
Poly(1,1-bis(dialkylamino)propan-1,3-diyl)s; conformationally-controlled oligomers bearing electroactive groups

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Electronic Supplementary Material

1,2-Di(2-furyl)-1-ethanone¹

Freshly distilled chlorotrimethylsilane (5.43 g, 50 mmol) was added dropwise to a stirred solution of furoin (3.84 g, 20 mmol) and sodium iodide (7.80 g, 52 mmol) in CH₃CN (40 mL). Stirring was continued for 1 hour and the mixture was concentrated *in vacuo*. An ether solution (40 mL) of the residue was washed with 10% sodium thiosulphate solution (30 mL), water (30 mL) and brine (30 mL). The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure to give a dark oil. Flash column chromatography of the residue (Silica Gel 60H, hexane/ethyl acetate, 80:20) gave the desired product as a clear liquid (2.61 g, 73%). ¹H NMR (400 MHz; CDCl₃) δ 4.17 (2 H, s), 6.26 (1 H, dd, *J* = 3.2, 0.9 Hz), 6.35 (1 H, dd, *J* = 3.2, 2.0 Hz), 6.55 (1 H, dd, *J* = 1.7, 3.7 Hz), 7.24 (1 H, dd, *J* = 3.6, 0.7 Hz), 7.37 (1 H, dd, *J* = 1.7, 0.7), 7.61 (1 H, dd, *J* = 1.8, 0.8 Hz); ¹³C NMR (100 MHz; CDCl₃) δ 38.1 (CH₂, t), 108.4 (furyl C-4, d), 110.7 (furoyl C-4, d), 112.4 (furyl C-3, d), 118.2 (furoyl C-3, d), 142.1 (furyl C-5, d), 146.8 (furoyl C-5, d), 147.7 (furyl C-2, s), 152.0 (furoyl C-2, s), 183.8 (C-1, s); MS *m/z* (EI) 176 (M⁺, 15), 160 (4), 149 (4), 95 (100)

2-[2-(2-Furyl)ethyl]furan¹

A mixture of 1,2-di(2-furyl)-1-ethanone (3.34 g, 18.8 mmol) and hydrazine monohydrate (2.50 mL, 51.5 mmol) was added at room temperature to a solution of potassium hydroxide (3.40 g, 60.6 mmol) in diethylene glycol (135 mL). The reaction mixture was warmed to 120°C and kept at that temperature for 30 mins and then at 185°C for 1.5 hours. The product was extracted with diethyl ether (5 × 30 mL) and the extract washed with water (2 × 30 mL), brine (2 × 30 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. Column chromatography of the residual oil on neutral alumina and elution with hexane afforded the desired product as a colourless liquid (2.06 g, 67%). ¹H NMR (400 MHz; CDCl₃) δ 2.98 (4 H, s), 5.99 (2 H, br d, *J* = 3.1 Hz), 6.28 (2 H, dd, *J* = 3.2, 2.0 Hz), 7.31 (2 H, dd, *J* = 1.9, 0.9 Hz); ¹³C NMR (100 MHz; CDCl₃) δ 26.7 (C-1, t), 105.2 (C-3, d), 110.1 (C-4, d), 141.0 (C-5, d), 154.9 (C-2, s)

N-[2-(Hexanoylamino)phenyl]hexanamide

A solution of triethylamine (9.36 g, 92.4 mmol) and *o*-phenylenediamine (4.00 g, 37.0 mmol) in dichloromethane (100 mL) was stirred under nitrogen. The solution was cooled to 0°C and hexanoyl chloride (12.46 g, 92.4 mmol) was added dropwise with stirring. The solution was warmed to room temperature and stirred for 17 hours. Work-up was completed by washing with NaHCO₃ (saturated solution, 2 × 30 mL), water (2 × 30 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. Brown flakes were crystallised in dichloromethane/pentane to yield the desired product as a white crystalline powder (9.41 g, 84%). Mp 115-118°C; ¹H NMR (400 MHz; CDCl₃) δ 0.93 (6 H, t, *J* = 6.8 Hz), 1.35 (8 H, m), 1.67 (4 H, m), 2.29 (4 H, t, *J* = 7.5 Hz), 7.16 (2 H, dd, *J* = 3.4, 3.4 Hz), 7.28 (2 H, dd, *J* = 3.4, 3.3 Hz), 8.31 (2 H, br s); ¹³C NMR (100 MHz; CDCl₃) δ 14.0 (C-6', q), 22.5 (C-5', t), 25.4 (C-4', t), 31.5 (C-3', t), 37.2 (C-2', t), 125.6 (C-2, d), 126.1 (C-3, d), 130.7 (C-1, s), 173.0 (C-1', s); MS *m/z* (EI) 304 (M⁺, 24) 206 (70), 189 (31), 150 (33), 145 (30) 135 (63), 133 (53), 108 (100), 71 (21); IR (ATR) $\nu_{\max}/\text{cm}^{-1}$ 2930 (C-H), (NC=O) & 1178, 1109, 944 (1,2-disubstituted benzene).

