

The Synthesis of Alkoxybromotriphenylenes: New Discotic Liquid Crystals and Valuable Precursors to 'Mixed Tail' Discotics

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The phenolic moieties of hydroxyalkoxytriphenylenes are derivatized and reduced to yield alkoxytriphenylenes possessing reactive sites for aromatic substitution; simple bromination affords the first triphenylene discotic liquid crystal having only three alkoxy tails.

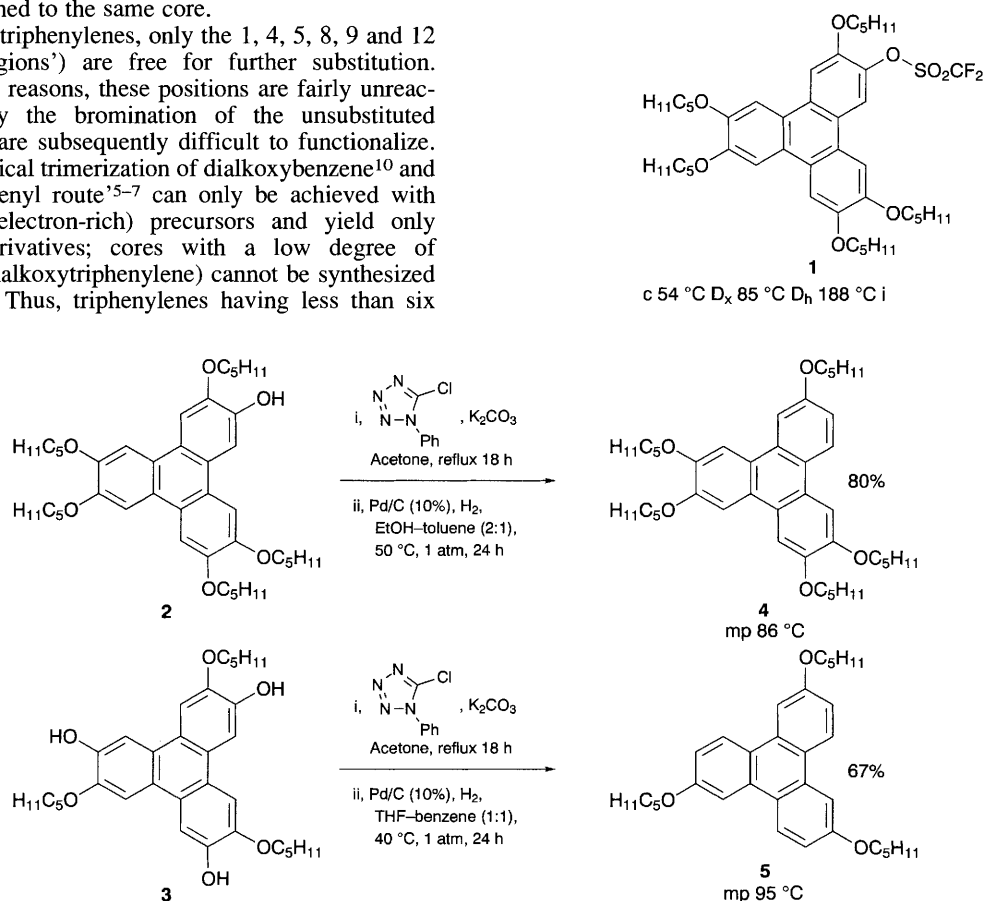
Discotic triphenylene derivatives represent a promising new class of liquid crystalline materials owing to their pronounced photoconductivity. Charge carrier mobilities of $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (hole mobility) have been observed in the mesophase of hexapentyloxytriphenylene and a dimer derived from the same molecule,¹ exceeding the values for commonly used photoconducting polymers by two or three orders of magnitude.² In an effort to further explore these potentially useful discotics, powerful synthetic methods for the preparation of highly substituted triphenylene cores have been recently described.³⁻⁷ Despite the desire for other core substitution, hexaalkoxytriphenylenes remain the most studied derivatives. An even higher charge carrier mobility of $1 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been observed in the highly ordered helical columnar phase of hexahexylthiotriphenylene.⁸ This enhanced photoconductivity has been attributed to long range order occurring along the columns of the helical phase. Clearly, the gross structure of the supramolecular assembly plays a crucial role in the photoconductivity of these systems. Interestingly, this helical columnar phase occurs only in alkylthio derivatives and not alkoxytriphenylenes. Thus, in an effort to investigate and better understand the molecular level origins of this highly ordered helical phase, we have begun the synthesis of triphenylene derivatives containing alternating alkoxy and alkylthio tails attached to the same core.

