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-ethanone

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 CH₂CN (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 (2.06 g, 67%). 1H NMR (400 MHz; CDCl₃) δ 7.51 (2H, d, J = 7.5 Hz), 7.16 (2H, dd, J = 3.4, 3.3 Hz), 6.26 (1H, dd, J = 3.4, 0.9 Hz), 6.35 (1H, dd, J = 3.2, 2.0 Hz), 6.55 (1H, dd, J = 1.7, 3.7 Hz), 7.24 (1H, dd, J = 3.6, 0.7 Hz), 7.37 (1H, dd, J = 1.7, 0.7 Hz), 7.61 (1H, dd, J = 1.8, 0.8 Hz); 13C NMR (100 MHz; CDCl₃) δ 140.0 (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); MS m/z (EI) 176 (M+, 15), 160 (4), 149 (4), 95 (100)

2-[2-(2-Furyl)ethyl]furan

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 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), brine (2×30 mL) and the extract washed with water (2×30 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 white crystalline powder (4.37 g, 78%). Mp 115-118°C 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 7.5 (2H, d, J = 7.5 Hz), 7.15 (2H, dd, J = 3.4, 3.3 Hz), 6.26 (1H, dd, J = 3.4, 0.9 Hz), 6.35 (1H, dd, J = 3.2, 2.0 Hz), 6.55 (1H, dd, J = 1.7, 3.7 Hz), 7.24 (1H, dd, J = 3.6, 0.7 Hz), 7.37 (1H, dd, J = 1.7, 0.7 Hz), 7.61 (1H, dd, J = 1.8, 0.8 Hz); 13C NMR (100 MHz; CDCl₃) δ 140.0 (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); MS m/z (EI) 176 (M+, 15), 160 (4), 149 (4), 95 (100)

N-[2-(Hexanoylamino)phenyl]hexanamide

A solution of triethylamine (9.36 g, 92.4 mmol) and hexanoyl chloride (12.46 g, 92.4 mmol) was added dropwise with vigorous stirring. The solution was warmed to room temperature and stirred for 17 hours. Freshly distilled chlorotrimethylsilane (5.43 g, 50 mmol) was added dropwise to a stirred solution of furoin (3.84 g, 20 mmol) and lithium chloride (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 9.3 (6H, t, δ = 6.8 Hz), 1.35 (8H, m), 1.67 (4H, m), 2.29 (4H, t, J = 7.5 Hz), 7.16 (2H, dd, J = 3.4, 3.4 Hz), 7.28 (2H, dd, J = 3.4, 3.3 Hz), 8.31 (2H, br s); 13C NMR (100 MHz; CDCl₃) δ 140.0 (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) νmax/cm⁻¹ 2930 (C-H), (NC=O) & 1178, 1109, 944 (1,2-disubstituted benzene). An alternative preparation involved reacting hexanoic anhydride (8.33 g, 38.85 mmol) and o-phenylenediamine (2.00 g, 18.55 mmol) in a flask under nitrogen. The solution was cooled to 0°C and lithium chloride (o-phenylenediamine) was added slowly over a 1 hour
period with stirring. The solution was refluxed for 19 hours. Water was added to the reaction flask to external
filtering, until excess LiAlH₄ was hydrolysed. The solution was filtered through Celite and
cooling provided, until excess LiAlH₄ was hydrolysed. The solution was filtered through Celite and
solvent was removed under reduced pressure. The crude powder was purified by column
and dried under vacuum to give the desired product (40.30 g, 73%). The
and dried under vacuum to give the desired product (40.30 g, 73%). The
the solution was slightly basic to litmus yielding a yellow solid. The solid was filtered, washed with
in THF (100 mL) and the reaction re-fluxed overnight. Work-up was as described above for
2-Methyl-1,2-Dimethylperimidinyl Methiodide4
Iodomethane (58.7 g, 0.41 mol) was added dropwise to a solution of 1,2-dimethyl-1H-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. 200-202°C; 1H NMR (400 MHz; CDCl3) 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) 13C NMR (100 MHz; CDCl3) δ 21.3 (C-1'-i, q), 31.7 (C-1'-q), 100.5 (C-4'-d), 118.7 (C-6'-d), 123.3 (C-5'-s), 127.5 (C-5'-d), 134.0 (C-3a'-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) νmax/cm⁻¹ 3100 (aromatic C-H), 2900 (aliphatic C-H), 1374 (vamide), 1739, 1639 & 817 (1,2,3-trisubstituted aromatic).
(22), 127 (75), 105 (15), 98 (11); IR (ATR) ν/cm⁻¹ 3300 ("amine salt), 3100 (aromatic C-H), 2870 (aliphatic C-H), 1376 ("amine), 1738, 1640 & 818 (1,2,3-trisubstituted aromatic).

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

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;