

**Synthesis and complexation properties of 1,3-alternate stereoisomers of *p*-tert-butylthiacalix[4]arenes tetrasubstituted at the lower rim by the phthalimide group**

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*5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-[2'-(N-phthalimido)-ethoxy]-2,8,14,20-tetrathiacalix[4]arene 2.* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.14 (s, 9H, Me<sub>3</sub>C), 1.19 (s, 18H, Me<sub>3</sub>C), 1.20 (s, 9H, Me<sub>3</sub>C), 4.44 (t, 2H, NCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 5.1 Hz), 4.59 (t, 2H, OCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 5.1 Hz), 7.51 (d, 2H, H<sub>Ar1</sub>, <sup>4</sup>J<sub>HH</sub> 2.4 Hz), 7.54 (s, 2H, H<sub>Ar2</sub>), 7.57 (d, 2H, H<sub>Ar1</sub>, <sup>4</sup>J<sub>HH</sub> 2.4 Hz), 7.58 (s, 2H, H<sub>Ar3</sub>), 7 (m, 2H, H<sub>Ar4</sub>), 7 (m, 2H, H<sub>Ar4</sub>), 8.88 (s, 2H, OH), 9.38 (s, 1H, OH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 34.4, 30.94, 31.2, 31.3, 34.0, 34.1, 37.8, 74.2, 119.9, 120.6, 120.7, 123.3, 128.2, 132.5, 133.6, 135.6, 135.64, 136.1, 136.8, 143.2, 143.9, 149.3, 156.2, 156.8, 157.1, 168.7. IR (Vaseline oil, ν/cm<sup>-1</sup>): 1268 (COC), 1718, 1778 (C=O), 3364 (OH). MS (ESI), *m/z*: 916.3 (calc. for [M + Na<sup>+</sup>]: 916.3). Found (%): C, 66.97; H, 6.18; N, 1.27; S, 14.11. Calc. for C<sub>50</sub>H<sub>52</sub>NO<sub>6</sub>S<sub>4</sub> (%): C, 67.16; H, 6.20; N, 1.57; S, 14.34.

*5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[3'-(N-phthalimido)-propoxy]-2,8,14,20-tetrathiacalix[4]arene 3.* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.18 (s, 36H, Me<sub>3</sub>C), 1.68 (tt, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 6.6 Hz, <sup>3</sup>J<sub>HH</sub> 8.1 Hz), 3.64 (t, 8H, NCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 6.6 Hz), 3.94 (t, 8H, OCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 8.1 Hz), 7.32 (s, 8H, H<sub>Ar1</sub>), 7.67–7.74 (m, 8H, H<sub>Ar2</sub>), 7.78–7.85 (m, 8H, H<sub>Ar2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 28.7, 31.1, 34.1, 35.2, 67.5, 123.2, 128.3, 129.0, 132.1, 133.8, 145.7, 157.2, 168.1. IR (Vaseline oil, ν/cm<sup>-1</sup>): 1266 (COC), 1715, 1773 (C=O). Found (%): C, 68.82; H, 5.49; N, 3.84; S, 9.07. Calc. for C<sub>84</sub>H<sub>84</sub>N<sub>4</sub>O<sub>12</sub>S<sub>4</sub> (%): C, 68.64; H, 5.76; N, 3.81; S, 8.72.

*5,11,17,23-Tetra-tert-butyl-25,26,27-tris[(ethoxycarbonyl)methoxy]-28-[2'-(N-phthalimido)ethoxy]-2,8,14,20-tetrathiacalix[4]arene 4.* <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.24 (s, 9H, Me<sub>3</sub>C), 1.25 (s, 9H, Me<sub>3</sub>C), 1.29 (s, 18H, Me<sub>3</sub>C), 1.00 (m, 9H, OCH<sub>2</sub>Me), 4.00 (m, 2H, NCH<sub>2</sub>), 4.00 (m, 8H, OCH<sub>2</sub>Me, NCH<sub>2</sub>CH<sub>2</sub>O), 4.32 (s, 2H, OCH<sub>2</sub>C=O), 4.62 (AB, 4H, OCH<sub>2</sub>C=O, <sup>4</sup>J<sub>HH</sub> 14.1 Hz), 7.46 (d, 2H, H<sub>Ar1</sub>, <sup>4</sup>J<sub>HH</sub> 2.5 Hz), 7.47 (s, 2H, H<sub>Ar2</sub>), 7.53 (s, 2H, H<sub>Ar3</sub>), 7.73 (d, 2H, H<sub>Ar1</sub>, <sup>4</sup>J<sub>HH</sub> 2.5 Hz), 7.00 (m, 2H, H<sub>Ar4</sub>), 7.00 (m, 2H, H<sub>Ar4</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.16, 14.21, 30.99, 31.02, 31.2, 34.2, 34.3, 37.0, 60.4, 60.5, 66.4, 67.6, 68.1, 122.3, 127.68, 127.72, 127.8, 128.3, 128.5, 132.16, 132.23, 132.9, 133.6, 133.9, 146.3, 146.4, 156.6, 157.1, 157.7, 167.9, 167.7. IR (Vaseline oil, n/cm<sup>-1</sup>): 1268 (COC), 1717, 1778 (C=O). MS (EI), *m/z*: 1151.5 (calc. for [M<sup>+</sup>]: 1151.4). Found (%): C, 64.89; H, 6.10; N, 1.23; S, 11.23. Calc. for C<sub>62</sub>H<sub>75</sub>NO<sub>12</sub>S<sub>4</sub> (%): C, 64.61; H, 6.38; N, 1.22; S, 11.13.