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Received June 7, 1999

Crown ethers containing a thiazole subcyclic unit are prepared from the reactions of 1,3-bis[2(4-hydroxymethylthiazoyl)]benzene with di-*p*-tosylates of corresponding di, tri, tetra, pentaethylene glycols in the presence of potassium hydride. However, if the cavity size in the ring system is small, [2+2] cyclization adduct also is formed.

*J. Heterocyclic Chem.*, **36**, 1285 (1999).

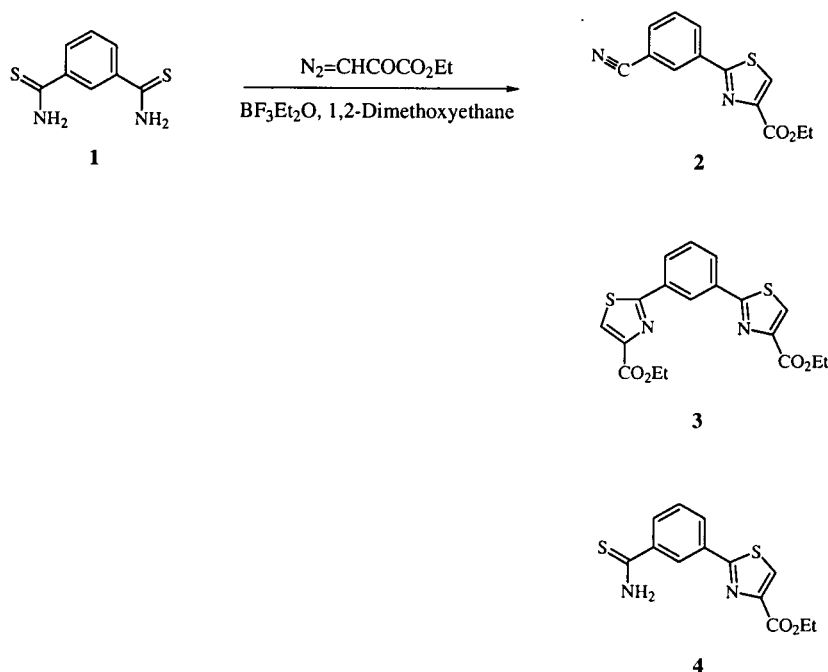
The crown ethers have been the subject of much interest in the field of host-guest chemistry during the past decade because of their different binding characteristics. Many crown ethers containing a heterocyclic unit in their ring systems have been synthesized and studied [1]. Recently we reported the synthesis of thiazole-containing polyether podands and benzo-crown ethers. [2,3]. In continuation of our research work, we attempted to synthesize 1,3-bis(thiazolyl)benzene crown ethers, and report our results here.

The requisite starting material for the synthesis of the 1,3-bis(thiazolyl)benzene crown ethers **6-10** was 1,3-bis[2(4-carbomethoxythiazolyl)]benzene **3**. The preparation of **3** is shown in Scheme 1. Thioisophthalamide **1** was prepared from isophthalamide, which was obtained from the reaction of isophthaloyl chloride with aqueous ammonium hydroxide in 94% yield. Thionation of isophthal-

amide with Lawesson's reagent in tetrahydrofuran provided **1** in 90% yield. Cyclocondensation of thioisophthalamide **1** with ethyl diazopyruvate in the presence of boron trifluoride in dimethoxyethane resulted in 1,3-bis[2(4-carbomethoxythiazolyl)]benzene **3** (83%) along with nitrile **2** (12%) and thioamide **4** (1%). [4,5] We have found that dry condition in this reaction is quite essential to improve the yield of **3**. Thus, when the reaction was carried out in the presence of magnesium sulfate or molecular sieve (4Å), **3** was obtained as a predominant product.

The structures of compounds **2**, **3** and **4** were confirmed by spectroscopic and analytical data. Compound **2** exhibited a characteristic nitrile absorption band at 2228 cm<sup>-1</sup> in the ir spectrum and nitrile signal at δ 117.8 in the <sup>13</sup>C nmr spectrum. The <sup>1</sup>H nmr spectrum of **3** showed one H-2 proton of benzene at δ 8.56 as doublet, which is due to the long range coupling between H-2 and H-4, H-6 protons of

