Synthesis and Structural Study of Thiacyclophanes Utilizing Dibromides and Methane Dithiolate

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ABSTRACT: The synthesis of a series of thiacyclophanes and optically active binaphthol based chiral thiacyclophanes is reported with XRD structure. Two diastereomeric tetrathiacyclophanes are designed and synthesized. The two diastereomers are evidenced by crystal structure; the single-crystal X-ray studies revealed that one of the isomers to possesses an inherent property of self-assembling into vertical stack of tunnel-like structures.

CONTENTS

S2-S4 : General experimental procedure; spectroscopic and analytical data for reported cyclophanes.

S5 : $^1$H NMR spectrum of Cyclophane 13.


S7-S9 : ORTEP diagram of Cyclophanes 6, 12, 13, 15 and 16 at 50% probability level.

Supporting Information

**General Experimental Procedure:** A mixture of dibromide (5 mmol) and CS₂ (10 mmol) in dry THF (75 mL) was added to a slurry of NaBH₄ (20 mmol) in THF (25 mL) at room temperature, and the resulting solution was refluxed for 6 h. The reaction mixture was then quenched with aqueous ammonium chloride, solvent was evaporated under reduced pressure and crude product was extracted with CHCl₃ (2×100 mL) and dried over sodium sulfate. The product was purified by column chromatography (SiO₂) using ethyl acetate/hexane solvent mixture as eluent.

**Cyclophanes 5:** (27%) as a colorless solid; mp 194-196 °C ¹H NMR (CDCl₃) δ 2.95 (s, 2H), 3.63 (s, 4H), 5.09 (s, 4H), 6.48 (d, 4H, J = 8.6 Hz), 6.89 (d, 4H, J = 8.6 Hz), 7.38-7.43 (m, 4H); ¹³C NMR (CDCl₃) δ 158.8, 131.1, 130.9, 130.2, 129.0, 115.0, 114.1, 69.8, 37.9, 35.3; MS (EI) (m/z) 46, 78, 104 (100%), 138, 195, 208, 309, 347, 394 (M⁺); Anal. Calcd for C₂₃H₂₂O₂S₂: C, 70.02; H, 5.62. Found: C, 70.21; H, 5.76.

**Cyclophanes 6:** (48%) as a colorless solid; mp 148-150 °C ¹H NMR (CDCl₃) δ 3.02 (s, 2H), 3.58 (s, 4H), 5.15 (s, 4H), 6.64 (d, 4H, J = 8.3 Hz), 6.89 (d, 4H, J = 8.3 Hz), 7.25 (d, 2H, J = 8.2 Hz), 7.35 (t, 1H, J = 8.2 Hz), 7.57 (s, 1H); ¹³C NMR (CDCl₃) δ 156.7, 137.9, 129.6, 129.0, 126.5, 126.3, 115.2, 69.1, 35.0, 29.4; MS (EI) (m/z) 57, 78, 104 (100%), 136, 209, 315, 348, 394 (M⁺); Anal. Calcd for C₂₃H₂₂O₂S₂: C, 70.02; H, 5.62. Found: C, 70.18; H, 5.75.
**Cyclophanes 7:** (32%) as a colorless solid; mp 196-198 °C \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.03 (s, 2H), 3.53 (s, 4H), 5.19 (s, 4H), 6.73 (d, 4H, \(J = 8.8\) Hz), 6.83 (d, 4H, \(J = 8.8\) Hz), 7.30 (d, 2H, \(J = 7.8\) Hz), 7.62 (t, 1H, \(J = 7.8\) Hz); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 156.8, 156.7, 135.7, 129.8, 129.6, 122.3, 114.9, 70.2, 34.9, 29.3; MS (EI) \((m/z)\) 78, 105 (100%), 213, 216, 316, 349, 395 (M\(^+\)); Anal. Calcd for C\(_{22}\)H\(_{21}\)NO\(_2\)S\(_2\): C, 66.80; H, 5.35; N, 3.54. Found: C, 66.98; H, 5.47; N, 3.48.

