Synthesis of Dihomocalix[4]naphthalenes: First Members of a New Class of [1.2.1.2](1,3)Naphthalenophanes

Paris E. Georghiou,* Zhaopeng Li, Muhammad Ashram, and David O. Miller†

Department of Chemistry and X-ray Crystallography Unit, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

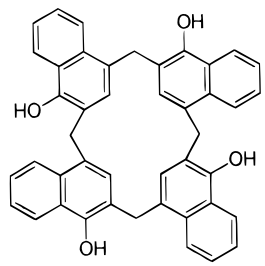
Received November 22, 1995

In 1944 Zincke and Ziegler[1] first reported that cyclic oligomeric compounds are formed by the acid- or base-catalyzed reaction of substituted phenols with formaldehyde. It is only in recent years, however, that the overwhelming wealth of research has appeared dealing with the chemistry and properties of what have since become known as the calix[*n*]arenes.[2,3] A factor which has caused this has been the realization that the calixarenes are a readily available and versatile group of "host" molecules that can, among other applications, be used to probe various aspects of enzyme function.[4] In a recent review, Brodesser and Vögtle present the argument that no single type of molecular structure can provide a basis for the mimicry of all enzyme behavior[5] and thus new molecules whose architecture can be controlled are desirable. This paper reports the synthesis of a new class of such molecules.

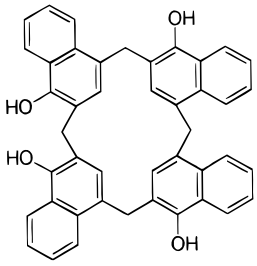
The syntheses of several novel structures which are analogous to the calixarenes and which we named "calix[4]naphthalenes" were recently reported.[6,7] These calix[4]naphthalenes are inherently chiral[8] cyclic oligomers of 1-naphthol and formaldehyde and were originally synthesized by base-catalyzed condensation of 1-naphthol and formaldehyde. Since this condensation afforded only three (**1**−**3**) of four possible isomers and involved a tedious purification step, we developed convergent synthetic approaches to all four isomers, including **4**.[9] In this paper we report the syntheses of the first examples of homologues ("dihomocalix[4]naphthalenes") of these compounds (**5**−**7**) which will allow for their evaluation as new potential host molecules and supramolecular building blocks in general.

Results and Discussion

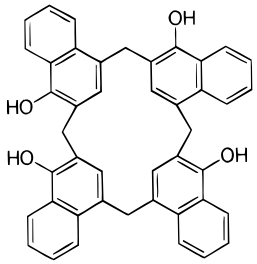
Calix[4]naphthalenes **1**−**4** can be considered to be examples of [1.1.1.1](1,3)naphthalenophanes, and the homologues **5** and **6** to be examples of [2.1.2.1](1,3)-naphthalenophanes. The procedures employed to synthesize **5** and **6** were methods commonly employed in cyclophane chemistry.[10,11] Scheme 1 outlines the procedure used to synthesize **5**. The precursor dithia compound **7** was synthesized by a nucleophilic coupling of the corresponding bis(mercaptomethyl) **8** with **9**. Bis(bromomethyl) **9** was formed from the corresponding bis(hydroxymethyl) **10**, which, in turn, was obtained by $LiAlH_4$ reduction of the bisester **11**. Photochemical irradiation[11] of **7** in triethyl phosphite afforded **5** in 22% yield.



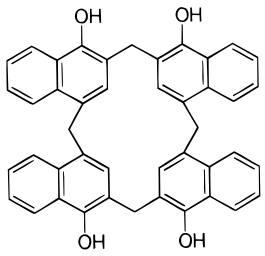
1



2



3



4

The ambient temperature ^{1}H NMR spectrum of **7** indicates that it is conformationally flexible since all signals are sharp and well-defined, implying that there is an averaging of the nonequivalent resonances. Using variable-temperature (VT) ^{1}H NMR, it can be seen (Figure 1) that the signal due to the *para*−*para* methylene bridge at $\delta = 4.86$ (at −20 °C) does not broaden significantly or split, even on cooling to temperatures of at least −65 °C. The signal due to the sulfide methylene bridges which appears at $\delta = 3.86$ (at −20 °C) by contrast has a coalescence temperature of approximately −45 °C. The methoxy signal which originally appears at $\delta = 3.35$ (at −20 °C) separates into three broad signals which are centred at $\delta = 4.00$, 3.35, and 2.85 (at −65 °C) in a 1:1:2 ratio, respectively. Of these signals, the one centered at $\delta = 2.85$ suggests a conformer in which two methoxy groups are shielded by two opposing naphthalene rings. A similar finding was noted for the tetramethoxy derivative of calixnaphthalene **3**.[9]