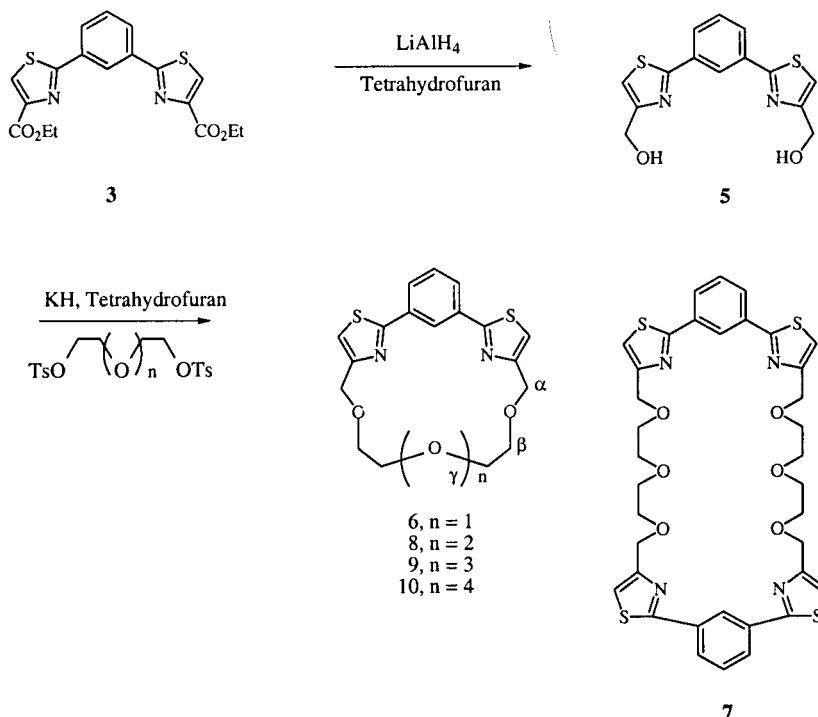
Scheme 1



benzene. The thiazole, H-4 and H-6 of benzene, and methylene and methyl protons of **3** observed at  $\delta$  8.21, 8.12, 4.46, and 1.44 in the  $^1\text{H}$  nmr spectrum. The thiazole carbons of **3** appeared at  $\delta$  161.3, 148.3, and 125.2 in the  $^{13}\text{C}$  nmr spectrum. The mass spectrum of **3** showed the molecular ion at 388 (55% relative abundance).

The synthesis of thiazole containing coronands **6**, **7**, **8**, **9** and **10** were carried out by the reaction sequences shown in Scheme 2. Reduction of **3** with lithium aluminum hydride at  $-78^\circ$  provided the 1,3-bis[2(4-hydroxymethyl)thiazolyl]benzene **5** in 99% yield. The hydroxyl signal of **5** was observed at  $\delta$  4.42 as broad singlet in the

Scheme 2



Compound **3** showed an ester carbonyl absorption in the ir spectrum at  $1728\text{ cm}^{-1}$ . Compound **4** exhibited, in its  $^1\text{H}$  nmr spectrum, signals of two thioamide protons at  $\delta$  8.97 and 9.12 as a broad singlet and one thiazole proton at  $\delta$  8.48. Due to the dissymmetry of the molecule, the  $^{13}\text{C}$  nmr spectrum of **4** showed six signals for benzene carbons at  $\delta$  140.0, 132.0, 129.2, 128.8, 128.2, 127.1, and thioamido carbon at  $\delta$  200.4. The mass spectrum of **4** displayed the molecular ion at 292 (38% relative abundance).

Table 1  
Synthesis of Thiazole Containing Crown Ethers

Compound	n	Yield (%) [a]
<b>6</b>	1	14
<b>7</b>	-	12
<b>8</b>	2	55
<b>9</b>	3	44
<b>10</b>	4	30

[a] Isolated yield.

$^1\text{H}$  nmr spectrum and the hydroxyl absorption band was shown at  $3450\text{--}3100\text{ cm}^{-1}$  in the ir spectrum. Treatment of **5** with potassium hydride in tetrahydrofuran then subsequently with di-*p*-tosylates of the corresponding poly(ethylene glycol) yielded corresponding 1,3-bis(thiazolyl)benzene crown ethers. The results of these reactions are shown in Table 1. From the reaction of **5** with tri, tetra, and pentaethylene glycol di-*p*-tosylate, we isolated crown ethers **8**, **9** and **10** in 55, 44, and 30% yield, respectively. It is suggested that if the cavity size in the crown ether ring system is large enough, the cyclization occurs readily. However, in the case of the crown ether **6**, the cavity size is small and the cyclization occurs two ways, *i.e.*, we could isolate not only the [1+1] adduct **6** but also the [2+2] adduct **7** in 14 and 12% yield, respectively. The difficulty of the cyclization between diethylene glycol di-*p*-tosylate and **5** could be due to ring strain induced during attempted cyclization.

