($M^+$, 2), 362 (100), 347 (29), 331 (23). Anal. Calcd for $C_{25}H_{24}O_8$: C, 66.37; H, 5.35. Found: C, 66.59; H, 5.52.

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**Registry No.** 5, 77422-59-4; 6, 67122-25-2; 7, 79919-76-9; 9, 77422-62-9; 10, 77422-60-7; 11, 76811-56-8; 12, 42082-94-0; 13, 13207-03-9; 14, 79899-11-9; 15, 79899-12-0; 16, 79899-13-1; 17, 79899-14-2; 18, 76527-50-9; 19, 79899-15-3; 20, 79899-16-4; 21, 77422-64-1; 22, 79899-17-5; 23, 65818-84-0; 24, 79899-18-6; 25, 79899-19-7; 26, 79899-20-0; 27, 79899-21-1; 28, 5471-63-6; 29, 79899-22-2; 30, 79899-23-3; 31, 79899-24-4; 32, 79899-25-5; 33, 79899-26-6; 1,4-dihydroxy-2,3-dimethylanthraquinone, 25060-18-8; 1,4-dimethoxy-2,3-dimethylanthraquinone, 67122-24-1; methyl vinyl ketone, 78-94-4; 2,3-butanedione, 431-03-8.

# Synthesis of Selectively Protected Tri- and Hexaamine Macrocycles

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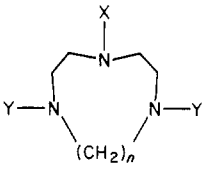
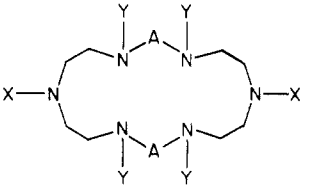
A general route to tri- and hexaamine macrocycles containing selectively protected diethylenetriamine units has been developed. Condensation of the *N'*-benzoyl-*N,N''*-bis(*p*-tolylsulfonyl)diethylenetriamine *N,N''*-disodium salt with bissulfonate esters of two-, four-, and six-carbon diols at high reactant concentrations gave the corresponding 9- and 18- (85% and <1%), 11- and 22- (30% and 20%), and 13- and 26- (56% and 17%) membered tri- and hexaamine macrocycles, respectively. The benzoyl group was selectively removed with potassium *tert*-butoxide in ca. 90% yield, and the macrocycles were conveniently separated by chromatography. Details of the synthetic procedures and characterization of the new selectively protected tri- and hexaamine macrocycles are described.

A significant property of macrocyclic polyamines is their ability to form stable complexes with transition metal ions. In this regard, cyclic tetraamines have been the most extensively studied macrocycles.[1,2] However, there is now considerable interest in elucidating the coordination properties of tri- and hexaamine macrocycles due to the novel structural features of the resulting metal complexes. Recent studies[3-5] with small, cyclic triamines such as **1a** ($n$ = 2, 3) indicate that the metal complexes have cis coordination geometries and distorted structures. Current work with the larger hexaamines **2a** ($n$ = 5)[6] and **2b**[7] shows that they readily bind two metals to yield discrete binuclear complexes. Binuclear compounds of these ligands may be especially useful as models for bimetallic metalloproteins and as bimetallic catalysts.

Synthesis of the triamines **1a** ($n$ = 2, 3) is conveniently accomplished by using Richman and Atkins'[8] modification of the method of Koyama and Yoshino.[9] The symmetric 18-membered hexaamine **2a** ($n$ = 2) has been synthesized by an adaptation of this general procedure.[10] The synthetic method relies on the condensation of bissulfonamide sodium salts and compounds having sulfonate ester leaving groups to facilitate ring closure at high reactant concentrations. This obviates the need for employing high-dilution or template techniques. When compounds **1b** ($n$ = 5, 6) were synthesized by this procedure, it was noted that the corresponding 2:2 cyclization products **2c** were also formed in 10-15% yield.[8] It has been suggested[11] that restricted rotation in the tosylated reactants (i.e., internal entropy effects) are the reason for the high yields achieved in these cyclizations. We are unaware of any reports detailing the application of this procedure to provide selectively protected macrocycles of types **1d** and **2f**, although this possibility has been mentioned as an extension of this method.[8] A route to the 24-membered selectively protected hexaamine **2d** which uses high-dilution methods in the



