Pseudo-Rodlike Molecules with Hockey-Stick-Shaped Mesogen

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Supplementary Information

2. Experimental

2.1. Synthesis of compound 3a

A mixture of compound **1** (0.6 g, 0.93 mmol), 2,3,4-trifluorobenzoic acid (0.16 g, 0.90 mmol), DCC (0.18 g, 0.87 mmol), and DMAP (0.01 g, 0.08 mmol) in DCM (60 ml) was stirred at room temperature for 24 h. The urea formed was removed by filtration, the filtrate was washed with 5% aqueous acetic acid and water, and the solvent was evaporated *in vacuo*. The solid residue was purified by flash column chromatography on silica gel using chloroform as eluent. Yield: 40%; IR (KBr pellet, cm^{-1}): 3075 (aromatic C–H stretch), 2917, 2850 (aliphatic C–H stretch), 1739 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1273, 1193, 1166 (C–O, C–F stretch); ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 8.35–8.25 (t, 4H, Ar–H), 8.2–8.14 (d, 1H, Ar–H), 8.11–8.08 (s, 1H, Ar–H), 7.96–7.89 (m, 1H, Ar–H), 7.66–7.59 (t, 1H, Ar–H), 7.58–7.53 (d, 1H, Ar–H), 7.44–7.34 (m, 4H, Ar–H), 7.18–7.07 (m, 3H, Ar–H), 6.97–6.89 (d, 2H, Ar–H), 3.99–3.91 (t, 2H, Ar–O–CH₂–), 1.83–1.72 (m, 2H, Ar–O–CH₂–CH₂–), 1.5–1.4 (m, 2H, Ar–O–CH₂–CH₂–CH₂–), 1.4–1.18 (m, 18H, –CH₂–), 0.92–0.84 (t, 3H, –CH₃); Anal. Calcd for $\text{C}_{46}\text{H}_{43}\text{F}_3\text{O}_9$: C 69.34, H 5.44; Found: C 69.93, H 5.75.

2.2. Synthesis of compound 3b

Quantities: compound **1** (0.5 g, 0.78 mmol), 3,4,5-trifluorobenzoic acid (0.13 g, 0.73 mmol), DCC (0.15 g, 0.72 mmol), and DMAP (0.01 g, 0.08 mmol). The experimental procedure was as described for the preparation of compound **3a**. Yield: 35%; IR (KBr pellet, cm^{-1}): 3075 (aromatic C–H stretch), 2920, 2850 (aliphatic C–H stretch), 1736 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1273, 1197, 1163 (C–O, C–F stretch); ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 8.34–8.24 (t, 4H, Ar–H), 8.18–8.13 (d, 1H, Ar–H), 8.05–8.03 (s, 1H, Ar–H), 7.91–7.82 (t, 1H, Ar–H), 7.65–7.58 (t, 1H, Ar–H), 7.54–7.48 (d, 1H, Ar–H), 7.42–7.33 (m, 4H, Ar–H), 7.13–7.07 (d, 2H, Ar–H), 6.94–6.88 (d, 2H, Ar–H), 3.97–3.91 (t, 2H, Ar–O–CH₂–), 1.81–1.72 (m, 2H, Ar–O–CH₂–CH₂–), 1.48–1.39 (m, 2H, Ar–O–CH₂–CH₂–CH₂–), 1.37–1.16 (m, 18H, –CH₂–), 0.9–0.83 (t, 3H, –CH₃); Anal. Calcd for $\text{C}_{46}\text{H}_{43}\text{F}_3\text{O}_9$: C 69.34, H 5.44; Found: C 69.93, H 5.75.

2.3. Synthesis of compound 3c

Quantities: compound **1** (0.5 g, 0.78 mmol), 2,4,6-trifluorobenzoic acid (0.13 g, 0.73 mmol), DCC (0.15 g, 0.72 mmol), and DMAP (0.01 g, 0.08 mmol). The experimental procedure was as described for the preparation of compound **3a**. Yield: 42%; IR (KBr pellet, cm^{-1}): 3075 (aromatic C–H stretch), 2920, 2850

(aliphatic C–H stretch), 1745 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1263, 1197, 1166 (C–O, C–F stretch); ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 8.32–8.24 (t, 4H, Ar–H), 8.17–8.12 (d, 1H, Ar–H), 8.09–8.07 (s, 1H, Ar–H), 7.64–7.57 (t, 1H, Ar–H), 7.57–7.52 (d, 1H, Ar–H), 7.44–7.33 (m, 4H, Ar–H), 7.14–7.07 (d, 2H, Ar–H), 6.95–6.88 (d, 2H, Ar–H), 6.85–6.77 (t, 2H, Ar–H), 3.97–3.91 (t, 2H, Ar–O–CH₂–), 1.81–1.72 (m, 2H, Ar–O–CH₂–CH₂–), 1.49–1.39 (m, 2H, Ar–O–CH₂–CH₂–CH₂–), 1.38–1.16 (m, 18H, –CH₂–), 0.9–0.83 (t, 3H, –CH₃); Anal. Calcd for $\text{C}_{46}\text{H}_{43}\text{F}_3\text{O}_9$: C 69.34, H 5.44; Found: C 69.68, H 5.79.

Figure 1. DSC thermograms of compounds (rate = 10 °C/min): lower curve: second heating; middle curve: first heating; upper curve: first cooling.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 2. Cross-polarizing optical micrographs (magnification 200 $\times$). Compound **3a**: (a) on cooling, $T = 168^{\circ}\text{C}$; (b) on heating, $T = 166^{\circ}\text{C}$; (c) after shearing, $T = 166^{\circ}\text{C}$. Compound **3b**: on cooling, (d) $T = 167^{\circ}\text{C}$; (e) $T = 163^{\circ}\text{C}$; (f) on heating, $T = 166^{\circ}\text{C}$.

Figure 3. Sets of 1D WAXD powder patterns of **3b** obtained at various temperatures during heating (a) and cooling (b) at a rate of 2.5 °C/min.