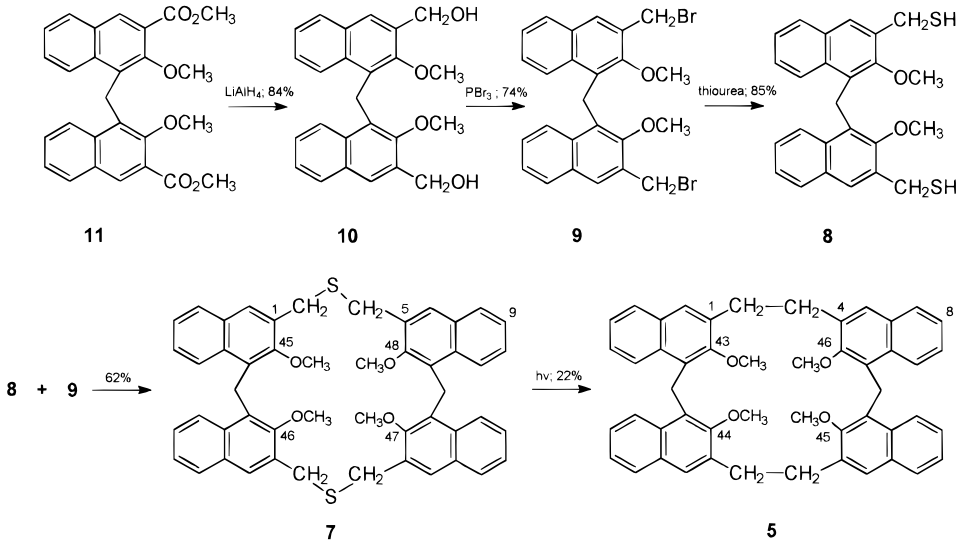
The ambient temperature ^{1}H NMR spectrum of **5** (Figure 2) indicates conformational flexibility similar to that seen with **7**. However, a coalescence temperature of approximately −20 °C can be discerned for the signal at $\delta = 3.06$ due to the ethano bridges. Unlike what was observed in the VT NMR spectra for **7**, the signal due to the methoxy groups in **5** does not divide, even on cooling to −60 °C. The *para*−*para* methylene bridge at $\delta = 4.68$ does not broaden or split, either. Since the methoxy groups appear as a broad singlet at $\delta = 2.91$ (as opposed to $\delta = 3.29$ in the case of **7**), this suggests that they are

† X-ray Crystallography Unit.

(1) Zincke, A.; Ziegler, E. *Ber.* **1944**, *77*, 264.
(2) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K., 1989.
(3) Vicens, J.; Böhmer, V. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(4) Gutsche, C. D. *Acc. Chem. Res.* **1983**, *16*, 161.
(5) Brodesser, G.; Vögtle, F. In *Calixarenes 50th Anniversary: Commemorative Issue*; Vicens, J., Asfari, Z., Harrowfield, J. M., Eds.; Kluwer Academic Publishers: Dordrecht, 1994; p 111.
(6) Georghiou, P. E.; Li, Z. *Tetrahedron Lett.* **1993**, *34*, 2887.
(7) Georghiou, P. E.; Li, Z. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 55.
(8) Böhmer, V.; Kraft, D.; Tabatabai, M., ref 5, p 17.
(9) Georghiou, P. E.; Ashram, M.; Li, Z.; Chaulk, S. G. *J. Org. Chem.* **1995**, *60*, 7284.
(10) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.
(11) Yamoto, T.; Miyazawa, A.; Tashiro, M. *Chem. Ber.* **1993**, *126*, 2505.

S0022-3263(95)02065-2 CCC: $12.00

Scheme 1



shielded by the naphthalene rings, thus precluding a "crown"-like conformation in solution. In both **5** and **7** there still appears to be conformational flexibility at temperatures as low as −60 °C since their respective methylene protons do not appear as AB-type quartets.

We were able to obtain a X-ray diffraction single-crystal structure on **5**, which is depicted in Figure 3. This is the first X-ray structure that we have been able to obtain on a calixnaphthalene-type compound. In the solid state, the structure of **5** contains a center of symmetry as its only symmetry element and has a "1,2-alternate" type of orientation of the naphthalene rings. It can also be seen that one pair of symmetry-related methoxy groups (methoxy groups on C-43 and C-45) is situated closer (3.52 Å) to its opposite symmetry-related naphthalene planes than the other pair (6.26 Å).

The synthesis of **6** was achieved in a similar manner as **5** and is outlined in Scheme 2. The precursor dithia molecule **12** was synthesized in 85% yield by reacting bis-(mercaptomethyl) **13** (derived from **14**[9]) with **9**. Again, the ambient temperature ^{1}H NMR spectrum of **12** indicates conformational mobility since all signals are sharp and well-defined. The molecule has C_{2v} symmetry as evidenced by among other features the two singlets due to two sets of equivalent methoxyl groups at $\delta = 3.94$ (at C-5 and C-21) and $\delta = 3.34$ (at C-43 and C-44) and two sets of methylene protons at $\delta = 4.84$ and $\delta = 4.58$. Examination of molecular models indicates that of two possible C_{2v}-symmetry conformations one is crown-like

