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# **The Self-ordering Properties of Novel Phthalocyanines with Out-of-plane Alkyl Substituents**

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**2,2-didodecyl-1-indanone:** To a mixture of 1-bromododecane (28 g, 113 mmol), potassium *t*-butoxide (12 g, 113 mmol) in toluene (50 ml) was added dropwise a solution of 1-indanone (5 g, 38 mmol) in toluene (25 ml). The reaction was heated at 80 °C for 4 h. On cooling, aq. HCl (1M, 200 ml) was added and the mixture extracted with diethyl ether (5 x 25 ml). The combined organic phases were dried (MgSO<sub>4</sub>), filtered and the solvent and excess 1-bromododecane removed under reduced pressure to give the product as a viscose oil which was used without further purification, (5.30 g, 30%);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.3-1.45 (m, 40H), 1.65 (m, 4H), 3.03 (s, 2H), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 486 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

The following compounds were prepared from the appropriate 1-bromoalkane using a similar procedure.

**2,2-dihexyl-1-indanone:** 91% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.30-1.55 (m, 16H), 1.65 (m, 4H), 3.03 (s, 2H); 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 318 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

**2,2-diheptyl-1-indanone:** 92% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.30-1.55 (m, 20H), 1.65 (m, 4H), 3.03 (s, 2H), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 346 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

**2,2-dioctyl-1-indanone:** 80% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.30-1.55 (m, 24H), 1.65 (m, 4H), 3.03 (s, 2H), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 364 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

**2,2-dinonyl-1-indanone:** 91% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.30-1.55 (m, 28H), 1.65 (m, 4H), 3.03 (s, 2H), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 402 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

**2,2-didodecyl-1-indanone:** 80% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.30-1.55 (m, 32H), 1.65 (m, 4H), 3.03 (s, 2H), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 430 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

**2,2-diundecyl-1-indanone:** 92% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.30-1.55 (m, 36H), 1.65 (m, 4H), 3.03 (s, 2H), 7.40 (t, 1H), 7.47 (d, 1H), 7.62 (t, 1H), 7.76 (d, 1H);  $m/z$  (CI) 458 (M<sup>+</sup> NH<sub>4</sub><sup>+</sup>).

**2,2-didodecylindane:** A solution of 2,2-didodecyl-1-indanone (7.92 g, 17 mmol) and triethylsilane (5.2 ml, 36 mmol) in TFA (30 ml) was heated at 80 °C for 48 h with the addition of 4 further portions (0.5 ml) of triethylsilane during this period. On completion of the reaction, as monitored by thin layer chromatography (hexane), the reaction mixture was added to saturated aq. NaHCO<sub>3</sub> (150 ml) the product extracted with diethyl ether (5 x 25 ml). The combined organic phases were dried (MgSO<sub>4</sub>), filtered and the solvent and byproducts removed under reduced pressure. The residue was passed through a silica column (hexane) and the solvent removed under reduced pressure to give the product as a viscose oil which was used without further purification, (4.49 g, 61%);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 40H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 486 (M<sup>+</sup>).

The following indanes were prepared from the appropriate 2,2-dialkyl-1-indanone using a similar procedure.

**2,2-dihexylindane:** 56% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 16H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 286 (M<sup>+</sup>).

**2,2-diheptylindane:** 28% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 20H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 314 (M<sup>+</sup>).

**2,2-dioctylindane:** 46% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 24H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 346 (M<sup>+</sup>).

**2,2-dinonylindane:** 56% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 28H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 370 (M<sup>+</sup>).

**2,2-didodecylindane:** 55% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 32H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 398 (M<sup>+</sup>).

**2,2-diundecylindane:** 36% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.35 (m, 36H), 1.40 (m, 4H), 2.75 (s, 4H), 7.15-7.20 (m, 4H);  $m/z$  (EI) 426 (M<sup>+</sup>).