The crown ethers obtained were characterized by spectroscopic and analytical data. In the  $^1\text{H}$  nmr spectrum, the most notable feature is chemical shift of the H-2 of ben-

zene. Due to the anisotropic effect of benzene and thiazole ring, H-2 proton of benzene is shifted to downfield. In the  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectrum, the methylene protons and carbons of the ethylene glycol units were shifted to downfield by the following order:  $\delta_\alpha > \delta_\beta > \delta_\gamma$ . It is regarded that these effects are also due to anisotropic effect of the thiazole ring.

Thus, the present procedure provides a series of crown ethers, which contain thiazole subcyclic unit. Future publications will describe utilization of some of these crown ethers in supramolecular chemistry.

## EXPERIMENTAL

General procedures are as described elsewhere. [3] All reactions were carried out under an atmosphere of argon. Solvents were dried and purified according to the known method. [6]

### Thioisophthalamide (1).

To a suspension of isophthalamide (4 g, 24.4 mmoles) in 20 ml of tetrahydrofuran was added Lawesson's reagent (9.9 g, 24.4 mmoles) at room temperature, and the mixture was refluxed until it became a homogeneous solution. After removal of the solvent, the residue was dissolved in dichloromethane and allowed to solidify. The precipitate was filtered, allowed to air-dry and then recrystallized from acetone and hexane to give a yellow solid (4.3 g, 90%), mp 203° (acetone-hexane) (200°, ref. [7]; 212°, ref. [8]); ir (potassium bromide): 3292, 3276, 3157, 1632, 1412, 1292, 888, 799, 652, 590  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuterioacetone):  $\delta$  9.12 (bs, 2H,  $\text{NH}_2$ ), 9.0 (bs, 2H,  $\text{NH}_2$ ), 8.43 (t,  $J = 1.8$  Hz, 1H), 8.10 (d,  $J = 7.8$  Hz, 2H), 7.46 (t,  $J = 7.8$  Hz, 1H); ms:  $m/z$  196 ( $\text{M}^+$ , 94), 162 (100), 128 (56);  $R_f$  0.40 (ethyl acetate-hexane, 1:1).

1-Cyano-3-[2(4-carbethoxy)thiazolyl]benzene (2), 1,3-bis[2-(4-Carbethoxy)thiazolyl]benzene (3) and 1-Thioamido-3-[2(4-carbethoxy)thiazolyl]benzene (4).

To a solution of 1 (1 g, 5.6 mmoles) and boron trifluoride etherate (1.3 ml, 10.4 mmoles) in dry dimethoxyethane (15 ml) was added a solution of ethyl diazopyruvate (1.45 g, 10.4 mmoles) in dry dimethoxyethane (5 ml) for 3 hours at room temperature. The resulting mixture was heated at 45° for 6 hours. The mixture was cooled to room temperature and poured into water and extracted with ethyl acetate. The organic layer was washed with water, saturated solution of sodium bicarbonate and brine, dried over anhydrous sodium sulfate and evaporated. Analysis by tlc (silica gel, ethyl acetate-hexane 1:1) indicated three components with  $R_f$ 's of 0.30, 0.46 and 0.54. These were separated by flash chromatography (silica gel, ethyl acetate-hexane 1:4) to give 2 (174 mg, 12%), 3 (1.81 g, 83%) and 4 (16 mg, 1%), respectively.

Compound 2 was obtained as a solid, which was recrystallized from dichloromethane and hexane, mp 128-129°; ir (potassium bromide): 3131, 3061, 2988, 2228, 1723, 1474,

1402, 1368, 1335, 1289, 1206, 1088, 1011, 802, 762, 683  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  8.33 (s, 1H, H-5), 8.24 (t,  $J = 4.1$  Hz, 2H), 7.74 (d,  $J = 7.5$  Hz, 1H), 7.60 (t,  $J = 7.8$  Hz, 1H), 4.47 (q,  $J = 7.1$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 1.45 (t,  $J = 7.2$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  nmr (deuteriochloroform): d 165.9 (C=O), 161.0 (C-2), 148.5 (C-4), 133.9, 133.6, 130.9, 130.3, 129.9, 127.8, 117.8 (CN), 113.4, 61.7 ( $\text{OCH}_2\text{CH}_3$ ), 14.3 ( $\text{OCH}_2\text{CH}_3$ ); ms:  $m/z$  258 ( $\text{M}^+$ , 31), 213 (45), 186 (100), 57 (54);  $R_f$  0.54 (ethyl acetate-hexane, 1:1).

