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The effect of molecular broadening on liquid crystal behaviour in oligoaryl mesogens

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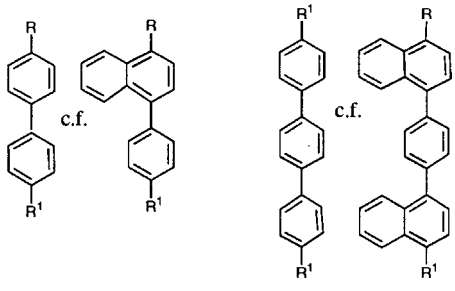
The synthesis and phase behaviour of a series of broadened oligoaryls, in which replacement of one or two of the phenyl groups of bi- and ter-phenyl mesogens has been made by 1,4-substituted naphthalene, is reported. The novel materials, which are not mesogenic, can be compared with the liquid crystalline 2,6-substituted isomers.

1. Introduction

Substituted bi- and ter-phenyls are in many ways archetypal calamitic mesogens. They have been widely studied and exploited in electro-optic display applications. These compounds present a roughly cylindrical profile which fits in well with the supramolecular organization of uniaxial liquid crystal phases. This paper describes a first series of experiments aimed at further elucidating the effects of molecular broadening on mesophase behaviour in oligoaryl mesogens. Such broadened, polyaromatic materials could be highly birefringent and offer the potential of giving or inducing biaxial mesophases with application in fast switching devices. Our study has involved synthesizing analogues of the oligoaryl mesogens in which replacement of one or two of the benzene rings is made by naphthalene units. The final compounds thus present a non-cylindrical molecular profile but retain a degree of flexibility. In many ways the materials represent a contrast (intermediate) to both calamitic and discotic mesogens.



2. Synthesis

The novel oligoaryls were all synthesized following broadly similar strategies. 1-Naphthol was alkylated with *n*-hexyl bromide. Bromination using NBS in acetonitrile [1] gave 4-bromo-1-hexyloxynapthalene. Palladium-catalysed Suzuki coupling [2] of the bromide with 4-hexyloxyphenylboronic acid **3** yielded phenylnapthalene derivative **2** (scheme 1). 1-Bromo-4-hexyloxynaphthalene was converted to the corresponding Grignard reagent (by treatment with magnesium) and reacted with trimethyl borate to give, after aqueous work-up, 4-hexyloxynaphth-1-ylboronic acid **4**. Suzuki coupling of **4** with 4-iodobenzontrile gave cyanobiaryl **5** (scheme 1).

Alkyl derivatives were similarly prepared (scheme 2). 1-Hexylnaphthalene was synthesized by nickel-catalysed cross-coupling [3] of 1-bromonaphthalene with *n*-hexylmagnesium bromide. Bromination to give **6** was effected with either molecular bromine in dichloromethane or, more conveniently, using NBS in acetonitrile [4]. Palladium-catalysed Suzuki coupling with 4-hexyloxyphenylboronic acid yielded biaryl **7**. Naphthylboronic acid **8** was prepared from **6** via the Grignard reagent in a procedure analogous to that described for **4**. Subsequent Suzuki coupling with 4-iodobenzonitrile gave cyanobiaryl **9**. Hydrolysis of **9** was achieved with NaOH by boiling in aqueous ethanol to give the carboxylic acid **10**. Symmetrical terphenyl derivative **11** was synthesized by direct Suzuki coupling of naphthylboronic acid **8** with 1,4-diiodobenzene.

3. Results and discussion

The mesophase behaviour of the novel oligoaryl derivatives is compared with reported data for related systems in the table.