**1a**, X = Y = H
**b**, X = Y = tosyl
**c**, X = benzoyl; Y = tosyl
**d**, X = H; Y = tosyl



**2a**, X = Y = H; A = $(CH_2)_n$
**b**, X = Y = H; A = $(CH_2CH_2)_2O$
**c**, X = Y = tosyl; A = $(CH_2)_n$
**d**, X = H; Y = tosyl; A = $(CH_2CH_2)_2O$
**e**, X = benzoyl; Y = tosyl; A = $(CH_2)_n$
**f**, X = H; Y = tosyl; A = $(CH_2)_n$

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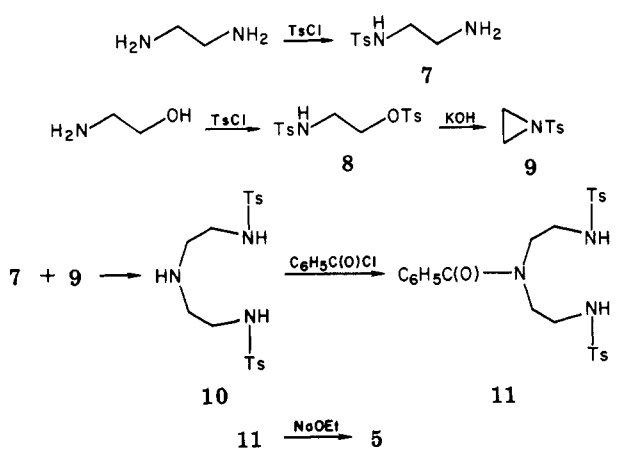
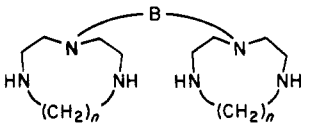
Scheme I

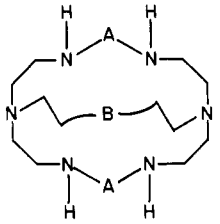


cyclization step has been reported.[12]

Our interest in the metal complexation properties of the modified diethylenetriamine-containing macrocycles **1** (as a function of different ring sizes and X, Y substituents) as well as the potentially binucleating macrocycles **3**[13] and **4**[12] led us to investigate the synthesis of selectively pro-

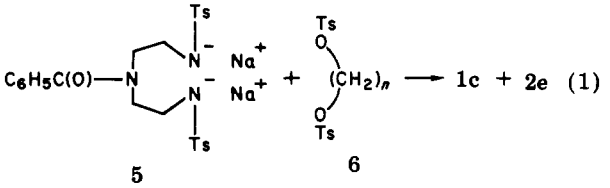


3, B = bridge (e.g., *p*-xylyl)



4a, A = $(CH_2CH_2)_2O$; B = $(N(H)CH_2CH_2)_2O$
b, A = $(CH_2)_n$; B = $(CH_2)_m$

tected polyamines **1d** and **2f** of varying ring sizes. Consequently, we examined the condensation of the selectively protected diethylenetriamine bissulfonamide salt **5** and a series of bissulfonate esters **6** where $n$ = 2, 4, 6 (see eq 1)



(1)

5 6

to determine the efficiency of the cyclizations and product distribution ratios for formation of small and large rings. We report here the convenient synthesis developed for the new selectively protected macrocyclic polyamines and the product distribution results.