**5,6-dibromo-2,2-didodecyl-1-indane:** Bromine (1.14 ml, 19.8 mmol) was added dropwise to a mixture of 2,2-didodecyl-1-indane (4.49 g, 9.88 mmol), iron granules (0.5 g) and iodine (50 mg) in DCM (20 ml), maintained at 0 °C. The mixture was warmed to 25 °C and stirred for 2h. A saturated aq. solution of sodium bisulfite (20 ml) was added and the organic layer extracted with DCM (2 x 20 ml) and the solvent removed under reduced pressure to give the product as a viscous oil which was used without further purification (5.00 g, 83%);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.37 (m, 40H), 1.43 (m, 4H), 2.78 (s, 4H), 7.40 (s, 4H);  $m/z$  (EI) 610 (M<sup>+</sup>), 612 (M<sup>+</sup>+2), 614 (M<sup>+</sup>+4).

The following dibromoindanes were prepared from the appropriate 2,2-dialkylindane using a similar procedure.

**5,6-dibromo-2,2-dihexyl-1-indane:** 84% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 16H), 1.42 (m, 4H), 2.75 (s, 4H), 7.45 (s, 2H);  $m/z$  (EI) 442 (M<sup>+</sup>), 444 (M<sup>+</sup>+2), 446 (M<sup>+</sup>+4).

**5,6-dibromo-2,2-diheptyl-1-indane:** 83% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.35 (m, 20H), 1.40 (m, 4H), 2.75 (s, 4H), 7.45 (s, 2H);  $m/z$  (EI) 470 (M<sup>+</sup>), 472 (M<sup>+</sup>+2), 474 (M<sup>+</sup>+4).

**5,6-dibromo-2,2-dioctyl-1-indane:** 75% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.35 (m, 24H), 1.40 (m, 4H), 2.75 (s, 4H), 7.45 (s, 2H);  $m/z$  (EI) 498 (M<sup>+</sup>), 500 (M<sup>+</sup>+2), 502 (M<sup>+</sup>+4).

**5,6-dibromo-2,2-dinonyl-1-indane:** 84% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.35 (m, 28H), 1.40 (m, 4H), 2.75 (s, 4H), 7.45 (s, 2H);  $m/z$  (EI) 526 (M<sup>+</sup>), 528 (M<sup>+</sup>+2), 530 (M<sup>+</sup>+4).

**5,6-dibromo-2,2-didecyl-1-indane:** 80% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.35 (m, 32H), 1.40 (m, 4H), 2.75 (s, 4H), 7.45 (s, 2H);  $m/z$  (EI) 554 (M<sup>+</sup>), 556 (M<sup>+</sup>+2), 558 (M<sup>+</sup>+4).

**5,6-dibromo-2,2-diundecyl-1-indane:** 67% yield;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.35 (m, 36H), 1.40 (m, 4H), 2.75 (s, 4H), 7.45 (s, 2H);  $m/z$  (EI) 582 (M<sup>+</sup>), 584 (M<sup>+</sup>+2), 586 (M<sup>+</sup>+4).

**5,6-Dicyano-2,2-didodecylindane:** Copper(I) cyanide (2.9 g, 33 mmol) was added to a stirred solution of 5,6-dibromo-2,2-didodecylindane (5.02 g, 8.2 mmol) in dry DMF (150 ml) under nitrogen. The reaction mixture was heated at 150 °C overnight. The reaction mixture was allowed to cool and aqueous ammonia (100 ml) was added. The mixture was stirred for a further 30 minutes. The organic material was extracted into ether (3 x 50 ml) and the combined extracts were washed with water (3 x 50 ml) and dried (MgSO<sub>4</sub>). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: hexane /dichloromethane). On removal of solvent under reduced pressure a viscous oil was obtained which was used without further purification (0.76 g, 18 %),  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.94 (t, 6H), 1.25-1.35 (m, 40H), 1.45 (m, 4H), 2.88 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 504 (M<sup>+</sup>),

The following compounds were prepared from the appropriate 5,6-dibromo-2,2-dialkylindane using a similar procedure.

**5,6-Dicyano-2,2-dihexylindane:** 43% yield;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 16H), 1.45 (m, 4H), 2.87 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 336 (M<sup>+</sup>).

**5,6-Dicyano-2,2-diheptylindane:** 98% yield;  $\mathbf{u}$  (KBr)/ $\text{cm}^{-1}$  2220 (CN);  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 20H), 1.45 (m, 4H), 2.87 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 364 ( $\text{M}^+$ ).

