Synthesis of a New Liquid Crystal with a 4,4′-Biphenanthryl Core

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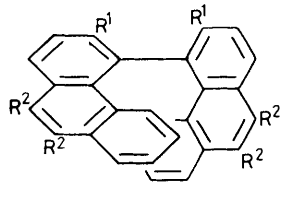
4,4′-Biphenanthryl carrying six long tails forms a stable thermotropic liquid crystalline mesophase.

The control of liquid crystalline molecular alignment including that in the discotic mesophase is being actively investigated for elaboration of molecular materials.[1] Of particular interest are chiral mesogens such as those giving phases of the cholesteric or chiral smectic type,[2] from the viewpoint of electric stimulus-response. In the course of investigation of new functional mesogens,[3] we found that the 4,4′-biphenanthryl derivative (**1**), which carries six long tails, forms a stable liquid crystalline mesophase. This is the first example of a 'pseudo'-discotic mesogen, the core of which may potentially possess molecular asymmetry, opening a route to a new class of chiral liquid crystal other than the cholesteric and chiral smectic types.

The mesogen (**1**) was prepared as follows (Scheme 1): (±)-3,3′-dihydroxy-4,4′-biphenanthryl (**2**) was obtained through the oxidative coupling of 3-phenanthrol[4] as previously reported.[5] Treatment of (**2**) with dodecyl bromide in the presence of Bu^{t}OK in tetrahydrofuran (THF) gave 3,3′-bis(dodecyloxy)-(±)-4,4′-biphenanthryl (**3**) in 85% yield. Oxidation of (**3**) to the corresponding bis-*o*-quinone, 3,3′-bis(dodecyloxy)-(±)-4,4′-biphenanthryl-9,9′,10,10′-tetraone (**4**), was successfully carried out using CrO_3 in acetic acid [37% yield; *m/z* 783 (M^+); ^{1}H n.m.r. ($CDCl_3$) δ 0.7—1.4(46H), 3.6—3.9(4H), 6.8—8.4(12H); $\nu_{C=O}$ (KBr) 1660 cm^{-1}. The bis-*o*-quinone (**4**) was readily reduced with $Na_2S_2O_4$ to afford 3,3′-bis(dodecyloxy)-9,9′,10,10′-tetrahydroxy-(±)-4,4′-biphenanthryl, (**5**). Compound (**5**) was, however, re-oxidized by air very readily to (**4**), therefore the reduced (**5**) (without isolation) was condensed with dodecanoic acid using dicyclohexylcarbodiimide (DCC) in THF. Silica gel chromatographic purification provided the desired compound, (**1**), the spectral (i.r. and n.m.r.) data for which were in agreement with the assigned structure [see Figure 1 for the 400 MHz ^{1}H n.m.r. spectrum of (**1**)].

The liquid crystalline properties of (**1**) were studied by differential scanning calorimetry (d.s.c.) and polarized light microscopy. A quite stable thermotropic mesophase was observed above 64 °C (at this temperature an endothermic d.s.c. peak appeared). Up to 200 °C no other d.s.c. peak appeared, but the birefringent texture for the turbid, viscous mesophase was found to be stable under the polarized light microscope. At *ca.* 200–260 °C, however, a slight brown

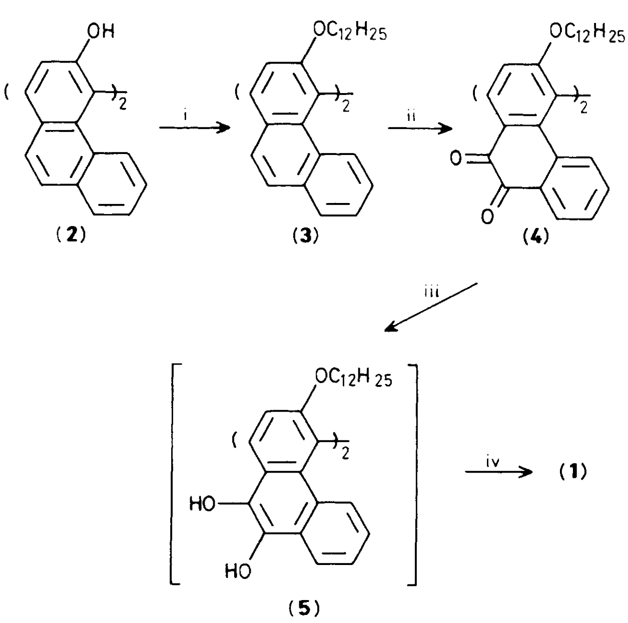


(±)-(**1**)

$R^1 = OC_{12}H_{25}$

$R^2 = OCOC_{11}H_{23}$

[Only the (+) isomer structure is shown in this figure for simplicity.]