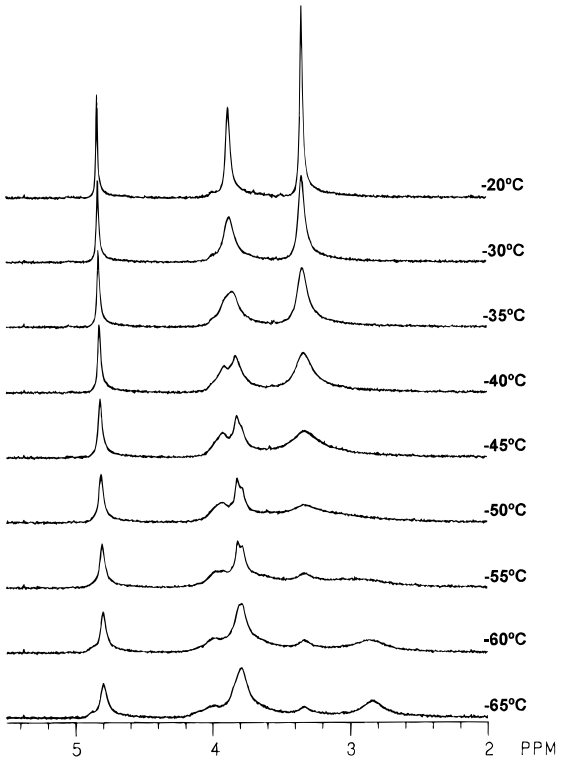


Figure 1. Variable-temperature ^{1}H NMR spectra of dithia-dihomocalix[4]naphthalene **7**.

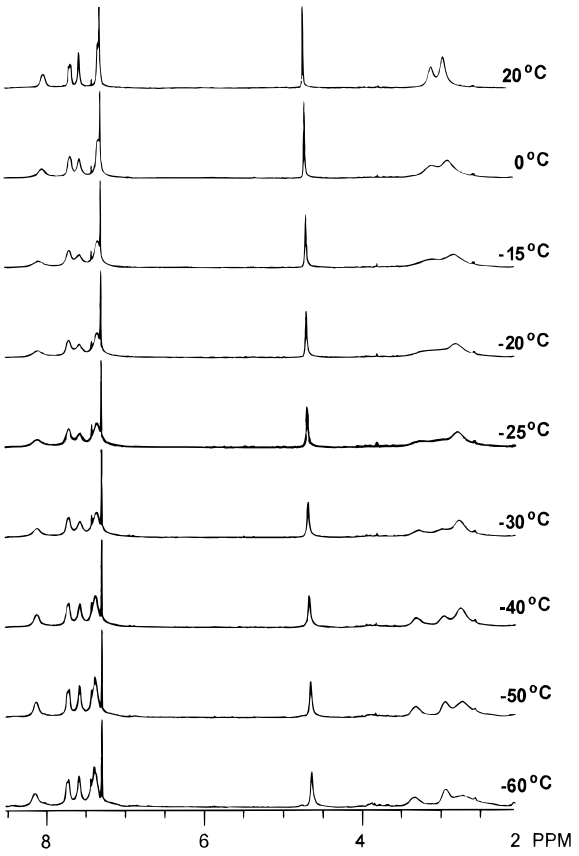


Figure 2. Variable-temperature ^{1}H NMR spectra of dihomocalix[4]naphthalene **5**.

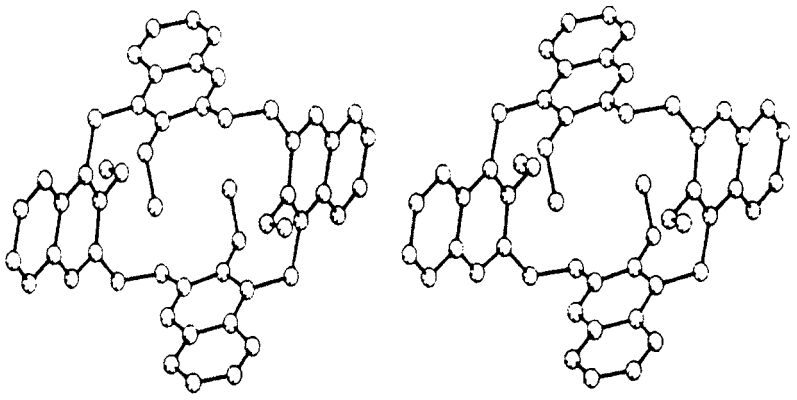
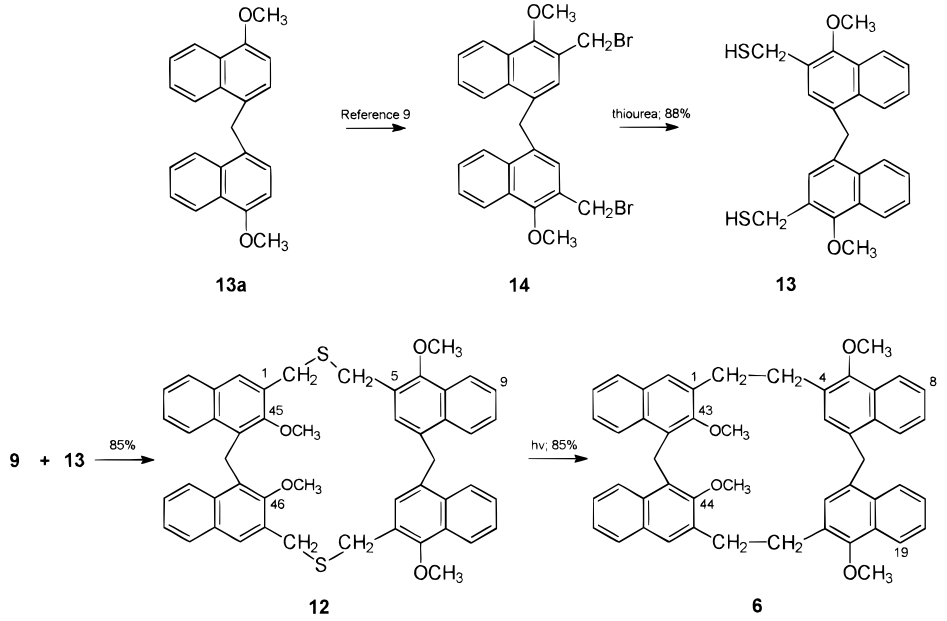