An alternative preparation² involved reacting hexanoic anhydride (8.33 g, 38.85 mmol) and *o*-phenylenediamine (2.00 g, 18.5 mmol) in a flask under nitrogen with stirring. The solution was cooled to 0°C and lithium chloride (39.2 mg, 0.925 mmol) was added in small portions with vigorous stirring. The solution was warmed to room temperature and stirred for 4 hours. Work-up was completed by extracting with ethyl acetate (3 × 30 mL), washing with water (2 × 20 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. Brown flakes were crystallised in dichloromethane/pentane to yield the desired product as a crystalline white powder (4.37 g, 78%). Mp 115-118°C; ¹H NMR (400 MHz; CDCl₃) δ 0.93 (6 H, t, *J* = 6.8 Hz), 1.35 (8 H, m), 1.67 (4 H, m), 2.29 (4 H, t, *J* = 7.5 Hz), 7.16 (2 H, dd, *J* = 3.4, 3.4 Hz), 7.28 (2 H, dd, *J* = 3.4, 3.3 Hz), 8.31 (2 H, br s); ¹³C NMR (100 MHz; CDCl₃) δ 14.0 (C-6, q), 22.5 (C-5, t), 25.4 (C-4, t), 31.5 (C-3, t), 37.2 (C-2, t), 125.6 (C-2, d), 126.1 (C-3, d), 130.7 (C-1, s), 173.0 (C-1, s).

N,N-Dihexyl-1,2-benzenediamine

Anhydrous THF (100 mL) was added to LiAlH₄ (95 %) powder (2.31 g, 57.82 mmol) in a flask under nitrogen. This solution was cooled to -40°C and *N*-[2-(hexanoylamino)phenyl]hexanamide was added slowly over a 1 hour

period with stirring. The solution was refluxed for 19 hours. Water was added to the reaction flask with external cooling provided, until excess LiAlH_4 was hydrolysed. The solution was filtered through Celite and dichloromethane (100 mL) was added. Work-up was completed by washing with brine (2×40 mL), drying over MgSO_4 , filtered and the solvent was removed under reduced pressure. The crude powder was purified by column chromatography (neutral alumina, dichloromethane/hexane, 20:80) to afford the desired product as green crystals (6.25 g, 86%). Mp 118-119 °C; ^1H NMR (400 MHz; CDCl_3) δ 0.90 (6 H, t, $J = 7.0$ Hz), 1.29-1.38 (8 H, br m), 1.38-1.46 (4 H, m), 1.61-1.70 (4 H, m), 3.06 (4 H, t, $J = 7.0$ Hz), 3.18 (2 H, br s), 6.68 (2 H, dd, $J = 3.6, 3.3$ Hz), 6.78 (2 H, dd, $J = 3.3, 3.6$ Hz); ^{13}C NMR (100 MHz; CDCl_3) δ 14.1 (C-6', q), 22.7 (C-5', t), 27.1 (C-4', t), 29.8 (C-3', t), 31.7 (C-2', t), 44.6 (C-1', t), 111.6 (C-2, d), 119.0 (C-3, d), 137.6 (C-1, s).