*Anal.* Calcd. For  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ : C, 60.45; H, 3.90; N, 10.85. Found: C, 60.43; H, 3.85; N, 10.96.

Compound 3 was obtained as a solid, which was recrystallized from dichloromethane and hexane, mp 143-144°; ir (potassium bromide): 3133, 3059, 2978, 1728, 1589, 1478, 1441, 1343, 1273, 1207, 1098, 1026, 793, 745, 719, 691, 635  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  8.56 (d,  $J = 1.6$  Hz, 1H), 8.21 (s, 2H, H-5), 8.12 (dd,  $J = 7.8, 1.6$  Hz, 2H), 7.56 (t,  $J = 7.8$  Hz, 1H), 4.46 (q,  $J = 7.1$  Hz, 4H,  $\text{OCH}_2\text{CH}_3$ ), 1.44 (t,  $J = 7.1$  Hz, 6H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  167.6 (C=O), 161.3 (C-2), 148.3 (C-4), 133.7, 129.9, 129.0, 127.5, 125.2 (C-5), 61.5 ( $\text{OCH}_2\text{CH}_3$ ), 14.3 ( $\text{OCH}_2\text{CH}_3$ ); ms:  $m/z$  388 ( $\text{M}^+$ , 55), 343 (22), 316 (100), 270 (68), 186 (26);  $R_f$  0.46 (ethyl acetate-hexane, 1:1).

*Anal.* Calcd. For  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4\text{S}_2$ : C 55.65 H, 4.16, N 7.21. Found: C, 55.80; H, 4.14; N, 6.99.

Compound 4 was obtained as a solid, which was recrystallized from dichloromethane and hexane, mp 188°; ir (potassium bromide): 3320, 3219, 3137, 2973, 1713, 1626, 1472, 1424, 1337, 1277, 1217, 1101, 1011, 806, 756, 685  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform-deuteriomethyl sulfoxide):  $\delta$  9.12 (bs, 1H,  $\text{NH}$ ), 8.97 (bs, 1H,  $\text{NH}$ ), 8.48 (s, 1H, H-5), 8.23 (s, 1H), 8.11 (d,  $J = 7.7$  Hz, 1H), 8.04 (d,  $J = 7.7$  Hz, 1H), 7.48 (t,  $J = 7.8$  Hz, 1H), 4.43 (q,  $J = 7.1$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 1.28 (t,  $J = 7.1$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  nmr (deuteriochloroform-deuteriomethyl sulfoxide):  $\delta$  200.4 (CSNH<sub>2</sub>), 167.2 (C=O), 160.6 (C-2), 147.4 (C-4), 140.0, 132.0, 129.2, 128.8, 128.2, 127.1, 124.9 (C-5), 60.8 ( $\text{OCH}_2\text{CH}_3$ ), 13.8 ( $\text{OCH}_2\text{CH}_3$ ); ms:  $m/z$  292 ( $\text{M}^+$ , 38), 261 (41), 211 (46), 184 (100), 144 (26), 128 (28), 56 (37);  $R_f$  0.30 (ethyl acetate-hexane, 1:1).

*Anal.* Calcd. For  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$ : C, 53.41; H, 4.14; N, 9.58. Found: C, 52.98; H, 4.12; N, 9.90.

### 1,3-Bis[2(4-hydroxymethyl)thiazolyl]benzene (5).

To a suspension of lithium aluminum hydride (198 mg, 5.2 mmoles) in 15 ml of tetrahydrofuran was added 3 (1 g, 2.6 mmoles) at -78°. Then the mixture was stirred at -78° for 2 hours, warmed to room temperature and then poured into the water. The mixture was acidified with 5% hydrochloric acid solution and then extracted with ethyl acetate. The organic layer was washed with water and brine, dried over sodium sulfate and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate-hexane 2:1) to give 5 (755 mg, 99%), which was recrystallized from methanol and water, mp 134-135°; ir (potassium bromide): 3450-3100 (OH), 3109, 2917, 2859, 1526, 1451, 1344, 1275, 1138, 1026, 1003, 866, 802, 777, 679  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriomethanol):  $\delta$  8.47 (d,  $J = 1.4$  Hz, 1H), 7.94 (dd,  $J = 7.8, 1.5$  Hz, 2H), 7.50 (t,  $J = 7.8$

Hz, 1H), 7.40 (s, 2H, H-5), 4.75 (s, 4H, CH<sub>2</sub>OH), 4.42 (bs, 2H, OH); <sup>13</sup>C nmr (deuteriomethanol): δ 168.9 (C-2), 159.6 (C-4), 135.6, 131.0, 129.0, 125.1, 116.5 (C-5), 61.3 (CH<sub>2</sub>OH); ms: m/z 305 (M<sup>+</sup>, 100), 304 (73), 303 (44), 287 (22), 286 (36), 257 (21); R<sub>f</sub> 0.45 (ethyl acetate).