Figure 3. Stereoview of **5**.

Scheme 2



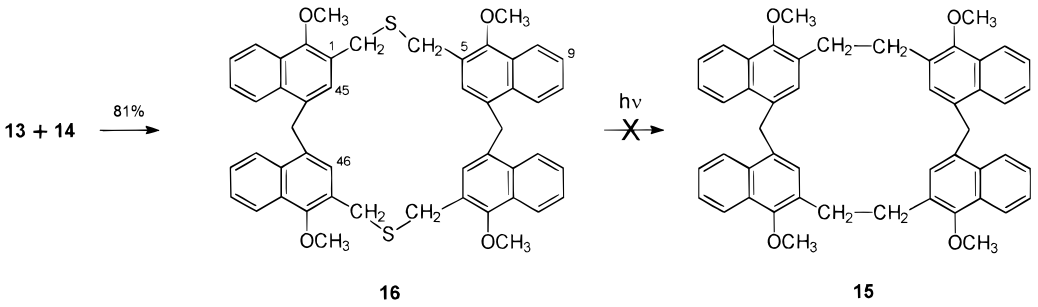
and the other is 1,2-alternate-like. The latter conformation is the only one which can account for the fact that one set of equivalent methoxyl groups is at higher field than the other. Further evidence for the assignment of the higher field signals to the intraannular methoxyl groups derives from the following complexation experiment conducted with **12**. When a THF solution of **12** was treated with a silver nitrate solution,[12] a crystalline product (**12a**) was obtained which unfortunately was not suitable for X-ray diffraction analysis. It's ^{1}H NMR spectrum however reveals that complexation has occurred since the higher field methoxyls now appear as a very broad signal centered at $\delta = 3.39$, whereas the lower field methoxyl signal at $\delta = 4.03$ is much sharper. Of the two methylene signals it is the higher field one at $\delta = 4.64$ which has broadened out. These findings are consistent with a complex formed between silver ion and half of the molecule, most likely with the methoxyls at C-43 and C-44, as revealed with molecular models. THF is also evident in the ^{1}H NMR spectrum and could be present as an inclusion molecule, but this has yet to be verified.

Photolytic conversion of **12** to **6** was achieved in 15% yield. The ambient temperature ^{1}H NMR spectrum of **6** also indicates conformational mobility, but it is evident that the ethano groups have restricted mobility since they appear as broad signals at $\delta = 3.04$ and $\delta = 2.85$. VT ^{1}H NMR indicates a first coalescence temperature at approximately this temperature. The signal of the pair of methoxy groups which is at $\delta = 3.16$ is also broader than that of the other pair which is at $\delta = 3.84$. This evidence is consistent with the assignment of the higher field signals to the intrannular methoxyls in both this product and in **7** and the corresponding compounds **6** and **5**, respectively.

Attempts to produce a third isomer **15** by an approach similar to that of photolytic conversion of **16** as was used for **5** and **6** has thus far not been successful (Scheme 3). Compound **16**, which was synthesized by reaction of **14** with its corresponding bis(mercaptomethyl) analogue **13**, is insoluble in all commonly available solvents, except warm DMSO. Its irradiation as a suspension in triethyl phosphite did not change the starting material. A silver ion complex (**16a**) can also be produced from **16**. Interestingly, **16a** is much more soluble than its precursor, but when a suspension of **16a** was irradiated as before in triethyl phosphite, the only change discernable was reversion back to **16**. Other procedures for the sulfur extrusion reaction have been investigated but with no success achieved. In summary, we have succeeded in synthesizing the first two members of a novel class of

(12) Xu, W.; Puddephatt, R. J.; Muir, K. W.; Torabi, A. A. *Organometallics* **1994**, *13*, 3054.