**5,6-Dicyano-2,2-dioctylindane:** 74% yield;  $\mathbf{u}$  (KBr)/ $\text{cm}^{-1}$  2220 (CN);  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 24H), 1.45 (m, 4H), 2.87 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 392 ( $\text{M}^+$ ).

**5,6-Dicyano-2,2-dinonylindane:** 39% yield;  $\mathbf{u}$  (KBr)/ $\text{cm}^{-1}$  2220 (CN);  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 28H), 1.45 (m, 4H), 2.87 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 420 ( $\text{M}^+$ ).

**5,6-Dicyano-2,2-didecylindane:** 35% yield;  $\mathbf{u}$  (KBr)/ $\text{cm}^{-1}$  2220 (CN);  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 32H), 1.45 (m, 4H), 2.87 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 448 ( $\text{M}^+$ ).

**5,6-Dicyano-2,2-diundecylindane:** 25% yield;  $\mathbf{u}$  (KBr)/ $\text{cm}^{-1}$  2220 (CN);  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 0.92 (t, 6H), 1.25-1.35 (m, 32H), 1.45 (m, 4H), 2.87 (s, 4H), 7.60 (s, 2H);  $m/z$  (EI) 476 ( $\text{M}^+$ ).

**2,2-Diethyl-1,3-benzodioxole:** A mixture of catechol (6.0 g, 54 mmol), 3-pentanone (4.7 g, 54 mmol) and *p*-toluenesulphonic acid (0.05g) in toluene was heated under reflux for 48 hours. Water was removed by azeotropic distillation using a Dean-Stark trap. The reaction mixture was allowed to cool and the solvent removed under reduced pressure. The residue was purified by column chromatography (silica gel, petroleum ether 60-80) to give a colourless oil which was used in the subsequent reaction without further purification (7.0 g, 73 %)  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 1.01 (t, 6H), 1.94 (q, 4H), 6.77 (m, 4H);  $m/z$  (EI) 178, ( $\text{M}^+$ ).

The following compounds were prepared from catechol and the appropriate dialkylketone using a similar procedure.

**2,2-Dipentyl-1,3-benzodioxole:** (66% yield);  $\mathbf{d}_\text{H}$  ( $\text{CDCl}_3$ , 300 MHz, 25 °C) 0.90 (6H, t), 1.25-1.55 (m, 12H), 1.90 (t, 4H), 6.77 (m, 4H);  $m/z$  (EI) 262, ( $\text{M}^+$ ).

**2,2-Dihexyl-1,3-benzodioxole:** (68% yield);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.55 (m, 16H), 1.90 (t, 4H), 6.77 (m, 4H);  $m/z$  (EI) 290, (M<sup>+</sup>).

**2,2-Diheptyl-1,3-benzodioxole:** (75% yield);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.25-1.55 (m, 20H), 1.90 (t, 4H), 6.77 (m, 4H);  $m/z$  (EI) 318, (M<sup>+</sup>).

**2,2-Dioctyl-1,3-benzodioxole:** (87% yield);  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.25-1.55 (m, 24H), 1.90 (t, 4H), 6.75 (m, 4H);  $m/z$  (EI) 346, (M<sup>+</sup>).

**2,2-Dinonyl-1,3-benzodioxole:** (86% yield); m.p. 18-20 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.25-1.55 (m, 28H), 1.90 (t, 4H), 6.75 (m, 4H);  $m/z$  (EI) 374, (M<sup>+</sup>).

**2,2-Didodecyl-1,3-benzodioxole:** (64% yield); m.p. 36-38 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.25-1.55 (m, 32H), 1.90 (t, 4H), 6.75 (m, 4H);  $m/z$  (EI) 402, (M<sup>+</sup>).

**2,2-Diundecyl-1,3-benzodioxole:** (80% yield); m.p. 40-41 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.25-1.55 (m, 36H), 1.90 (t, 4H), 6.75 (m, 4H);  $m/z$  (EI) 430, (M<sup>+</sup>).

**2,2-Didodecyl-1,3-benzodioxole:** (96% yield); m.p. 57-59 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.25-1.55 (m, 40H), 1.90 (t, 4H), 6.75 (m, 4H);  $m/z$  (EI) 458, (M<sup>+</sup>).