## Results and Discussion

The selectively protected diethylenetriamine **10** was readily prepared in large quantities from reaction of the monotosylated ethylenediamine **7** and *N*-tosylaziridine **9** (see Scheme I) in ca. 75% yield. Compound **7** was synthesized by reacting a threefold excess of ethylenediamine with tosyl chloride.[14] Removal of bissulfonamide byproduct from **7** was readily accomplished by treatment with MeOH, in which only the monosulfonamide is appreciably soluble. The tosylaziridine **9** used in this sequence was conveniently obtained from the ditosylated ethanolamine **8** in a two-phase reaction. It was isolated as a white crystalline solid in 90% yield. Treatment of **10** with benzoyl chloride resulted in high-yield conversion to the selectively protected triamine **11**. The benzoyl protecting group was chosen since it was expected to provide efficient cyclization in the ring-closure reaction[8,11] due to restricted rotation of the amide linkage, to be stable to the cyclization conditions, and to be selectively removed in high yield after the ring closure. The disodium salt of the selectively protected bissulfonamide **5** was prepared by slight modification of the reported procedure for the tritosylated triamine analogue.[10] The bissulfonate esters **6** ($n$ = 2, 4, 6) were prepared by reaction of the appropriate diol with tosyl chloride in pyridine[15,16] and were obtained as highly pure white crystalline solids upon recrystallization from ethanol.

The ring-closure reaction (eq 1) gave a high yield of cyclized product when $n$ = 2 (85% **1c**, <1% **2e**), although cyclization yields were poorer with longer chain lengths ($n$ = 4, 30% **1c**, 20% **2e**; $n$ = 6, 56% **1c**, 17% **2e**). These results agree reasonably well with those previously reported[8] for the reaction of the tritosylated diethylenetriamine analogue, except that the yield of **1c** ($n$ = 4) is unusually low. The overall cyclization yield of ca. 50% was reproducibly obtained in several experiments. It is not obvious why the yields in the case of $n$ = 4 are consistently low. Molecular models do not indicate any unusual steric constraints for this case compared to $n$ = 2 and $n$ = 6. The presence of an impurity would not seem to be consistent with the relatively high yield of the 2:2 cyclization product. The 1:1 and 2:2 selectively protected macrocycles were separated from one another by column chromatography on silica. The remaining crude product contained presumably polymeric materials which were relatively insoluble and remained as an immobile band at the origin of the chromatography column under conditions where the rings were quite mobile.

The selective removal of the benzoyl group was accomplished in ca. 90% yield by the procedure of Gassman[17] for the hydrolysis of tertiary amides, using potassium *tert*-butoxide, to give the di- and tetratosylamides **1d** and **2f** from **1c** and **2e** respectively. This method is conveniently carried out on the crude reaction mixture obtained from the ring-closure reaction. Separation of the product macrocycles by chromatography is somewhat easier than for the selectively protected precursors.

The analyses of the products indicate in several cases the presence of residual solvent ($CH_2Cl_2$) which is not readily removed by drying in vacuo. This affinity of macrocycles for solvent has previously been noted.[18]

In conclusion, a route leading to the synthesis of new selectively protected triaza and hexaaza macrocycles has been developed. These rings can readily be deprotected

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to give free amines. Work is currently underway in our laboratory to prepare more complex ligands such as **3** and **4** from these compounds. In addition, we are investigating a synthetic route leading exclusively to the cyclic hexaamines.

## Experimental Section

All reagents (Aldrich, Fisher) were used as supplied unless otherwise noted. $^1$H NMR spectra were obtained on a Perkin-Elmer R-12 magnetic resonance spectrometer ($CDCl_3$ solvent, $Me_4Si$ reference unless otherwise noted). Infrared spectra were recorded as KBr pellets, using a Unicam SP1100 infrared spectrophotometer. Melting points were determined on a Laboratory Devices Mel-Temp and are uncorrected. Molecular-weight determinations were made on a Hitachi Perkin-Elmer 115 vapor pressure osmometer, using $CH_2Cl_2$ as the solvent. Analyses were performed by Micro-Analysis, Inc., Wilmington, DE.

***N*-(2-Aminoethyl)-*p*-tolylsulfonamide (7).** The procedure of Kirsanov and Kirsanova[14] was followed to provide a white solid, which was recrystallized from hot $H_2O$ to give 64 g (60%) of white plates: mp 124.5–126.0 °C (lit.[14] mp 122–123 °C); $^1$H NMR ($D_2O$, external $Me_4Si$) $\delta$ 7.73 (dd, 4 H), 2.82 (m, 7 H), 2.46 (s, 3 H); IR 3360 (br), 1300 (s), 1150 (s).