Scheme 3



naphthalenophanes or dihomocalixnaphthalenes and obtaining the first solid state structure of a calixnaphthalene-type of molecule. We are continuing our synthetic investigations into these and related compounds since they are potentially more versatile and possess larger cavities than the calix[4]arenes and the calix[4]-naphthalenes previously reported. Their complexation properties are also being further evaluated. These studies will be the subject of forthcoming reports.

Experimental Section

For general experimental procedures, see ref 9. All ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, and in CD_3Cl unless otherwise noted. Photochemical transformations were conducted in a Pyrex tube fitted with a reflux condenser and placed in a Rayonet reactor fitted with RPR 3500 Å lamps.

Dihomocalixnaphthalene (5). A solution of **7** (200 mg, 0.26 mmol) in triethyl phosphite (50 mL) was maintained under Ar and was stirred vigorously while being irradiated for 18 h. The solvent removed by vacuum distillation, and the residue was crystallized from CH_2Cl_2:hexane to give **5** (41 mg 22%) as colorless fine crystals, mp = 163−165 °C: ^{1}H NMR δ = 2.91 (br s, 12H), 3.06 (br s, 8H), 4.68 (s, 4H), 7.26−7.28 (m, 8H), 7.52 (s, 4H), 7.63−7.65 (m, 4H), 7.97−7.98 (m, 4H); ^{13}C NMR δ = 23.7, 30.2, 60.3, 123.5, 123.6, 124.7, 127.5, 127.6, 128.3, 130.7, 132.2, 134.7, 156.2; MS *m*/*z* (%) 709 (100), 677 (6), 537 (8), 354 (25), 308 (11), 265 (9), 185 (18); HRMS M^+ 708.3130, calcd for $C_{50}H_{44}O_4$ 708.3240.

X-ray Data for 43,44,45,46-Tetramethoxy[2.1.2.1](1,3)-naphthaleneophane (5). Crystal data for **5**: $C_{50}H_{44}O_4$, triclinic, space group *P*1 (No. 2), a = 10.343(3) Å, b = 11.240(6) Å, c = 8.992(4) Å, α = 96.15 (4)°, β = 110.13 (3)°, γ = 104.46°, Z = 1, D_{calc} = 1.267 g/cm^3, crystal size = 0.400 × 0.200 × 0.400 mm. Intensity data were measured at 299 K on a Rigaku AFC6S diffractometer with Mo Kα (λ = 0.710 69 Å) to $2\theta_{max}$ (deg) = 50.2°; 3304 unique reflections converged to a final R = 0.042, for 2392 reflections with $I > 2.00\sigma(I)$; R_w = 0.038, gof = 2.54. Atomic coordinates of the structure have been deposited with the Cambridge Crystallographic Data Centre. These coordinates are available, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EK, U.K.

Dihomocalixnaphthalene (6). A solution of **12** (96 mg, 0.13 mmol) in triethyl phosphite (50 mL) was maintained under Ar and was stirred vigorously while being irradiated for 22 h. The solvent was removed by vacuum distillation, and the residue was dissolved in a minimum volume of $CHCl_3$ and purified by preparative layer chromatography ($CHCl_3$:petroleum ether 50:50) to give **6** (13 mg 13%) as colorless fine crystals, mp = 153−155 °C: ^{1}H NMR δ = 2.85 (br s, 4H), 3.04 (br s, 4H), 3.16 (br s, 6H), 3.84 (s, 6H), 4.43 (s, 2H), 4.84 (s, 2H), 6.77 (s, 2H), 7.18−7.25 (m, 4H), 7.31−7.45 (m, 4H), 7.51 (s, 2H), 7.61 (dd, 2H), 7.74 (br dd, 2H), 7.87 (dd, 2H), 8.05 (dd, 2H); ^{13}C NMR δ = 23.9, 30.5, 31.1, 34.7, 60.7, 61.1, 61.9, 122.5, 123.4, 124.0, 124.1, 124.9, 125.2, 126.9, 127.9, 128.2, 128.3, 129.8, 130.6, 130.8, 131.9, 132.0, 134.9, 152.4, 155.8; MS *m*/*z* (%) 709 (21), 707 (100), 676 (5), 354 (17); HRMS M^+ 708.3230, calcd for $C_{50}H_{44}O_4$ 708.3240.

Dithiadihomocalixnaphthalene (7). A solution consisting of **8** (300 mg, 0.71 mmol) and **9** (370 mg, 0.72 mmol) was prepared in benzene (50 mL). This solution was added dropwise, over a 10 h period, into a solution of ethanolic KOH (230 mg in 120 mL of 95% ethanol). The mixture was stirred vigorously during the addition, and after the addition was completed, for an additional 12 h period. The mixture was neutralized with sulfuric acid, and the solvent was evaporated on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (200 mL), and the solution was washed with water (100 mL). The water washing was reextracted with two 50 mL portions of CH_2Cl_2, and the combined organic solutions were dried over anhydrous $MgSO_4$ and treated in the usual manner, to afford a solid product. Crystallization from chloroform:hexane gave **7** (342 mg, 62%) as colorless fine needles, mp > 300 °C dec: ^{1}H NMR δ = 3.29 (s, 12H), 3.86 (s, 8H), 4.81 (s, 4H), 7.26−7.36 (m, 8H), 7.71 (s, 4H), 7.72−7.75 (m, 4H), 7.93−7.96 (m, 4H); ^{13}C NMR δ = 24.1, 32.1, 61.7, 123.9, 124.4, 125.9, 128.4, 128.9, 129.1, 130.9, 131.3, 132.9, 155.5; +FAB MS (matrix: 3-nitrobenzyl alcohol) *m*/*z* (%) 794 (3), 772 (1); HRMS M^+ 772.2671, calcd for $C_{50}H_{44}O_4S_2$ 772.2681.