### **5,6-Dibromo-2,2-diethyl-1,3-benzodioxole**

*N*-Bromosuccinimide (2.0 g, 11.2 mmol) was added in small portions to a stirred solution of 2,2-diethyl-1,3-benzodioxole (1.0g, 5.6 mmol) in DMF (10 ml). The reaction mixture was stirred at room temperature for 2 days. Water (10 ml) was added and the organic material was extracted into ether (2 x 20 ml) and the combined extracts were washed with water (2 x 20 ml) and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether) and crystallised (petroleum ether) to give colourless crystals (1.6 g,

85%); m.p. 84-86 °C (lit. m.p. 86 °C)<sup>7</sup>;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 1.01 (t, 6H), 1.94 (q, 4H), 6.96 (s, 2H);  $m/z$  (EI) 334 (M<sup>+</sup>), 336 (M<sup>+</sup> + 2), 338 (M<sup>+</sup> + 4).

The following compounds were prepared from the appropriate 2,2-dialkyl-1,3-benzodioxole using a similar procedure.

**5,6-Dibromo-2,2-dipentyl-1,3-benzodioxole:** (85% yield); m.p. 32-33 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.45 (m, 12H), 6.98 (s, 2H);  $m/z$  (EI) 418 (M<sup>+</sup>), 420 (M<sup>+</sup> + 2), 422 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-dihexyl-1,3-benzodioxole:** (80% yield); m.p. 34-36 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.45 (m, 16H), 6.98 (s, 2H);  $m/z$  (EI) 446 (M<sup>+</sup>), 448 (M<sup>+</sup> + 2), 450 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-diheptyl-1,3-benzodioxole:** (88% yield); m.p. 36-38 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.25-1.45 (m, 20H), 6.98 (s, 2H);  $m/z$  (EI) 474 (M<sup>+</sup>), 476 (M<sup>+</sup> + 2), 478 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-dioctyl-1,3-benzodioxole:** (80% yield); m.p. 39-40 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.25-1.45 (m, 24H), 6.98 (s, 2H);  $m/z$  (EI) 502 (M<sup>+</sup>), 504 (M<sup>+</sup> + 2), 506 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-dinonyl-1,3-benzodioxole:** (46% yield); m.p. 41-42 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.25-1.45 (m, 28H), 6.98 (s, 2H);  $m/z$  (EI) 530 (M<sup>+</sup>), 532 (M<sup>+</sup> + 2), 534 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-didecyl-1,3-benzodioxole:** (72% yield); m.p. 43-44 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.25-1.45 (m, 32H), 6.98 (s, 2H);  $m/z$  (EI) 558 (M<sup>+</sup>), 560 (M<sup>+</sup> + 2), 562 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-diundecyl-1,3-benzodioxole:** (90% yield); m.p. 44-46 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.25-1.45 (m, 36H), 6.99 (s, 2H);  $m/z$  (EI) 586 (M<sup>+</sup>), 588 (M<sup>+</sup> + 2), 590 (M<sup>+</sup> + 4).

**5,6-Dibromo-2,2-didodecyl-1,3-benzodioxole:** (68% yield); m.p. 44-46 °C;  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.25-1.45 (m, 40H), 6.99 (s, 2H);  $m/z$  (EI) 614 (M<sup>+</sup>), 616 (M<sup>+</sup> + 2), 618 (M<sup>+</sup> + 4).

**5,6-Dicyano-2,2-diethyl-1,3-benzodioxole:** Copper(I) cyanide (0.95 g, 10.6 mmol) was added to a stirred solution of 5,6-dibromo-2,2-diethyl-1,3-benzodioxole (1.2 g, 3.6 mmol) in dry DMF (15 ml) under nitrogen. The reaction mixture was heated at 140 °C overnight. The reaction mixture was allowed to cool and aqueous ammonia (20 ml) was added. The mixture was stirred for a further 30 minutes. The organic material was extracted into ether (3 x 50 ml) and the combined extracts were washed with water (3 x 50 ml) and dried (MgSO<sub>4</sub>). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: petroleum ether/dichloromethane) followed by crystallisation from petroleum ether to give colourless crystals (0.35 g, 60 %), m.p. 112-114 °C, (Found: C, 68.20; H, 5.41; N, 12.20%. C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> requires C, 68.41; H, 5.31; N, 12.27%);  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 1.02 (t, 6H), 1.97 (q, 4H), 7.08 (s, 2H);  $m/z$  (EI) 228 (M<sup>+</sup>).