Scheme 1. *Reagents*: i, $C_{12}H_{25}Br$, Bu^{t}OK; ii, CrO_3, AcOH; iii, $Na_2S_2O_4$, aq. THF; iv, $C_{11}H_{23}CO_2H$, DCC–THF.

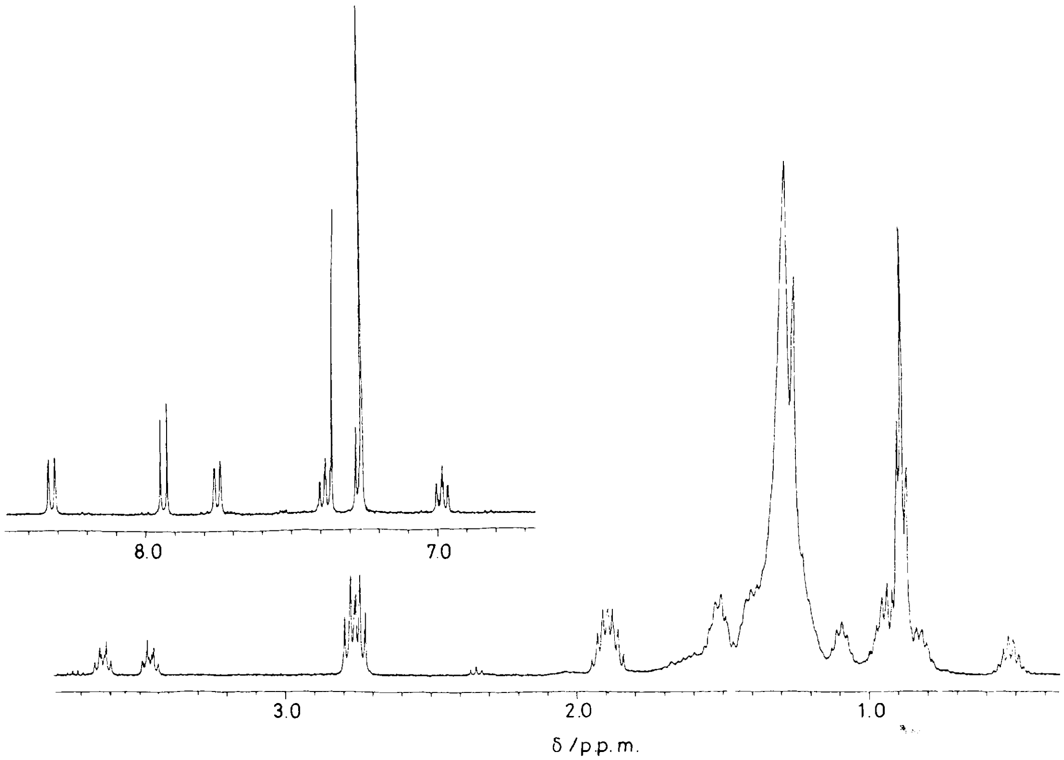


Figure 1. The 400 MHz ^{1}H n.m.r. spectrum of mesogen (**1**) in $CDCl_3$.

colouration of the mesogen began, suggesting a thermal decomposition, which continued up to *ca.* 300 °C. We are currently attempting to determine the molecular organization and alignment of the mesophase including *X*-ray studies.

There has been no previous report of a mesogen having a 'pseudo'-discotic core with a skewed structure like that of (**1**). The synthetic route described herein promises to provide a method for preparing new, chiral biphenanthryl-based mesogens, since the chiral resolution of biphenanthryl has been achieved by Yamamoto.[5]

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