Bis-(2-methoxy-3-(mercaptomethyl)naphthyl)methane (8). A solution of **9** (2.0 g, 3.9 mmol) and thiourea (0.59 g, 7.8 mmol) in THF (100 mL) was refluxed for 4 h, under N_2. The solvent was evaporated on a rotary evaporator, and the residue was dissolved in 250 mL of aqueous 1% NaOH. The mixture was refluxed for 4 h, cooled to room temperature, and neutralized with 3 M HCl. The white precipitate was filtered and dried under vacuum. Flash chromatography of the crude product using 20:80 ethyl acetate:hexane afforded **8** (1.4g, (85%) as colorless crystals, mp 134−135 °C: ^{1}H NMR δ = 3.95 (s, 6H), 3.96 (s, 4H), 3.99 (s, 2H, exchangeable with D_2O), 4.95 (s, 2H), 7.21−7.26 (m, 4H), 7.60−7.63 (m, 2H), 7.64 (s, 2H), 8.12−8.15 (m, 2H); ^{13}C NMR δ = 23.0, 24.7, 62.7, 124.7, 124.8, 125.9, 127.8, 127.9, 129.0, 131.1, 132.9, 133.8, 153.6; MS *m*/*z* (%) 420 (100), 355 (20), 352 (22), 309 (16), 308 (14), 265 (12), 217 (24), 185 (180) 171 (61); HRMS M^+ 420.1235, calcd for $C_{25}H_{24}O_2S_2$ 420.1218.

Bis-(2-methoxy-3-(bromomethyl)naphthyl)methane (9). To a solution of **10** (0.50 g, 1.3 mmol) in CH_2Cl_2 (30 mL) was added PBr_3 (0.40 mL, 4.1 mmol), dropwise via a dropping funnel over 30 min. The reaction solution was stirred at room temperature for 4 h. Workup of the reaction was effected by diluting the mixture with an additional 20 mL of CH_2Cl_2 and washing with three 30 mL portions of water. After the solution was dried over $MgSO_4$ and filtered, the solvent was removed in the usual manner to afford, after flash chromatography (ethyl acetate:hexane 30:70), **9** (0.49 g, 74%), mp 191−193 °C: ^{1}H NMR δ = 4.05 (s, 6H), 4.80 (s, 4H), 4.95 (s, 2H), 7.22−7.29 (m, 4H), 7.63 (m, 2H), 7.75 (s, 2H), 8.11 (m, 2H); ^{13}C NMR δ = 23.0, 29.4, 62.9, 124.5, 124.8, 126.5, 128.1, 129.1, 130.4, 130.5, 130.9, 133.7, 153.6; MS *m*/*z* (%) 514 (70), 512 (35), 435 (20), 433 (18), 412 (7), 308 (18), 265 (61), 263 (63), 155 (100); HRMS M^+ 511.9994, calcd for $C_{25}H_{22}O_2Br_2$ 511.9986.

Bis-(2-methoxy-3-(hydroxymethyl)naphthyl)methane (10). To a mixture of $LiAlH_4$ (0.64 g 16.8 mmol) in anhydrous THF (30 mL) under Ar at −78 °C was added dropwise a solution of **11** (4.9 g, 11 mmol) in THF (40 mL) over 30 min. After the addition was complete, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The mixture was stirred for an additional 4 h at room temperature and was worked up by adding water dropwise until excess hydride decomposed, followed by the addition of 40 mL of aqueous 10% H_2SO_4. The organic layer was separated and washed with aqueous 5% $NaHCO_3$, followed by two 20 mL portions of saturated NaCl. After the solution was dried over

anhydrous $MgSO_4$ and filtered, the solvent was removed in the usual manner to afford, after vacuum drying, crude **10** (4.3 g). The crude product was sufficiently pure by TLC to be used for the subsequent step without further purification. For characterization, 50 mg of the crude reaction product was purified by p.l.c. using 30:70 ethyl acetate:hexane. Isolation of the major band afforded colorless crystalline **10** (42 mg, 84%),[13] mp 89−90 °C; ^{13}C NMR δ = 22.7, 61.5, 62.2, 124.4, 124.8, 126.0, 127.1, 128.3, 126.6, 131.1, 133.1, 153.8, 166.6; MS *m*/*z* (%) 388 (32), 352 (18), 339 (13), 337 (28), 325 (11), 323 (13), 321 (19), 309 (24) 265 (19), 252 (21); HRMS M^+ 388.1667, calcd for $C_{25}H_{24}O_4$ 388.1673.