A number of features emerge. Alkylalkoxybiaryl **7**, in which one phenyl ring is replaced with 1,4-substituted naphthalene, shows a low melting point of 29°C which probably reflects the difficulty in packing experienced by the broadened molecule. Binary mixture studies with

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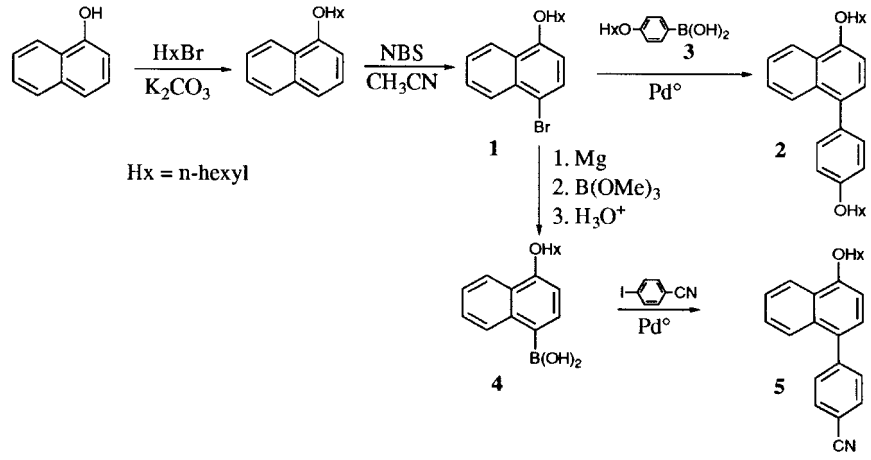
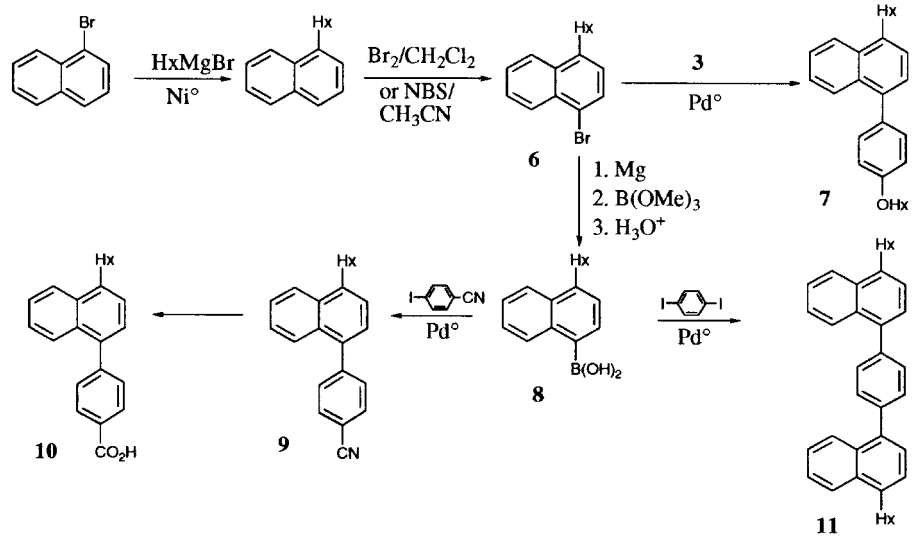
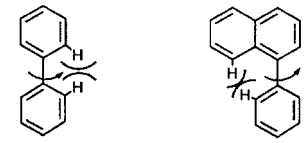


Scheme 1. Synthesis of alkoxy-naphthyl biaryls.



Scheme 2. Synthesis of alkyl-naphthyl bi- and ter-aryls.