***N*-[2-[(*p*-Tolylsulfonyl)oxy]ethyl]-*p*-tolylsulfonamide (8).** A modification of the procedure of Hope and Horncastle[19] was used to obtain compound **8**, a yellowish solid. Recrystallization from EtOH afforded a white solid: 138 g (68%); mp 86.5–88.5 °C (lit.[19] mp 86–87 °C); $^1$H NMR $\delta$ 7.55 (dd, 8 H), 5.27 (t, 1 H), 4.04 (t, 2 H), 3.20 (m, 2 H), 2.42 (s, 6 H); IR 3280 (s), 1360 (s), 1320 (s), 1180 (s), 1145 (s).

***N*-(*p*-Tolylsulfonyl)aziridine (9).** A solution of 20% aqueous KOH (375 mL) was rapidly added to **8** (93.5 g, 0.253 mol) in 2 L of benzene. The two-phase mixture was vigorously stirred, resulting in the appearance of a pink color and a white solid. The reaction was monitored by TLC with silica and was complete in 0.5 h. The mixture was then shaken with $H_2O$ and the benzene solution dried over $Na_2SO_4$. Evaporation provided the white crystalline product: 46.9 g (94%); mp 63–64 °C (lit.[20] mp 64.2–64.4 °C); $^1$H NMR $\delta$ 7.55 (dd, 4 H), 2.41 (s, 4 H), 2.31 (s, 3 H); IR 1595 (sh), 1318 (s), 1155 (s). Occassionally, batches were found to melt at 52.5–53.0 °C, in agreement with an earlier literature value of 52 °C.[21] No difference in spectra or reactivity was noted.

***N*,*N*″-Bis(*p*-tolylsulfonyl)diethylenetriamine (10).** Compound **7** (45.2 g, 0.211 mol) was dissolved in $CH_3CN$ (1 L, dried over molecular sieves) and heated to reflux under an inert atmosphere. **9** (41.6 g, 0.211 mol) in 0.5 L of $CH_3CN$ was added dropwise over a period of several hours. The mixture was cooled and evaporated to leave a yellow oil, which was crystallized from $CH_2Cl_2$/ether to give **10** (66.5 g, 77%) as a white solid: mp 59–61 °C; $^1$H NMR $\delta$ 7.55 (dd, 8 H), 4.32 (br, 3 H), 2.95 (m, 4 H), 2.62 (m, 4 H), 2.42 (s, 6 H); IR 3300 (br), 1330 (s), 1155 (s).

***N*′-Benzoyl-*N*,*N*″-bis(*p*-tolylsulfonyl)diethylenetriamine (11).** Compound **10** (50.0 g, 0.121 mol) was slurried under $N_2$ in benzene (700 mL, distilled under $N_2$ from $CaH_2$) to which triethylamine (21.0 mL, 0.15 mol; distilled under $N_2$ from 2% phenyl isocyanate) had been added. Dropwise addition of benzoyl chloride (15.0 mL, 0.129 mol) was regulated to keep the temperature <50 °C. After the mixture was stirred overnight, the white solid was filtered and washed with benzene and $H_2O$. It was dissolved in $CH_2Cl_2$ and washed with $H_2O$ to remove residual triethylamine hydrochloride. The organic layer was dried with $K_2CO_3$ and evaporated to give a white solid. Recrystallization from $CH_2Cl_2$/hexane afforded 49.9 g (80%) of the white, crystalline product: mp 171.0–172.8 °C; $^1$H NMR $\delta$ 7.51 (m, 13 H), 5.79 (br, 2 H), 3.55 (m, 4 H), 3.15 (m, 4 H), 2.40 (s, 6 H); IR 3310 (br), 1620 (s), 1332 (s), 1148 (s), 1080 (s). Anal. Calcd for $C_{25}H_{29}N_3O_5S_2$: C, 58.23; H, 5.67; N, 8.15. Found: C, 58.34; H, 5.55; N, 8.04.