Bis-(methyl-2-methoxy-3-naphthoyl)methane (11). A solution of 2-hydroxy-3-naphthoic acid (2.0 g, 10.6 mmol) and paraformaldehyde (0.43 g, 14. 2 mmol HCOH) in 0.5% H_2SO_4−glacial acetic acid (20 mL) was refluxed for 10 h. After the solution was cooled to room temperature, a light yellow precipitate formed which was filtered and washed twice with 5 mL portions of a saturated NaCl solution. The product was dried under vacuum to give 3.9 g (95%) of bis(2-hydroxy-3-naphthoyl)-methane as a light yellow powder, mp >300 °C. This was used directly in the following step. To a solution of 3.9 g of in CH_2Cl_2 (15 mL) were added water (30 mL), 0.5 mL of the phase-transfer catalyst Adogen, and aqueous 10% NaOH (10 mL). To the vigorously stirred mixture at room temperature were added dimethyl sulfate (6.5 mL, 60 mmol) dropwise over a period of 15 min at room temperature. The mixture was stirred at room temperature for an additional 10 h. After separation of the two layers, the aqueous layer was extracted twice with 20 mL portions of CH_2Cl_2. The solvent was removed on a rotary evaporator, and the residue was mixed with 10 mL water and diethyl ether (50 mL). The ether layer was separated and washed twice with 10 mL portions of aqueous 2.0 M NH_4OH in order to remove the excess dimethyl sulfate. The ether layer was washed twice with 60 mL portions of saturated NaCl and then was dried over anhydrous $MgSO_4$, filtered, and evaporated on a rotary evaporator. After the solution was dried under vacuum, the crude product was flash chromatographed using 40:60 ethyl acetate:hexane to give **11** (2.1 g 95%) as a cream-colored solid, mp 113−115 °C (lit.[13] mp 133 °C, methanol): ^{13}C NMR δ = 22.6, 52.3, 62.7, 123.7, 124.7, 125.2, 128.3, 129.3, 129.8, 130.0, 132.3, 135.2, 153.6, 166.8; MS *m*/*z* (%) 444 (100), 412 (81), 397 (76), 381 (8), 353 (56), 337 (43), 324 (50), 280 (20); HRMS M^+ 444.1578, calcd for $C_{27}H_{24}O_6$ 444.1573.

Dithiadihomocalixnaphthalene (12). A solution consisting of **9** (1.96 g, 3.83 mmol) and **13** (1.60 g, 3.82 mmol) was prepared in benzene (200 mL). This solution was added dropwise, over a 15 h period, into a solution of ethanolic KOH (2.5 g in 500 mL 95% ethanol) under N_2. The mixture was stirred vigorously during the addition and for an additional 24 h after the addition was completed. A colorless precipitate formed which was filtered by suction filtration, washed with water, and air dried. The product was flash chromatographed (CH_2Cl_2: petroleum ether 80:20) to give **12** (350 mg). The filtrate was concentrated to 50 mL, and the colorless crystals which separated were filtered and washed with aqueous 10% HCl, cold water, ethanol and finally petroleum ether to give **12** (2.15 g) whose melting point was identical to that of the first crop obtained from the first filtration. The total yield of **12** was 2.50 g (85%), mp 173−175 °C: ^{1}H NMR: δ = 3.34 (s, 6H), 3.81 (s, 4H), 3.82 (s, 4H), 3.94 (s, 6H), 4.58 (s, 2H), 4.84 (s, 2H), 6.87 (s, 2H), 7.32−7.36 (m, 4H), 7.39−7.44 (m, 2H), 7.48−7.54 (m, 2H), 7.69−7.74 (m, 4H), 7.88 (d, *J* = 8.1 Hz, 2H), 8.00−8.03 (m, 2H), 8.12 (dd, *J* = 8.1 Hz, 2H); ^{13}C NMR δ = 23.9, 30.8, 32.0, 34.9, 61.6, 62.7, 122.9, 123.7, 124.3, 124.5, 125.8, 126.0, 126.1, 128.2, 128.4, 128.6, 128.8, 129.0, 130.8, 131.2, 132.2, 132.6, 153.1, 155.3; MS *m*/*z* (%) 707 (3), 692 (2), 601 (5), 587 (3), 570 (3), 555 (8), 537 (4) 524 (6), 387 (48); HRMS M^+ 772.2658, calcd for $C_{50}H_{44}O_4S_2$ 772.2681.

Silver Ion Complex 12a. A solution of **12** (110 mg, 0.15 mmol) in 2.5 mL of THF was added dropwise to a solution of $AgNO_3$ (0.025g, 0.15 mmol) in THF (5.0 mL). The mixture was protected from light and stirred at room temperature for 24 h under Ar. The grey precipitate was filtered and vacuum dried to afford **12** (52 mg), mp 135−138 °C dec.): ^{1}H NMR δ = 1.61 (s, H_2O), 1.85 (m, THF), 3.40 (br, 6H), 3.75 (m, THF), 4.03 (s, 8H), 4.10 (br s, 6H), 4.64 (br, 2H), 4.85 (s, 2H), 6.93 (br, 2H), 7.33−7.50 (m, 6H), 7.53−7.55 (m, 4H), 7.69 (m, 2H), 8.08−8.19 (m, 6H); +FAB MS (matrix: 3-nitrobenzyl alcohol); *m*/*z* (%) 880 (M^+).