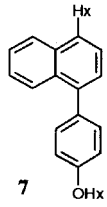
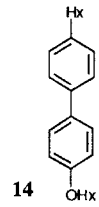
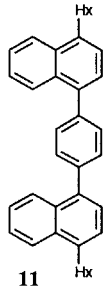
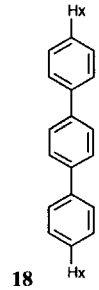
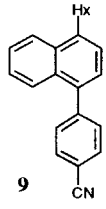
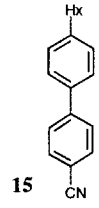
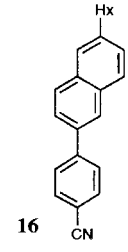
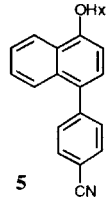
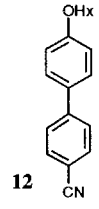
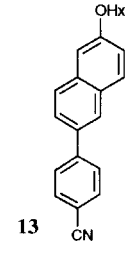
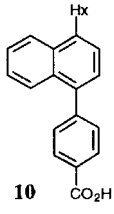
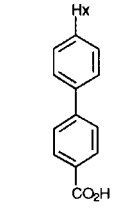
K15 (see the figure) indicate a virtual T_{N-I} of − 45°C for **7** whereas the parent biphenyl is liquid crystalline up to 68°C. Cyanobiaryls **9** and **5** show relatively high melting points. The virtual clearing point of **5** (− 5°C) is again substantially lower than the nematic clearing temperature for the related biphenyl **12** (T_{N-I} 76.5°C) [7]. The most informative comparison is between isomeric cyanobiaryls based on 1,4- and 2,6-substitution of the naphthalene. 1,4-Substitution, as in **5**, leads to a compound with a (virtual) clearing temperature substantially below the clearing point of the liquid crystalline 2,6-substituted isomer, demonstrating clearly the detrimental effect of molecular broadening on mesophase stability. As such, the results support earlier studies on naphthalenes [11] and lateral substitution in bi- and ter-phenyl mesogens [12]. A number of factors contribute to the reduction in mesophase stability in these broadened systems. In addition to disrupting the general rod-like molecular profile, the 1,4-substitution pattern influences the preferred conformation of the molecules. In both the crystalline solid and solution†, compound **2** adopts a (preferred) conformation in which the naphthalene and benzene rings are approximately orthogonal. In the fluid state the entropy of such systems is also severely affected because of restricted rotation around the aryl–aryl bond (the energy barrier is approximately 1.6 kcal mol^{-1} in 2-phenylnaphthalene [13] compared with 12.4 kcal mol^{-1} in 1-phenylnaphthalene [14]).



severe rotation barrier

† Determined by X-ray crystallography (twist angle = 57.9°) and NMR respectively.

Table. Phase behaviour of broadened and cylindrical oligoaryls. Transition temperatures in °C.

Oligoaryl	Related mesogens	
 **7** Cr 29 I	 **14** Cr 9 Sm 68 I [5]	
 **11** Cr 99 I	 **18** Cr 193 Sm 218 I [6]	
 **9** Cr 96 I	 **15** Cr 13·5 N 28 I [7]	 **16** Cr 59 N 116 I [8]
 **5** Cr 95 I	 **12** Cr 58 N 76·5 I [7]	 **13** Cr 100 N 148 I [9]
 **10** Cr 219 I	 Cr 165 Sm 244 N 264 I [10]	

4. Conclusions

We have synthesized a series of oligoaryl derivatives in which one or two benzene units of the archetypal ter- and bi-phenyl mesogens have been replaced by a 1,4-naphthyl group. As such, the compounds are isomeric with known 2,6-naphthalenes. These latter compounds (and the oligophenyls) are essentially cylindrical and give liquid crystal phases. The new materials