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 55.24; H, 3.97; N, 9.20. Found: C, 54.99; H, 4.12; N, 9.38.

1,3-Bis(thiazolyl)benzene Coronand 18-C-5 (BBC 18-C-5) (6) and 1,3-Bis(thiazolyl)benzene Coronand 34-C-10 (BBC 34-C-10) (7).

A mixture of **5** (61 mg, 0.2 mmole) and potassium hydride (16 mg, 0.4 mmole) in 100 ml of tetrahydrofuran was heated under reflux for 2 hours. A solution of diethylene glycol di-*p*-tosylate (83 mg, 0.2 mmole) in tetrahydrofuran (10 ml) was added to the resulting mixture via syringe pump for 2 hours. The mixture was refluxed an additional 6 hours. After removal of the solvent at reduced pressure, the residue was extracted with ethyl acetate. The organic layer was washed with 5% hydrochloric acid solution and brine, dried over sodium sulfate and evaporated. Analysis by tlc (silica gel, methanol/ethyl acetate 1:19) indicated two components with R<sub>f</sub>'s of 0.48 and 0.21. These were separated by preparative silica gel thin layer chromatography (methanol-ethyl acetate 1:19) to give **6** (11 mg, 14%) and **7** (18 mg, 12%), respectively.

Compound **6** was obtained as an oil; ir (neat): 3091, 2925, 2886, 1513, 1455, 1358, 1262, 1216, 1142, 1092, 1038, 961, 922, 845, 799, 749, 710, 695 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 9.29 (s, 1H), 7.70 (dd, J = 7.8, 2.1 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.08 (s, 2H, H-5), 4.71 (s, 4H, thiazole-CH<sub>2</sub>), 4.07 (t, J = 11.1 Hz, 4H), 3.85 (t, J = 11.1 Hz, 4H); <sup>13</sup>C nmr (deuteriochloroform): δ 167.0 (C-2), 155.3 (C-4), 134.4, 129.1, 127.1, 127, 115.1 (C-5), 70.8 (thiazole-CH<sub>2</sub>), 70.7, 68.1; ms: m/z 374 (M<sup>+</sup>, 74), 345 (32), 332 (30), 305 (39), 289 (93), 270 (80), 199 (47), 71 (100); R<sub>f</sub> 0.48 (ethyl acetate-methanol 19:1); hrms: Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: 374.0759. Found: 374.0761.

Compound **7** was obtained as a solid in 12% yield, mp 158-159° (dichloromethane and hexane); ir (potassium bromide): 3103, 2918, 2872, 1606, 1520, 1449, 1362, 1281, 1140, 1101, 1047, 999, 860, 799, 683 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 8.32 (t, J = 1.8 Hz, 2H), 7.96 (dd, J = 7.8 and 1.8 Hz, 4H), 7.43 (t, J = 7.8 Hz, 2H), 7.32 (s, 4H, H-5), 4.78 (s, 8H, thiazole-CH<sub>2</sub>), 3.82 (m, 8H), 3.77 (m, 8H); <sup>13</sup>C nmr (deuteriochloroform): δ 167.3 (C-2), 155.2 (C-4), 134.3, 129.5, 127.7, 124.7, 116.3 (C-5), 70.8 (thiazole-CH<sub>2</sub>), 70.2, 69.3. R<sub>f</sub> 0.21 (ethyl acetate-methanol 19:1).

*Anal.* Calcd. for C<sub>36</sub>H<sub>36</sub>N<sub>4</sub>O<sub>6</sub>S<sub>4</sub>: C, 57.73; H, 4.84; N, 7.48. Found: C, 57.76; H, 4.88; N, 7.22.

1,3-Bis(thiazolyl)benzene Coronand 21-C-6 (BBC 21-C-6) (8).