Bis-(4-methoxy-3-(mercaptomethy)lnaphthyl)methane (13). To a solution of **14**[9] (540 mg, 1.06 mmol) in DMSO (25 mL) was added thiourea (200 mg, 2.65 mmol) under N_2, and the solution was stirred at room temperature for 5 h. The reaction was quenched by pouring the solution into a cold aqueous 10% solution of NaOH (100 mL), and the resulting solution was left to stir at room temperature for 2 h. The mixture was neutralized at 0 °C by the addition of aqueous 10% HCl. The precipitate was filtered, washed repeatedly with water, and air dried to give **13** (391 mg, 88%), mp 134−135 °C: ^{1}H NMR δ = 1.76 (t, 2H), 3.82 (d, 4H), 4.02 (s, 6H), 4.75 (s, 2H), 7.02 (s, 2H), 7.57−7.44 (m, 4H), 7.98 (dd, *J* = 8.1 Hz, 2H), 8.17 (dd, 8.1 Hz, 2H); ^{13}C NMR δ = 23.1, 35.1, 62.7, 122.8, 124.4, 126.0, 126.2, 128.3, 129.1, 132.5, 132.5, 132.8, 152.0; MS *m*/*z* (%) 420 (66), 387 (45), 183 (100); HRMS M^+ 420.1240, calcd for $C_{25}H_{24}O_2S_2$ 420.1216.

Dithiadihomocalixnaphthalene (16). A solution consisting of **13** (0.28 g, 0.67 mmol) and **14** (0.34 g, 0.67 mmol) was prepared in benzene (40 mL). This solution was added dropwise, over a 10 h period, into a solution of ethanolic KOH (0.23 g in 110 mL of 95% ethanol), under N_2. The mixture was stirred vigorously during the addition and for an additional 18 h after the addition was completed. A colorless precipitate formed which was filtered by suction filtration, washed successively with aqueous 10% HCl, water, and ethanol, and, finally, air dried to give 0.42 g of **16** (81%), mp 285−290 °C: ^{1}H NMR δ = 3.76 (s, 8H), 3.85 (s, 12H), 4.61 (br s, 4H), 6.70 (s, 4H), 7.41−7.51 (m, 8H), 7.92−7.96 (m, 4H), 8.09−8.11 (m, 4H); ^{13}C NMR δ = 31.30, 34.47, 62.70, 122.69, 122.74, 122.82, 123.99, 124.16, 125.47, 125.53, 125.58, 125.81, 125.91, 125.96, 125.91, 125.96, 126.10, 128.17, 128.22, 128.25, 129.24, 129.40, 131.81, 132.78; MS *m*/*z* (%) 772 (5), 731 (6), 679 (6), 601 (16), 529 (10), 387 (20), 386 (22); HRMS M^+ 772.2695, calcd for $C_{50}H_{44}O_4S_2$ 772.2681.

Silver Ion Complex 16a. To a solution of **16** (121 mg, 0.157 mmol) in 6.0 mL of THF was added $AgNO_3$ (0.026 g, 0.15 mmol) in THF (5.0 mL). The mixture was protected from light and stirred at room temperature for 24 h under Ar. The grey precipitate was filtered and vacuum dried to afford **16a** (98 mg), mp 220−224 °C dec; ^{1}H NMR δ = 1.58 (s, H_2O), 1.85 (m, THF), 3.75 (m, THF), 3.98 (s, 12H), 4.25 (s, 8H), 4.72 (s, 4H), 7.15 (s, 4H), 7.52−7.60 (m, 4H), 8.17−8.09 (m, 4H); +FAB MS (matrix: 3-nitrobenzyl alcohol) *m*/*z* (%) 880 (M^+).

Acknowledgment. We are grateful to Mu'Tah University, Jordan for providing a scholarship to one of us (M.A.) and to Memorial University for providing financial assistance to Z.L. We thank Dr. C. R. Jablonski for the high-resolution NMR spectra and Dr. B. Gregory and Ms. M. Baggs for the mass spectra. All FAB/MS and some HRP/MS were obtained by Mr. D. Drummond, Department of Chemistry, University of New Brunswick.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectral data for the following new compounds: **5, 6, 7, 8, 9, 12, 12a, 13, 16, 16a**. Also included are signal assignments wherever determined. An ORTEP diagram of the X-ray structure of **5** is included (4 pages). This material is contained in libraries on microfiche, immediately follows the article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9520654

(13) Failla, S.; Finocchiaro, P.; Belsky, V. K.; Zavodnik, V. E.; Sobolev, A. N. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1993**, *15*, 247.