With hexaalkoxytriphenylenes, only the 1, 4, 5, 8, 9 and 12 positions ('bay regions') are free for further substitution. However, for steric reasons, these positions are fairly unreactive, as shown by the bromination of the unsubstituted triphenylene,⁹ and are subsequently difficult to functionalize. Moreover, the classical trimerization of dialkoxybenzene¹⁰ and the so-called 'biphenyl route'⁵⁻⁷ can only be achieved with highly activated (electron-rich) precursors and yield only hexasubstituted derivatives; cores with a low degree of substitution (*e.g.* trialkoxytriphenylene) cannot be synthesized by these methods. Thus, triphenylenes having less than six

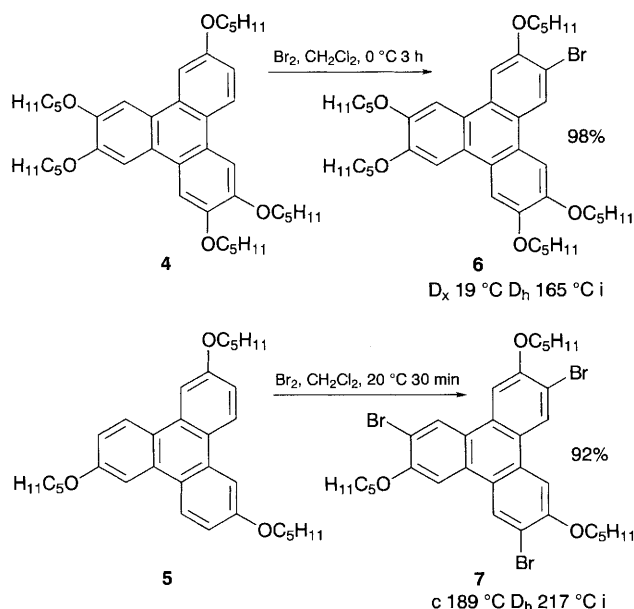
alkoxy groups would be valuable intermediates for linkage of new substituents. To date, such derivatives can only be prepared efficiently by the effective yet complicated 'terphenyl route'.³

Previously, we have shown that all possible isomers of hexasubstituted mono-, di- and tri-hydroxyalkoxytriphenylenes are accessible by simple strategies, often on a large scale.⁶ In an effort to extend the scope of these synthetic procedures and initiate the synthesis of 'mixed tail' systems we have tried to derivatize and substitute the phenolic group(s) on the core. Our first attempt involved the synthesis of triflate **1**† from hydroxyalkoxytriphenylene **2** in the hope that it could be reduced using previously reported methodology.¹¹ Although the reduction was not successful, we were pleased to discover that triflate **1** is mesogenic over a broad temperature range with an unidentified phase occurring below the hexagonal discotic phase.‡ Reduction of the phenolic groups of hydroxyalkoxytriphenylenes **2** and **3** has ultimately been accomplished by activation with a tetrazole unit followed by catalytic hydrogenation,¹² as shown in Scheme 1.

Compounds **4** and **5**§ now possess reactive sites capable of derivatization *via* classical aromatic substitution chemistry. In our first example, the bromination of **4** and **5** with Br_2 in



Scheme 1 Reduction of hydroxypentyloxytriphenylenes



Scheme 2 Bromination of alkoxytriphenylenes

methylene chloride affords the mesogenic bromoalkoxytriphenylenes **6** and **7** in 98 and 92% yields, respectively (Scheme 2).