***N*-[2-(Acetylamino)phenyl]acetamide**

N-[2-(Acetylamino)phenyl]acetamide was synthesised using acetic anhydride and lithium chloride.² *o*-Phenylenediamine (10.00 g, 92.4 mmol), acetic anhydride (20.78 g, 19.2 mol) and lithium chloride (196 mg, 4.62 mmol). Brown flakes were recrystallised from hot ethanol to yield the desired product as a crystalline white powder (11.5 g, 65%). M.p. 186-188°C; ^1H NMR (400 MHz; d_6 -DMSO) δ 2.06 (3 H, s), 7.11 (2 H, dd, $J = 3.7, 3.3$ Hz), 7.53 (2 H, dd, $J = 3.7, 3.6$ Hz), 9.32 (2 H, br s); ^{13}C NMR (100 MHz; d_6 -DMSO) δ 24.3 (C-2', q), 125.2 (C-2, d), 125.3 (C-3, d), 131.0 (C-1, s), 169.2 (C-1', s); MS m/z (EI) 192 (M^+ , 46), 174 (8), 150 (41), 132 (63), 108 (100); IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3019 (aromatic C-H), 1665 (NC=O), 1036, 971 (1,2-disubstituted benzene).

***N,N*-Diethyl-1,2-benzenediamine**

N-[2-(acetylamino)phenyl]acetamide (8.00 g, 41.62 mmol) was added slowly at -40°C to a solution of LiAlH_4 (3.60 g, 94.9 mmol) in THF (100 mL) and the reaction refluxed overnight. Work-up was as described above for *N,N*-dihexyl-1,2-benzenediamine. The resulting yellow oil was purified by column chromatography (neutral alumina, hexane/ethyl acetate, 99:1) affording the desired product as green crystals (5.67 g, 83%). ^1H NMR (400 MHz; CDCl_3) δ 1.28 (6 H, t, $J = 7.2$ Hz), 3.12 (4 H, q, $J = 7.3$ Hz), 3.10 (2 H, br s), 6.67 (2 H, dd, $J = 2.2, 3.7$ Hz), 6.78 (2 H, dd, $J = 3.3, 3.6$ Hz); ^{13}C NMR (100 MHz; CDCl_3) δ 15.2 (C-2', q), 39.0 (C-1', t), 111.5 (C-2, d), 119.2 (C-3, d), 137.5 (C-1, s); MS m/z (CI) 165 ($[\text{M}+\text{H}]^+$, 100); HRMS: found 164.1305, $\text{C}_{10}\text{H}_{16}\text{N}_2$ requires 164.1313; Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{N}_2$: C, 73.13; H, 9.82; N, 17.06. Found C, 73.44; H, 10.38; N, 17.20; IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3332 (N-H), 2967 (C-H), 1255 ($^{\text{sec}}$ amine), 1153, 1052, 901 (1,2-disubstituted benzene).

2-Methyl-1*H*-perimidine³

Acetic anhydride (270 g, 2.65 mol) was added dropwise to 1,8-naphthalenediamine (50.0 g, 0.32 mol) at 0°C with stirring under nitrogen. Formation of a mass of yellow needles of 2-methylperimidine acetate was rapid. Addition of aqueous ammonia to the aqueous solution liberated 2-methyl-1*H*-perimidine, which crystallised from methanol as greenish/yellow needles (54.7 g, 95%). M.p. 210-214°C, (Lit.,³ 215°C); ^1H NMR (400 MHz; d_6 -DMSO) δ 2.06 (3 H, s), 6.48 (2 H, br d, $J = 6.6$ Hz), 6.96 (2 H, dd, $J = 8.0, 1.0$ Hz), 7.10 (2 H, br dd, $J = 8.1, 7.7$ Hz), 10.5 (NH, br s); ^{13}C NMR (100 MHz; d_6 -DMSO) δ 21.9 (C-1, q), 118.5 (CH d), 121.8 (Cq s), 128.9 (CH d), 135.7 (CH d), 154.2 (Cq s), 154.7 (Cq, s), 173.0 (Cq s); MS m/z (EI) 182 (M^+ , 100), 140 (18), 127 (5), 115 (14), 91 (10), 78 (5); IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3400 (N-H), 3100 (aromatic C-H), 2900 (aliphatic C-H), 1338 ($^{\text{tert}}$ amine), 1299 ($^{\text{sec}}$ amine), 1607 & 820 (1,2,3-trisubstituted aromatic).