***N*′-Benzoyl-*N*,*N*″-bis(*p*-tolylsulfonyl)diethylenetriamine *N*,*N*″-Disodium Salt (5).** Compound **11** (30.2 g, 0.0586 mol) was slurried in absolute EtOH (300 mL) under $N_2$. Freshly prepared NaOEt (2.69 g, 0.117 mol of Na in 200 mL of EtOH) was added all at once. The solid rapidly dissolved, leaving a clear solution. After several hours, the solvent was removed by rotary evaporation under $N_2$. Distilled benzene was added several times and evaporated to remove residual EtOH. The white solid was dried under vacuum and stored in a drybox. The product was usually used in subsequent reactions without further treatment; however, it can be recrystallized from anhydrous EtOH under $N_2$. A yield of >95% was obtained; IR shows the loss of the tosylamide proton (3460 cm$^{-1}$ absent).

**General Procedure for Synthesis of the Bissulfonate Esters (6).** The diol (0.0273 mol) was dissolved in dry pyridine (200 mL) in a flask that could be tightly stoppered. The solution was chilled to 0 °C in an ice bath. Solid tosyl chloride (21 g, 0.108 mol) was then added in increments over a period of 1 h, and the orange solution was refrigerated overnight. The mixture was poured into 1 L of ice/$H_2O$ and 50 mL of concentrated HCl to give a white solid, which was recrystallized from absolute EtOH to give the bissulfonate esters in 60–80% yield.

**1,2-Bis[(*p*-tolylsulfonyl)oxy]ethane (6, *n* = 2):** mp 109–111 °C (lit.[22] mp 126 °C); $^1$H NMR $\delta$ 7.58 (dd, 8 H), 4.20 (s, 4 H), 2.46 (s, 6 H); IR 1598 (sh), 1363 (s), 1172 (s).

**1,4-Bis[(*p*-tolylsulfonyl)oxy]butane (6, *n* = 4):** mp 67.5–69.5 °C (lit.[22] mp ~70 °C); $^1$H NMR $\delta$ 7.70 (dd, 8 H), 4.06 (m, 4 H), 2.44 (s, 6 H), 1.72 (m, 4 H); IR 1600 (sh), 1368 (s), 1168 (s).

**1,6-Bis[(*p*-tolylsulfonyl)oxy]hexane (6, *n* = 6):** mp 70.0–71.5 °C (lit.[22] mp ~70 °C); $^1$H NMR $\delta$ 7.54 (dd, 8 H), 3.97 (t, 4 H), 2.42 (s, 6 H), 1.46 (m, 8 H); IR 2980–2850 (m), 1595 (sh), 1354 (s), 1168 (s).

**General Procedure for Synthesis of the Selectively Protected Macrocycles (1c and 2e).** Compound **5** (1.79 mmol) was dissolved in DMF (10 mL; dried over molecular sieves) under a $N_2$ atmosphere and heated to 95 °C. A solution of the appropriate bissulfonate ester **6** (*n* = 2, 4, or 6; 1.79 mmol) in DMF (5 mL) was added dropwise. The temperature was maintained for 2 h, after which the solution was allowed to cool to room temperature and 150 mL of $H_2O$ was added to precipitate the crude product. Separation of the tri- and hexaamine products for each *n* was effected by column chromatography on silica gel, as noted below. The products were recrystallized from $CH_2Cl_2$/hexane.

**Cyclization Results for *n* = 2. 4-Benzoyl-1,7-bis(*p*-tolylsulfonyl)-1,4,7-triazacyclononane (1c):** collected as the most mobile component upon elution with $CHCl_3$; isolated as a white solid, 85%; mp 108–110 °C; $^1$H NMR $\delta$ 7.48 (m, 13 H), 3.83 (br, 4 H), 3.45 (br, 8 H), 2.42 (s, 6 H); IR 1635 (s), 1600 (sh), 1345 (s), 1153 (s); mol wt calcd 542, found 508. Anal. Calcd for $C_{27}H_{31}N_3O_5S_2 \cdot 0.5CH_2Cl_2$: C, 56.54; H, 5.52. Found: C, 56.43; H, 5.59.

**4,13-Dibenzoyl-1,7,10,16-tetrakis(*p*-tolylsulfonyl)-1,4,7,10,13,16-hexaazacyclooctadecane (2e):** <1%; not characterized.