The procedure to prepare **8** was the same as for the preparation of **6** starting with **5** (61 mg, 0.2 mmole), triethylene glycol di-*p*-tosylate (92 mg, 0.2 mmole), potassium hydride (16 mg, 0.4 mmole) in tetrahydrofuran (200 ml). Compound **8** was obtained as a solid in 55% yield, mp 116-117° (dichloromethane and hexane); ir (potassium bromide): 3092, 2882, 2863, 1631, 1468,

1439, 1348, 1250, 1206, 1144, 1103, 1053, 999, 966, 920, 795, 762, 743, 712, 681 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 9.07 (s, 1H), 7.77 (dd, J = 7.6, 2.1 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.29 (s, 2H, H-5), 4.70 (s, 4H, thiazole-CH<sub>2</sub>), 3.96 (s, 4H), 3.93 (m, 4H), 3.83 (m, 4H); <sup>13</sup>C nmr (deuteriochloroform): δ 167.7 (C-2), 154.6 (C-4), 134.4, 129.2, 128.2, 124.7, 117.5 (C-5), 71.1 (thiazole-CH<sub>2</sub>), 70.7, 70.0, 68.1; ms: m/z 419 (M<sup>+</sup> + 1, 28), 301 (70), 285 (63), 270 (100), 199 (39); R<sub>f</sub> 0.5 (ethyl acetate-methanol, 3:1).

*Anal.* Calcd. for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 57.40; H, 5.30; N, 6.69. Found: C, 57.34; H, 5.40; N, 6.33.

1,3-Bis(thiazolyl)benzene Coronand 24-C-7 (BBC 24-C-7) (9).

The procedure to prepare **9** was the same as for the preparation of **6** starting with **5** (61 mg, 0.2 mmole), tetraethylene glycol di-*p*-tosylate (101 mg, 0.2 mmole), potassium hydride (16 mg, 0.4 mmole) in tetrahydrofuran (200 ml). Compound **9** was obtained as an oil in 44% yield; ir (neat): 3095, 2921, 2877, 1466, 1439, 1250, 1204, 1096, 1038, 965, 806, 749, 718, 687 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 8.99 (s, 1H), 7.76 (dd, J = 7.8, 1.8 Hz, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.26 (s, 2H, H-5), 4.76 (s, 4H, thiazole-CH<sub>2</sub>), 3.86 (m, 4H), 3.76 (m, 4H), 3.72 (s, 8H); <sup>13</sup>C nmr (deuteriochloroform): δ 167.4 (C-2), 155.2 (C-4), 134.5, 129.3, 128.0, 124.4, 116.9 (C-5), 71.0 (thiazole-CH<sub>2</sub>), 70.9, 70.8, 70.1, 68.6; ms: m/z 462 (M<sup>+</sup>, 32), 329 (24), 301 (100), 286 (70), 270 (55); R<sub>f</sub> 0.50 (ethyl acetate-methanol, 3:1); hrms: Calcd. for C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>: 462.1283. Found: 462.1267.

1,3-Bis(thiazolyl)benzene Coronand 28-C-8 (BBC 28-C-8) (10).

The procedure to prepare **10** was the same as for the preparation of **6** starting with **5** (61 mg, 0.2 mmole), pentaethylene glycol di-*p*-tosylate (109 mg, 0.2 mmole), potassium hydride (16 mg, 0.4 mmole) in tetrahydrofuran (200 ml). Compound **10** was obtained as an oil in 30% yield; ir (neat): 3106, 2921, 2863, 1455, 1354, 1250, 1100, 1041, 1003, 930, 799 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 8.82 (s, 1H), 7.86 (dd, J = 7.8, 1.8 Hz, 2H), 7.48 (t, J = 7.8 Hz, 1H), 7.38 (s, 2H, H-5), 4.77 (s, 4H, thiazole-CH<sub>2</sub>), 3.84 (m, 4H), 3.75-3.66 (m, 12H), 3.66 (s, 4H); <sup>13</sup>C nmr (deuteriochloroform): δ 167.4 (C-2), 155.2 (C-4), 134.5, 129.3, 128.1, 124.4, 116.9 (C-5), 71.0 (thiazole-CH<sub>2</sub>), 70.9, 70.8, 70.1, 68.6; ms: m/z 506 (M<sup>+</sup>, 21), 329 (27), 301 (100), 285 (63), 270 (37); R<sub>f</sub> 0.5 (ethyl acetate-methanol, 3:1); hrms: Calcd. for C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: 506.1545. Found: 506.1527.

#### Acknowledgment.

This work was supported by the grants from the Center for Biofunctional Molecules and the Basic Science Research Institute Program (1998-015-D00174), Ministry of Education, Korea.

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