The following compounds were prepared from the appropriate 5,6-dibromo-2,2-dialkyl-1,3-benzodioxole using a similar procedure.

**5,6-Dicyano-2,2-dipentyl-1,3-benzodioxole:** 24% yield; m.p. 102-104 °C (hexane); Found: C, 73.10; H, 7.90; N, 9.00%. C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> requires C, 73.05; H, 7.74; N, 8.97%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.22-1.45 (m, 12H), 2.00 (t, 2H), 7.02 (s, 2H);  $m/z$  (EI) 312 (M<sup>+</sup>).

**5,6-Dicyano-2,2-dihexyl-1,3-benzodioxole:** 35% yield; m.p. 92-93 °C (hexane); Found: C, 74.35; H, 8.60; N, 7.42%. C<sub>23</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> requires C, 74.08; H, 8.29; N, 8.23%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $d_H$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.22-1.45 (m, 16H), 2.00 (t, 2H), 7.02 (s, 2H);  $m/z$  (EI) 340 (M<sup>+</sup>).

**5,6-Dicyano-2,2-diheptyl-1,3-benzodioxole:** 29% yield; m.p. 84-86 °C (hexane); (Found: C, 74.15; H, 8.90; N, 8.12%. C<sub>21</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub> requires C, 74.96; H, 8.75; N, 7.60%);  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.88 (t, 6H), 1.22-1.45 (m, 20H), 2.00 (t, 2H), 7.02 (s, 2H);

**5,6-Dicyano-2,2-dioctyl-1,3-benzodioxole:** 31% yield; m.p. 75-77 °C (hexane); Found C, 75.90; H, 9.18; N, 7.12%; C<sub>25</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub> requires C, 75.70; H, 9.16; N, 7.06%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.89 (t, 6H), 1.22-1.45 (m, 24H), 1.95 (t, 4H), 7.05 (s, 2H);  $m/z$  (EI) 396 (M<sup>+</sup>).

**5,6-Dicyano-2,2-dinonyl-1,3-benzodioxole:** 38% yield; m.p. 73-75 °C (hexane); Found C, 76.56; H, 9.64; N, 6.54%; C<sub>27</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub> requires C, 76.37; H, 9.50; N, 6.60%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.22-1.45 (m, 28H), 1.95 (t, 4H), 7.05 (s, 2H);  $m/z$  (EI) 424 (M<sup>+</sup>).

**5,6-Dicyano-2,2-didecyl-1,3-benzodioxole:** 37% yield; m.p. 71-73 °C (hexane); Found C, 77.00; H, 9.91; N, 6.21%; C<sub>29</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub> requires C, 76.92; H, 9.81; N, 6.18%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.22-1.45 (m, 32H), 1.95 (t, 4H), 7.05 (s, 2H);  $m/z$  (EI) 452 (M<sup>+</sup>).

**5,6-Dicyano-2,2-diundecyl-1,3-benzodioxole:** 34% yield; m.p. 70-72 °C (hexane); Found C, 77.41; H, 9.97; N, 5.96%; C<sub>31</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub> requires C, 77.43; H, 10.08; N, 5.82%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.22-1.45 (m, 36H), 1.95 (t, 4H), 7.05 (s, 2H);  $m/z$  (EI) 476 (M<sup>+</sup>).

**5,6-Dicyano-2,2-didodecyl-1,3-benzodioxole:** 54% yield; m.p. 68-70 °C (hexane); Found C, 77.60; H, 10.50; N, 5.60%; C<sub>33</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub> requires C, 77.88; H, 10.32; N, 5.50%;  $\nu$  (KBr)/cm<sup>-1</sup> 2220 (CN),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 300 MHz, 25 °C) 0.90 (t, 6H), 1.22-1.45 (m, 40H), 1.95 (t, 4H), 7.05 (s, 2H);  $m/z$  (EI) 508 (M<sup>+</sup>).