy and differential scanning calorimetry (DSC). This benzotriphenylene was found to exhibit a liquid crystal phase between 35 °C and 88 °C; the enthalpies of these transitions were 51.4 J g^{-1} and 1.0 J g^{-1}, respectively. This mesophase exhibits the characteristic dendritic texture of a columnar hexagonal phase when examined under a microscope (Fig. 1). This assignment was confirmed by the X-ray diffraction pattern, which has two peaks in the small angle region that index to the (100) and (110) reflections of a two dimensional hexagonal lattice. We also observed a broad halo centred at 4.5 Å and a peak at 3.6 Å, which were assigned to the spacings between alkyl chains and the central π-systems, respectively.

It is interesting to compare the phase behaviour of this compound with that of the analogous **HAT** derivative, 2,3,6,7,10,11-hexadecyloxytriphenylene (**HAT10**). The XRD patterns of **1b** and **HAT10** are surprisingly similar; the latter possesses a lattice constant of 25.7 Å, whereas the intercolumnar distance observed for **1b** was 26.7 Å. This difference is smaller than anticipated based on the size of the two molecules, since the long axis of benzo[*b*]triphenylene is approximately 2.5 Å larger than that of triphenylene. The increase in core size may be somewhat offset in the columnar phase by a greater degree of interdigitation of the side chains for **1b**, leading to the relatively modest change in the intercolumnar spacing.

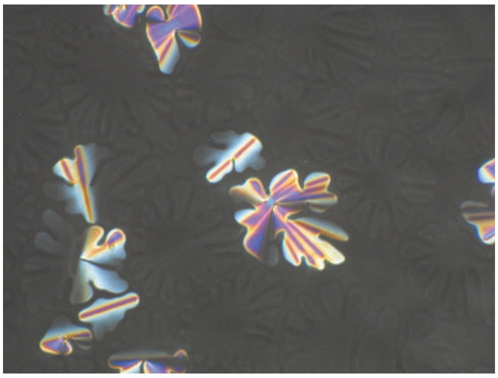

Fig. 1 Polarized optical micrograph of **1b** obtained from cooling at 85 °C (100×).

Despite the similarity in their XRD patterns, the benzotriphenylene mesogen is liquid crystalline over a much broader temperature range than **HAT10**, which forms a columnar hexagonal phase from only 58–69 °C.[12] This large difference likely reflects the greater propensity of the larger cores to self-assemble into columnar structures. Like many triphenylene derivatives,[13] compound **1b** becomes homeotropically aligned when slowly annealed from the isotropic phase.

The demonstration that compound **1b** exhibits a stable, easily aligned columnar liquid crystal phase at relatively low temperatures suggests that benzo[*b*]triphenylene derivatives may be promising candidates for practical applications where formation of a broad columnar phase at room temperature is highly desirable. We are currently investigating other members of this series in order to gain further insight into their phase behaviour and electronic properties.

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