**Cyclization Results for *n* = 4. 4-Benzoyl-1,7-bis(*p*-tolylsulfonyl)-1,4,7-triazacycloundecane (1c):** eluted with 0.25% MeOH/$CH_2Cl_2$ and collected as the first mobile band; isolated as a white solid, 30%; mp 145–147 °C; $^1$H NMR $\delta$ 7.46 (m, 13 H), 3.85 (m, 4 H), 3.33 (m, 8 H), 2.40 (s, 6 H), 2.00 (br, 4 H); IR 1634 (s), 1599 (sh), 1340 (s), 1153 (s); mol wt calcd 570, found 555. Anal. Calcd for $C_{29}H_{35}N_3O_5S_2$: C, 61.14; H, 6.19. Found: C, 61.19; H, 6.34.

**4,15-Dibenzoyl-1,7,12,18-tetrakis(*p*-tolylsulfonyl)-1,4,7,12,15,18-hexaazacyclodocosane (2e):** eluted from the column as the second mobile component upon increasing the MeOH to 1%; isolated as a white solid, 20%; mp 221–222 °C; $^1$H NMR $\delta$ 7.45 (m, 26 H), 3.70 (br, 8 H), 3.25 (br, 16 H), 2.39 (s, 12 H), 1.70 (br, 8 H); IR 1622 (s), 1605 (sh), 1346 (s), 1158 (s); mol wt calcd 1139, found 1120. Anal. Calcd for $C_{58}H_{70}N_6O_{10}S_4 \cdot 2CH_2Cl_2$: C, 55.04; H, 5.70. Found: C, 55.19; H, 5.70.

**Cyclization Results for *n* = 6. 4-Benzoyl-1,7-bis(*p*-tolylsulfonyl)-1,4,7-triazacyclotridecane (1c):** isolated as a white solid from the most mobile band on silica with 0.1% MeOH/$CHCl_3$, 56%; $^1$H NMR $\delta$ 7.52 (m, 13 H), 3.07–3.70 (br, 12 H), 2.41 (s, 6 H), 1.63 (br, 8 H); IR 2980–2860 (m), 1648 (s), 1348 (s), 1149 (s).

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**4,17-Dibenzoyl-1,7,14,20-tetrakis(*p*-tolylsulfonyl)-1,4,7,14,17,20-hexaazacyclohexacosane (2e)**: isolated as a white solid from the second mobile band on silica with 0.1% MeOH/$CHCl_3$, 17% $^1H$ NMR $\delta$ 7.44 (m, 26 H), 3.65 (br, 8 H), 3.14 (br, 16 H), 2.41 (s, 12 H), 1.35 (m, 16 H); IR 3000-2860 (s), 1645 (s), 1350 (s), 1158 (s).

**General Procedure for Deprotection of Selectively Protected Macrocycles.** The crude reaction mixture (**1c** and **2e**, $n$ = 6; 0.895 mequiv of benzoyl) was dissolved in THF (60 mL; distilled under $N_2$ from Na/benzophenone). To this was added $H_2O$ (3.6 mmol) and sublimed potassium *tert*-butoxide (1.23 g, 11.0 mmol). The brown slurry was refluxed under a $N_2$ atmosphere until TLC analysis on silica showed the reaction was complete (several hours). Addition of ice caused the precipitation of the crude product, a tan solid. The rings were separated by column chromatography on silica gel with $CHCl_3$/MeOH.

**1,7-Bis(*p*-tolylsulfonyl)-1,4,7-triazacyclotridecane (1d, *n* = 6)**: eluted as the first mobile band, using 0.5% MeOH/$CHCl_3$; isolated as a white solid in 91% yield (based on **1c**); mp 162-164 °C; $^1H$ NMR $\delta$ 7.49 (dd, 8 H), 3.00 (m, 12 H), 2.41 (s, 6 H), 1.55 (br, 9 H); IR 3345 (w), 1597 (sh), 1330 (s), 1145 (s); mol wt calcd 494, found 478. Anal. Calcd for $C_{24}H_{35}N_3O_4S_2$: C, 58.39; H, 7.15. Found: C, 58.00 H, 7.06.