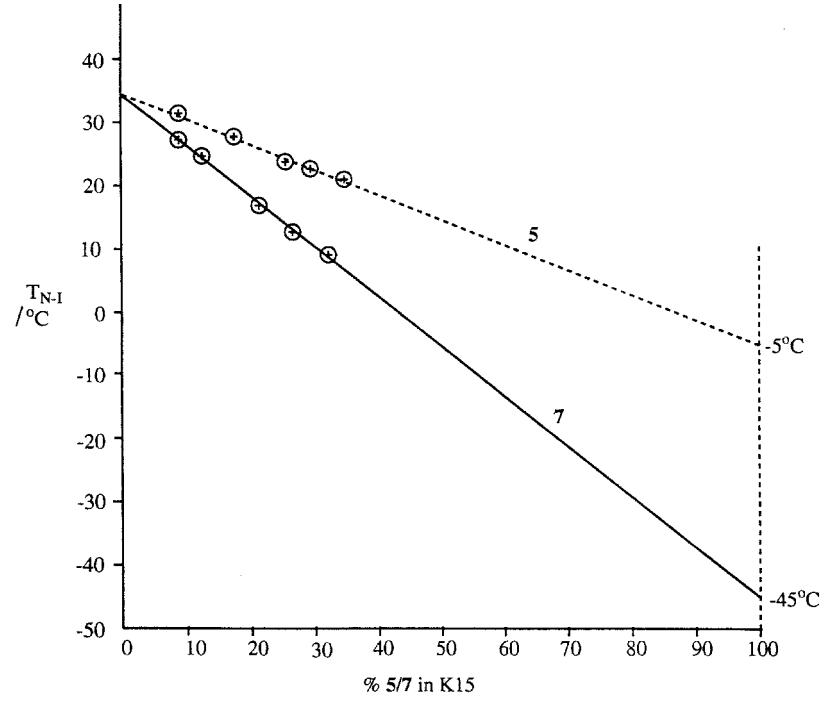


Figure. Determination of virtual T_{N-I} values for **5** and **7**.

discussed in this paper present a broadened molecular profile and our studies indicate that this modification disfavours mesophase formation (as is the case for simple lateral substituents and different substitution patterns in simpler naphthalenes) resulting in direct transition from crystal to isotropic liquid.

5. Experimental

^{1}H NMR spectra were measured at 60 MHz on a JEOL JNM-PMX 60, at 270 MHz on a JEOL EX 270 and at 300 MHz on a Varian Gemini 2000. Routine mass spectra (EI) were performed on a Kratos MS 25 mass spectrometer. Melting points/transition temperatures were obtained using an Olympus BH-2 polarizing microscope in conjunction with a Linkam TMS 92 thermal analyser with a Linkam THM 600 cell. Purity of products (> 99%) was confirmed by elemental analysis and/or high-field NMR spectroscopy.

5.1. *1-Hexyloxynaphthalene*

1-Naphthol (50 g, 347 mmol), 1-bromohexane (68.7 g, 416 mmol) and potassium carbonate (57.5 g, 416 mmol) were stirred in ethanol (250 ml) heated under reflux for 5 h. The ethanol was removed *in vacue* and water added. The organic material was extracted with dichloromethane and the solvent was removed *in vacuo*. The residue was distilled (190°C/15 mm Hg) to give 1-hexyloxynaphthalene as a pale yellow oil (58.2 g, 74%). ^{1}H NMR δ_H (60 MHz, $CDCl_3$): 8.2 (1H, m), 7.7 (1H, m), 7.4 (3H, m), 6.7 (1H, m), 4.0 (2H, t, $J = 6$ Hz, OCH_2), 1.4–0.9 (11H, m). EIMS *m/z*: 228 (M^+, 15%), 144 (100%), 116 (12%).

5.2. *1-Bromo-4-hexyloxynaphthalene (**1**)*

To a solution of 1-hexyloxynaphthalene (10 g, 43.8 mmol) in acetonitrile (150 ml) was added *N*-bromosuccinimide (8.58 g, 48.2 mmol). The mixture was stirred at room temperature for 16 h and then the acetonitrile was removed *in vacuo*. An aqueous solution of sodium hydrogen carbonate was added and the mixture was shaken with dichloromethane. The product was precipitated by addition of ethanol to the organic extract, filtered off and recrystallized from ethanol to give **1** as white crystals (11.1 g, 82%), m.p. 41°C. ^{1}H NMR δ_H (60 MHz, $CDCl_3$) 8.4–7.5 (5H, m), 6.6 (1H, d, $J = 9.6$ Hz), 4.1 (2H, t, $J = 7.2$ Hz, 1.5–0.9 (11H, m). EIMS *m/z*: 308 (M^+, ^{81}Br, 27%), 306 (M^+, ^{79}Br, 28%), 224 (98%), 222 (100%), 115 (24%).