1,2-Dimethyl-1*H*-perimidine⁴

Iodomethane (59.6 g, 0.42 mol) was added dropwise at room temperature over a period of 30 mins to a solution of 2-methyl-1*H*-perimidine (51.0 g, 0.28 mol) in *N,N*-dimethylformamide (100 mL) containing anhydrous potassium carbonate (40.1 g, 0.29 mol). The solution was heated to 100°C for 1 hour giving a yellow precipitate. After cooling, the yellow solid was filtered and suspended in 2L of water. Ammonia solution was added slowly with stirring until the solution was slightly basic to litmus yielding a yellow solid. The solid was filtered, washed with water, and dried under vacuum to give the desired product (40.30 g, 73%). The *N,N*-dimethylformamide filtrate from the first filtration was added to 1.5 L of water, and the solution was made alkaline with aqueous ammonia solution to yield a yellow green/solid. The solid was filtered, washed with water, and dried under reduced pressure to give an additional (13.09 g, 24%) of product. The product was used in the next reaction without purification. M.p. 200-202°C; ^1H NMR (400 MHz; CDCl_3) δ 2.30 (3 H, s), 3.18 (3 H, s), 6.23 (1 H, br dd, $J = 7.7, 1.1$ Hz), 6.81 (1 H, br dd, $J = 7.4, 0.8$ Hz), 7.17 (1 H, br dd, $J = 8.0, 7.3$ Hz), 7.22 (1 H, br dd, $J = 8.1, 7.7$ Hz), 7.53 (1 H, br dd, $J = 8.0, 8.1$ Hz), 7.61 (1 H, br d, $J = 8.1$ Hz); ^{13}C NMR (100 MHz; CDCl_3) δ 21.5 (C-1', q), 31.7 (C-1, q), 100.5 (C-4, d), 118.7 (C-6, d), 123.3 (C-9b, s), 127.3 (C-5, d), 134.0 (C-3a, s), 139.0 (C-6a, s), 154.4 (C-2, s); MS m/z (EI) 196 (M^+ , 26), 181 (26), 168 (100), 154 (26), 140 (23), 127 (75), 105 (18), 98 (12); IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3100 (aromatic C-H), 2900 (aliphatic C-H), 1374 ($^{\text{tert}}$ amine), 1739, 1639 & 817 (1,2,3-trisubstituted aromatic).

1,2-Dimethylperimidinyl Methiodide⁴

Iodomethane (58.7 g, 0.41 mol) was added dropwise to a solution of 1,2-dimethyl-1*H*-perimidine (54.1 g, 0.28 mol) in *N,N*-dimethylformamide (200 mL) and refluxed for 1 hour forming a yellow solid. After cooling, the yellow solid was filtered and dried under reduced pressure to give the desired salt (58.47 g, 63%) which was used in the next reaction without purification. M.p. 248-249°C; ^1H NMR (400 MHz; CDCl_3) δ 2.72 (3 H, s), 3.51 (6 H, s), 7.07 (2 H, br d, $J = 8.0$ Hz), 7.45 (2 H, br dd, $J = 8.0, 8.1$ Hz), 7.57 (2 H, br d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz; CDCl_3) δ 20.5 (C-1', q), 39.7 (C-1, q), 108.9 (C-4, d), 120.9 (C-9b, s), 123.6 (C-5, d), 129.9 (C-6, d), 134.0 (C-3a, s), 134.2 (C-6a, s), 162.9 (C-2, s); MS m/z (EI) 210 (M^+-I , 86), 195 (60), 181 (33), 168 (100), 154 (23), 140

(22), 127 (75), 105 (15), 98 (11); IR (ATR) $\nu_{\max}/\text{cm}^{-1}$ 3300 (*tert*-amine salt), 3100 (aromatic C-H), 2870 (aliphatic C-H), 1376 (*tert*-amine), 1738, 1640 & 818 (1,2,3-trisubstituted aromatic).

1,2,2,3-Tetramethyl-2,3-dihydro-1H-perimidine⁵

To a solution of *N,N*-dimethyl-1,8-naphthalenediamine (0.75 g, 4.03 mmol) and acetone (15 mL) was added *p*-toluenesulphonic acid (0.08 g, 0.40 mmol) in a flask under nitrogen with stirring. The solution was refluxed for 20 hours and the acetone was removed under reduced pressure. Dichloromethane (50 mL) was added and the solution was washed with NaHCO₃ (saturated solution, 2 × 20 mL), water (2 × 20 mL), dried over MgSO₄, filtered and concentrated under reduced pressure to give a brown solid. This solid was purified by column chromatography (neutral alumina, hexane/dichloromethane, 80:20) to afford the desired product as a white solid (0.78 g, 86%). M.p. 62-63°C;

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