**Cyclophanes 11:** (41%) as a colorless solid; mp 72-74 °C; \([\alpha]_D^{30} = -126.69, (c 0.0175, CHCl\(_3\))\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.04 (s, 2H), 3.16 (d, 2H, \(J = 13.5\) Hz), 3.39 (d, 2H, \(J = 13.5\) Hz), 4.85 (d, 2H, \(J = 12.4\) Hz), 4.91 (d, 2H, \(J = 12.4\) Hz), 6.59 (s, 2H), 6.84-7.31 (m, 14H), 7.78 (d, 2H, \(J = 8.0\) Hz), 7.84 (d, 2H, \(J = 9.0\) Hz); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 154.3, 138.2, 138.1, 137.9, 134.5, 129.9, 129.7, 128.8, 128.4, 128.3, 128.2, 128.1, 128.1, 126.8, 125.8, 121.4, 71.6, 36.4, 33.4; MS (EI) \((m/z)\) 58, 67, 105(100%), 134, 164, 190, 205, 236, 268, 284, 570 M\(^+\)); Anal. Calcd for C\(_{37}\)H\(_{30}\)O\(_2\)S\(_2\): C, 77.86; H, 5.30. Found: C, 77.68; H, 5.44.

**Cyclophanes 12:** (55%) as a colorless solid; mp 114-116 °C; \([\alpha]_D^{30} = -146.30, (c 0.0175, CHCl\(_3\))\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.30 (s, 2H), 3.53 (s, 4H), 5.04 (d, 2H, \(J = 13.2\) Hz), 5.22 (d, 2H, \(J = 13.2\) Hz), 6.67 (d, 4H, \(J = 8.0\) Hz), 6.91 (d, 4H, \(J = 8.0\) Hz), 7.26-7.40 (m, 8H\(_2\)), 7.77 (d, 2H, \(J = 8.0\) Hz), 7.84 (d, 2H, \(J = 9.0\) Hz); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 151.5, 135.1, 133.9, 132.1, 127.0, 127.0, 126.6, 125.8, 124.6, 124.3, 123.1, 121.5, 117.9, 113.0, 67.6, 33.1, 27.2; MS (EI) \((m/z)\) 52, 77, 89 (100%), 133, 185, 207, 218, 237, 286, 570 M\(^+\)); Anal. Calcd for C\(_{37}\)H\(_{30}\)O\(_2\)S\(_2\): C, 77.86; H, 5.30. Found: C, 78.05; H, 5.50.
Cyclophanes 13: (28%) as a colorless solid; mp 194-196 °C \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.36 (s, 4H), 3.72 (s, 8H), 6.95 (s, 2H), 7.18-7.27 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 36.1, 38.1, 127.6, 128.4, 129.5, 138.3; MS (EI) (m/z) 105 (100%), 135, 166, 198, 227, 364 (M\(^{+}\)); Anal. Calcd for C\(_{18}\)H\(_{20}\)S\(_4\): C, 59.29; H, 5.53. Found: C, 59.57; H, 5.71.

Cyclophanes 15: (27%) as a colorless solid; mp 222-225 °C \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.98 (d, 2H, \(J = 11.2\) Hz), 3.27 (d, 2H, \(J = 11.2\) Hz), 3.35 (d, 4H, \(J = 13.6\) Hz), 3.71 (s, 12H), 4.15 (d, 4H, \(J = 13.6\) Hz), 6.67 (s, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 151.2, 125.1, 113.6, 56.3, 30.4, 29.6; MS (EI) (m/z) 46, 91, 135, 164 (100%), 209, 242, 274, 319, 392, 438, 484 (M\(^{+}\)); Anal. Calcd for C\(_{22}\)H\(_{28}\)O\(_4\)S\(_4\): C, 54.51; H, 5.82. Found: C, 54.40; H, 5.76.

Cyclophanes 16: (18%) as a colorless solid; mp 206-208 °C \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.15 (s, 4H), 3.31 (d, 4H, \(J = 14\) Hz), 3.72 (s, 12H), 4.13 (d, 4H, \(J = 14\) Hz), 6.75 (s, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 151.4, 124.9, 113.0, 56.3, 30.2, 29.7; MS (EI) (m/z) 49, 91, 134, 165 (100%), 195, 242, 287, 328, 360, 484 (M\(^{+}\)); Anal. Calcd for C\(_{22}\)H\(_{28}\)O\(_4\)S\(_4\): C, 54.51; H, 5.82. Found: C, 54.75; H, 5.97.
$^1$H NMR spectrum of [5.5]metacyclophane 13
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Base: m/z 105; 28.3% FS TIC: 94759

Threshold: 3% of Base

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Mass spectrum of [5,5]metacyclophane 13
ORTEP drawing of cyclophane 6 showing 50% probability level.
ORTEP diagram of cyclophane 12 showing 50% probability level.

ORTEP drawing of cyclophane 13 showing 50% probability level.
ORTEP diagram of cyclophane 15 showing 50% probability level.

ORTEP drawing of cyclophane 16 showing 50% probability
Self assembly views of cyclophane 15

Front view of cyclophane 15

Perspective view of cyclophane 15

Linear view (chain) of cyclophane 15