5.3. *1-Hexyloxy-4-(4-hexyloxyphenyl)naphthalene **2***

A solution of 1-bromo-4-hexyloxynaphthalene (2 g, 6.5 mmol) in dimethoxyethane (DME) (40 ml) was degassed with nitrogen. Palladium chloride (0.02 g, 0.1 mmol) and triphenyl phosphine (0.06 g, 0.2 mmol) were added and the solution degassed for a further 10 min. Aqueous sodium carbonate solution (30 ml) and a solution of 4-hexyloxyphenylboronic acid (2.15 g, 9.75 mmol) in DME (10 ml) were added and the mixture heated under

reflux for 24 h under nitrogen. After cooling, the product was extracted with dichloromethane, the solvents were evaporated and the residue was purified by column chromatography (silica gel, dichloromethane/petroleum ether 50 : 50) and recrystallization from dichloromethane/ethanol to give **2** as colourless crystals (0.8 g, 30%), m.p. 44°C. ^{1}H NMR δ_H (270 MHz, $CDCl_3$) 8.38 (1H, m), 7.88 (1H, m), 7.48–7.34 (4H, m), 7.26 (1H, d, $J = 8$ Hz), 6.98 (2H, m), 6.80 (1H, d, $J = 8$ Hz), 4.12 (2H, t, $J = 6.5$ Hz), 3.99 (2H, t, $J = 6.6$ Hz), 1.90 (2H, m), 1.80 (2H, m), 1.6–1.25 (12H, m), 0.92 (6H, m). Found C 83.11, H 9.06; $C_{28}H_{36}O_2$ requires C 83.12, H 8.97%.

5.4. *4-Hexyloxynaphth-1-ylboronic acid* **4**

Magnesium turnings (0.58 g, 24 mmol) and a crystal of iodine were stirred in dry ether under nitrogen. 1-Bromo-4-hexyloxynaphthalene (7 g, 22 mmol) was added at such a rate as to maintain gentle boiling. Reflux conditions were maintained for a further 2 h before cooling the solution to room temperature and adding trimethyl borate (2.47 g, 24 mmol). The mixture was stirred for 24 h, quenched with dilute hydrochloric acid and shaken with ether. The combined ether extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The residue was washed with cold dichloromethane to leave crude **4** (2.6 g, 48%). ^{1}H NMR δ_H (60 MHz, CD_3OD) 8.3 (1H, m), 7.9–7.3 (4H, m), 6.8 (1H, d, $J = 8$ Hz), 4.8 (brs), 4.1 (2H, t, $J = 6$ Hz), 2.0–0.9 (11H, m).

5.5. *1-(4-Cyanophenyl)-4-hexyloxynaphthalene* **5**

Palladium acetate (97 mg, 0.4 mmol) and triphenylphospine (220 mg, 9 mmol) were added to a stirred solution of 4-iodobenzonitrile (1 g, 4.3 mmol) in DME (20 ml). The mixture was degassed with nitrogen for 15 min before addition of sodium carbonate solution (10 ml) and 4-hexyloxynaphth-1-ylboronic acid (1 g, 4.3 mmol) in DME (10 ml). The mixture was heated under reflux for 3 h under nitrogen, cooled and shaken (3 times) with ether. The organic solvents were removed *in vacuo* and the residue precipitated from dichloromethane/methanol. After filtering, the crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether 50 : 50) and recrystallization from ethanol to give 1-(4-cyanophenyl)-4-hexyloxynaphthalene **5** as colourless plates (0.56 g, 39%), m.p 95°C. ^{1}H NMR δ_H (270 MHz, $CDCl_3$) 8.40 (1H, d, $J = 7.8$ Hz), 7.76 (2H, d, $J = 8.1$ Hz), 7.60 (2H, d, $J = 8.1$ Hz), 7.56–7.26 (4H, m), 6.88 (1H, d, $J = 8.1$ Hz), 4.19 (2H, t, $J = 6.3$ Hz), 1.91 (2H, m), 1.66–1.29 (6H, m), 0.90 (3H, t, $J = 6.9$ Hz). EIMS *m/z*: 329 (M^+, 40%), 245 (100%). Found C 83.58, H 7.02, N 4.31; $C_{23}H_{23}NO$ requires C 83.85, H 7.04, N 4.25%.