Compound **6** exhibits a very broad range of mesogenicity and shows a transition from the hexagonal discotic phase into an unidentified phase just below room temperature. X-Ray investigations are now under way in order to identify this phase. In contrast to compound **6**, the tribromotriphenylene **7** possesses a much narrower hexagonal discotic phase but represents the first discotic triphenylene having only three alkoxy tails. The high melting point is probably a result of the symmetry of the molecule and the low number of alkoxy tails that induce disorder in the crystalline state. The fact that it has any mesogenicity at all is noteworthy given the steric bulk of the bromine atoms near the core.

As substrates capable of undergoing nucleophilic aromatic substitution, as well as metal-mediated coupling reactions (*e.g.* Castro–Stevens and Heck-type reactions), these new bromoalkoxytriphenylenes serve as versatile precursors to new mixed tail discotic systems.

The trialkoxytriphenylene **5** cannot be prepared directly by trimerization of alkoxybenzene or *via* the 'biphenyl route'. The pentaalkoxy derivative **4** could be made *via* the 'biphenyl route' but in very poor yield. Thus, our new findings greatly expand the synthetic utility of the previously reported hydroxyalkoxytriphenylenes. Efforts are now under way to synthesize mixed alkoxy/alkylthio triphenylene discotics as well as the various regioisomers of the haloalkoxy systems.

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Footnotes

† Selected data for **1**: $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 0.96 (t, J 6.83 Hz, 15H), 1.55 (m, 20H), 1.94 (m, 10H), 4.21 (m, 10H), 7.32 (s, 1H), 7.69 (s, 1H), 7.78 (s, 1H), 7.80 (s, 1H), 7.86 (s, 1H), 8.18 (s, 1H); MS (FD+) m/z 807.0 (M+); Satisfactory elemental analysis obtained.

‡ The transition seen at 54 °C (melting) was seen only in the first heating run and the compound remains in a super-cooled discotic mesophase for several days at room temperature. The transition at 85 °C was seen in all heating and cooling runs.

§ Selected data for **4**: mp 86 °C; $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 0.95 (t, J 6.91 Hz, 15H), 1.53 (m, 20H), 1.93 (m, 10H), 4.21 (m, 10H), 7.21 (dd, J 2.42, 9.17 Hz, 1H), 7.80 (s, 2H), 7.84 (d, J 2.42 Hz, 1H), 7.90 (s, 2H), 8.36 (d, J 9.17 Hz, 1H); MS (EI+) m/z 658.4 (M+). For **5**: mp 95 °C; $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 0.95 (t, J 7.09 Hz, 9H), 1.53 (m, 12H), 1.88 (m, 6H), 4.16 (t, J 6.52 Hz, 6H), 7.16 (dd, J 8.98, 2.39 Hz, 3H), 7.91 (d, J 2.39 Hz, 3H), 8.42 (d, J 8.98 Hz, 3H); MS (EI+) m/z 486.4 (M+), 276.1, 246.9, 43.4. Satisfactory elemental analyses were obtained.

¶ Selected data for **6**: $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 0.98 (t, J 6.45 Hz, 15H), 1.51 (m, 20H), 1.95 (m, 10H), 4.22 (m, 10H), 7.74 (s, 1H), 7.76 (s, 3H), 7.81 (s, 1H), 8.54 (s, 1H); MS (FD+) m/z 736.3 (M+). For **7**: $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 0.99 (t, J 7.03 Hz, 9H), 1.55 (m, 12H), 1.98 (m, 6H), 4.21 (t, J 6.45 Hz, 6H), 7.52 (s, 3H), 8.34 (s, 3H); MS (FD+) m/z 719.9 (M+). Satisfactory elemental analyses were obtained.

|| In ref. 7 the authors report the synthesis of 2,3,6,7-tetrahydroxy-10-methoxytriphenylene in 5% yield.

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