**1,7,14,20-Tetrakis(*p*-tolylsulfonyl)-1,4,7,14,17,20-hexaazacyclohexacosane (2f, *n* = 6)**: eluted from the column by increasing the MeOH to 2%; isolated as a white solid in 85% yield (based on **2e**); mp 145-147 °C; $^1H$ NMR $\delta$ 7.53 (dd, 16 H), 3.02 (m, 24 H), 2.42 (s, 12 H), 1.42 (br, 18 H); IR 3310 (w), 1598 (sh), 1340 (s), 1154 (s); mol wt calcd 987, found 1024. Anal. Calcd for $C_{48}H_{70}N_6O_8S_4$: C, 58.39; H, 7.15. Found: C, 57.83; H, 6.95.

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**Registry No.** **1c** ($n$ = 2), 77429-90-4; **1c** ($n$ = 4), 77429-91-5; **1c** ($n$ = 6), 77429-92-6; **1d** ($n$ = 6), 77450-07-8; **2e** ($n$ = 4), 77429-93-7; **2e** ($n$ = 6), 77429-94-8; **2f** ($n$ = 6), 77429-95-9; **5**, 77429-96-0; **6** ($n$ = 2), 6315-52-2; **6** ($n$ = 4), 4724-56-5; **6** ($n$ = 6), 4672-50-8; **7**, 14316-16-6; **8**, 6367-75-5; **9**, 3634-89-7; **10**, 77429-97-1; **11**, 77429-98-2.

# General Synthetic Route to Hexaamine Macrocycles

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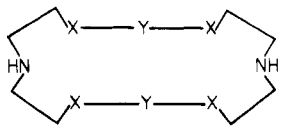
A general synthetic route has been developed for the preparation of hexaamine macrocycles containing two diethylenetriamine units joined by aliphatic hydrocarbon bridges of varying length. By use of this method, the new 20-, 22-, and 24-membered polyamines 1,4,7,11,14,17-hexaazacycloeicosane, 1,4,7,12,15,18-hexaazacyclodocosane, and 1,4,7,13,16,19-hexaazacyclotetracosane were prepared and isolated as crystalline solids. The synthetic details are described, and the characterization of the macrocycles is reported.

Macromonocycles 1 containing two distinct sets of donor atoms are of current interest due to their ability to form bimetallic complexes with transition-metal ions. The resulting binuclear compounds have the two metals positioned within a single ligand cavity and rely on the macrocylic framework rather than directly bridging groups between the metals to maintain structural integrity. Recent work with such macrocycles[1-3] has shown that discrete bimetallic complexes of this type do have unique structural, chemical, and physical properties. For macrocycle **1a**, an imidazolate-bridged dicopper complex was spontaneously formed upon addition of imidazolate to 1:1 mixtures of **1a** and Cu(II).[1] Additionally, this complex showed marked hydrolytic stability of the bridge compared to similar imidazolate-bridged complexes where the metals were not girdled by a macrocyclic ligand. In the case of **1c**, a dicopper(I) complex has been prepared[3] which has unusual reactivity with CO and $O_2$. A dicopper(II) complex of this same ligand which possessed two azide bridges between the metals was found to be completely diamagnetic at room temperature. Comparison of the structural data for this bridged dicopper compound with those for a nonbridged analogue indicated that the macrocycle is capable of accommodating intermetal distances spanning from ca. 5 to 7 Å[3]. Further studies of these and similar binuclear systems offer great promise for elucidating the reactivity of two metal sites, metal-exchange interactions, and multielectron redox phenomena, especially if the nature of the donor atoms and the intermetal separations can be systematically varied by synthetic control of the macrocyclic ligands.




**1a**, X = NH; Y = $(CH_2)_5$
**b**, X = NH; Y = $(CH_2CH_2)_2O$
**c**, X = S; Y = $(CH_2)_5$

To date, the macrocycles 1 capable of coordinating two metals have been reported only with five-atom bridges between the two diethylene tridonor units. The 18-membered homologues where Y is an ethylene bridge have been of little value in forming bimetallic complexes since they tend to encapsulate a single metal atom, yielding stable mononuclear complexes.[4,5] The reported synthetic routes to **1b**[6] and **1c**[7] are inconvenient for synthesis of large

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