5.6. *1-Hexylnaphthalene*

The Grignard reagent was prepared from 1-bromohexane (36.7 g, 223 mmol) and magnesium turnings (6 g, 247 mmol) in ether (200 ml). This was added over 30 min to a stirred solution of 1-bromonaphthalene (36.86 g, 178 mmol) and (1,2-bis(diphenylphosphino)ethane)-nickel(II) chloride (100 mg) in dry ether (200 ml) at 0°C. The reaction mixture was stirred under argon at reflux for 24 h. The mixture was cooled, quenched with water, separated and shaken with ether. The ether was removed *in vacuo* and the residue distilled under reduced pressure to give 1-hexylnaphthalene as a pale yellow oil (34.75 g, 92%), b.p. 165°C/15 mm Hg. ^{1}H NMR δ_H (60 MHz, $CDCl_3$) 8.2–7.3 (7H, m), 3.1 (2H, t, $J = 8$ Hz), 1.9–0.9 (11H, m).

5.7. *1-Bromo-4-hexylnaphthalene* **6**

N-Bromosuccinimide (32.11 g, 180 mmol) was added to a solution of 1-hexylnaphthalene (34.75 g, 164 mmol) in acetonitrile (450 ml). The mixture was stirred at room temperature for 24 h (dark) causing separation of a dense oil. Water was added and the mixture shaken (3 times) with dichloromethane. The organic solvents were removed *in vacuo* and the residue was distilled under reduced pressure to give 1-bromo-4-hexylnaphthalene as a yellow oil (39.38 g, 83%), b.p. 200°C/15 mm Hg. ^{1}H NMR δ_H (60 MHz, $CDCl_3$). 8.4 (1H, m), 7.9 (1H, m), 7.7–7.3 (3H, m), 6.9 (1H, d, $J = 8$ Hz), 2.9 (2H, t, $J = 7$ Hz), 1.7–0.8 (11H, m).

5.8. *1-Hexyl-4-(4-hexyloxyphenyl)naphthalene* **7**

A solution of 1-bromo-4-hexylnaphthalene (0.87 g, 3 mmol) in DME (14 ml) was degassed with nitrogen. Palladium acetate (0.1 g, 0.45 mmol) and triphenylphosphine (0.237 g, 0.9 mmol) were added and the solution degassed for a further 10 min. Aqueous sodium carbonate solution (0.047 g in 10 ml) and a solution of 4-hexyloxyphenylboronic acid (1 g, 4.5 mmol) in DME (10 ml) were added and the mixture stirred at reflux under nitrogen for 9 h. Palladium acetate (0.1 g, 0.45 mmol) and triphenylphosphine (0.237 g, 0.9 mmol) were added and the mixture was heated at reflux for a further 7 h. After cooling, the mixture was shaken with dichloromethane, the solvents were evaporated and the residue was purified by column chromatography (silica gel, petroleum ether then petroleum ether/ethyl acetate 99 : 1) and crystallized from aqueous ethanol to give **7** as colourless crystals (0.45 g, 39%), m.p. 29°C. ^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.10 (1H, d, $J = 8.4$ Hz), 8.04 (1H, d, $J = 8.5$ Hz), 7.53–7.25 (6H, m), 7.01 (2H, d, $J = 6.8$ Hz), 4.04 (2H, t, $J = 6.6$ Hz), 3.10 (2H, t, $J = 7$ Hz), 1.86–0.90 (22H, m). EIMS *m/z*: 388 (M^+, 33%), 254 (36%), 233 (11%), 171 (13%), 170 (100%). Found C 84.54, H 9.37; $C_{28}H_{36}O.0.5H_2O$ requires C 84.59, H 9.38%.

5.9. *4-Hexylnaphth-1-ylboronic acid* **8**

1-Bromo-4-hexylnaphthalene (20 g, 68.7 mmol) was converted to the corresponding Grignard reagent by reaction with magnesium turnings (1.81 g, 78 mmol) in dry ether (200 ml). A solution of tri-isopropyl borate (25.84 g, 137 mmol) in dry ether (200 ml) was added (room temperature) and the mixture stirred under nitrogen for 48 h at room temperature and 7 h at reflux. The solution was cooled and quenched with 10% hydrochloric acid. After stirring for 2 h, the mixture was shaken with ether. The combined organic solutions were concentrated and the residue was washed with petroleum ether to give colourless crystals of **8** which were used in subsequent steps without further purification.

5.10. *1-(4-Cyanophenyl)-4-hexylnaphthalene* **9**

A solution of 1-cyano-4-iodobenzene (0.45 g, 1.95 mmol) in DME (15 ml) was degassed with nitrogen. Palladium acetate (0.1 g, 0.45 mmol) and triphenylphosphine (0.24 g, 0.9 mmol) were added and the solution degassed for a further 15 min. Aqueous sodium carbonate solution (0.047 g in 10 ml) and a solution of 4-hexylnaphth-1-ylboronic acid (0.3 g, 1.17 mmol) in DME (10 ml) were added and the mixture was stirred at reflux under nitrogen for 6 h. DME was removed *in vacuo* and the remaining mixture was treated with dichloromethane. The solvent was evaporated and the residue purified by column chromatography (silica gel, dichloromethane/petroleum ether) and crystallized from dichloromethane/ethanol to give **9** as colourless crystals (180 mg, 49%), m.p 96°C. ^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.13 (1H, d, $J = 8.5$ Hz), 7.8–7.43 (9H, m), 3.12 (2H, t, $J = 7.5$ Hz), 1.76 (2H, m), 1.5–1.3 (6H, m), 0.91 (3H, t, $J = 6.5$ Hz). EIMS *m/z*: 313 (M^+, 100%), 242 (98%). Acc. mass (EI) 313.1816 (calculated for $C_{23}H_{23}N = 313.1830$).

5.11. *1-(4-Carboxyphenyl)-4-hexylnaphthalene* **10**

1-(4-Cyanophenyl)-4-hexylnaphthalene (80 mg, 0.25 mmol) was dissolved in a mixture of ethanol (10 ml) and water (10 ml). Sodium hydroxide (0.5 g) was added and the mixture stirred at reflux for 3 days. After cooling, the mixture was acidified with dilute hydrochloric acid and shaken with dichloromethane. The solvents were removed *in vacuo* and the residue was recrystallized from ethanol to give **10** as colourless crystals (75 mg, 89%), m.p 219°C. ^{1}H NMR δ_H (270 MHz, $CDCl_3$) 8.25 (2H, d, $J = 8.2$ Hz), 8.13 (1H, d, $J = 8.6$ Hz), 7.87 (1H, d, $J = 8.6$ Hz), 7.60 (2H, d, $J = 8.2$ Hz), 7.50–7.36 (4H, m), 3.12 (2H, t, $J = 7.6$ Hz), 1.75 (2H, m), 1.5–1.3 (6H, m), 0.94 (3H, t, $J = 6.9$ Hz). Acc. mass (EI) 332.1776, (calculated for $C_{23}H_{24}O_2 = 332.1776$).

5.12. *1,4-Bis-(4-hexylnaphth-1-yl)benzene* **11**

A solution of 1,4-di-iodobenzene (0.59 g, 1.77 mmol) in DME (8 ml) was degassed with nitrogen. Palladium acetate (0.1 g, 0.45 mmol) and triphenylphosphine (0.24 g, 0.9 mmol) were added and the solution was degassed for a further 15 min. Aqueous sodium carbonate solution (0.047 g in 10 ml) and a solution of 4-hexylnaphth-1-ylboronic acid (1 g, 3.91 mmol) in DME (10 ml) were added and the mixture was stirred at reflux under nitrogen for 16 h. DME was removed *in vacuo*, water added and the mixture shaken with dichloromethane. The solvent was evaporated and the residue purified by column chromatography (silica gel, dichloromethane/petroleum ether) and recrystallized from dichloromethane/petroleum ether to give **11** as colourless crystals (0.35 g, 39%), m.p 99°C. ^{1}H NMR δ_H (300 MHz, $CDCl_3$) 8.18–8.08 (4H, m), 7.60 (4H, s), 7.59–7.42 (8H, m), 3.14 (4H, t, $J = 7.8$ Hz), 1.83 (4H, m), 1.5–1.3 (12H, m), 0.93 (6H, t, $J = 6.9$ Hz). EIMS *m/z*: 498 (M^+, 21%), 422 (49%). Found C 90.16, H 8.32; $C_{38}H_{42}.0.5H_2O$ requires C 89.89, H 8.53%.

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