Cupped Azacyclophanes Based on a *m*-Terphenyl Framework: Conformational Features of Their *N*-Tosylamide Precursors

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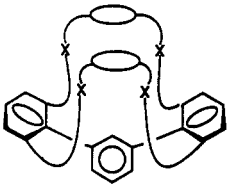
Tetrabromomethyl *m*-terphenyl **4** was used to construct tetrakis-*N*-tosylamide cuppedophanes **8–10** and, by detosylation, the corresponding tetraazacuppedophanes **17–19**. The para- and meta-bridged tosylamides **8** and **9** are conformationally rigid, but the ortho-bridged isomer **10** is conformationally mobile. At low temperatures diagonally opposite tosylamide groups are magnetically equivalent but form two nonequivalent sets which equilibrate (**10A** ⇌ **10B**) at higher temperatures ($\Delta G^{\ddagger}$ = 12.3 kcal mol^{-1}). Tetraamines **17** and **18** have cupped geometries, as deduced from shielding of the isolated aromatic proton on the central ring of the *m*-terphenyl moiety; also, **17** shows restricted rotation of the *p*-xylylene rings. Bis-*N*-tosylamides **11–13** and the corresponding diamines **20–22** were similarly prepared, from bis(bromomethyl)-*m*-terphenyl, **16**. Tosylamides **11** and **12** undergo a dynamic conformational change that involves macrocyclic ring inversion (**11A** ⇌ **11B** and **12A** ⇌ **12B**, $\Delta G^{\ddagger}$ = 14.0 and 10.4 kcal mol^{-1}, respectively), equivalent to conjoint rotation of the two outer *m*-terphenyl rings about the bonds that join them to the central ring of that moiety. Diamine **20** exhibits a similar conformational motion ($\Delta G^{\ddagger}$ = 12.8 kcal mol^{-1}).

Synthesis of azacyclophanes with sizeable cavities has received considerable attention recently,[1] one impetus for such studies being the use of their protonated forms as anion receptors[2] and hosts for neutral arenes[3] in aqueous media. Bicyclic azacyclophanes with heteroaromatic subunits have also been extensively investigated due to their selective cation complexing properties.[4]

We have recently prepared a new class of rapidly assembled cup-shaped tetrathiacyclophanes **1**.[5] It seemed desirable to extend these studies to the analogous azacyclophanes **3**, which could be approached[6] via the corresponding *N*-tosylamides **2**. We report here the synthesis



X = S 1
X = NTs 2
X = NH 3

of tetraazacyclophanes **17–19** and the novel conformational features of one of their tetrakis-*N*-tosylamide precursors **10** and the model bis-*N*-tosylamides **11** and **12**.

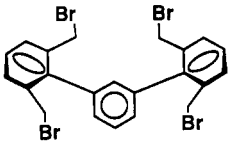
Table I. Chemical Shifts of Significant Aryl Protons in Tetrakis-*N*-tosylamides 8–10 and Bis-*N*-tosylamides 11–13[a]

compd	H_a	H_b	H_c	H_d
8[b]	6.25 (t, 1.5)	6.98–7.19 (m)		
9[b]	4.56 (br s)	6.77 (d, 7.7)	7.12–7.30 (m)	
10[c]	4.76 (br s)	5.72 (d, 7.6)	7.07 (t, 7.6)	7.62[e] (d, 7.7)
11[d]	6.62 (t, 1.6)	7.01 (dd, 7.6, 1.6)	7.13–7.40 (m)	
12[c]	6.34 (br s)	6.53 (d, 7.5)	6.70 (t, 7.5)	7.56 (dd, 7.5, 1.4)
13[d]	5.69 (br s)	6.93–7.46 (m)		7.78 (dd, 7.3, 1.3)

[a] δ (multiplicity, *J* in hertz). [b] $CDCl_3$, room temperature. [c] $CDCl_3$, 55 °C. [d] DMSO-d_6, 72 °C. [e] H_e, with which H_d is coupled, appeared at δ 7.43 (t, 7.7).

Results and Discussion

Synthesis of Tetrakis-*N*-tosylamides 8–10. The building blocks for **8–10** were the readily available tetrabromide **4**[5] and the bis-*N*-tosylamides **5–7**; of the latter, **6** was known[6b] and **5** and **7** were prepared from the appropriate diamine using the same procedure.



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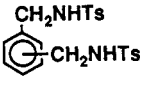

5 1,4-
6 1,3-
7 1,2-

Coupling of **4** with **5** in dimethylformamide (DMF) containing a suspension of cesium carbonate[7] at room temperature gave the tetrakis-*N*-tosylamide **8**, mp 314–316 °C, in 41% yield. Key features of its ^{1}H NMR spectrum are summarized in Table I. Particularly diagnostic was the internal hydrogen of the *m*-terphenyl moiety H_a, which appeared as a narrow triplet (*J* = 1.5 Hz; coupled with H_b on the same ring) at δ 6.25. This chemical shift is nearly

(1) (a) Takemura, H.; Suenaga, M.; Sakai, K.; Kawachi, H.; Shinmyozu, T.; Miyahara, Y.; Inazu, T. *J. Inclusion Phenomena* **1984**, *2*, 207–214. (b) Franke, J.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 219–221. (c) Murakami, Y.; Kikuchi, J.-i.; Tenma, H. *J. Chem. Soc., Chem. Commun.* **1985**, 753–755. (d) Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Org. Chem.* **1985**, *50*, 4478–4484. (e) Murakami, Y.; Kikuchi, J.-i.; *Pure Appl. Chem.* **1988**, *60*, 549–554. (f) Bukownik, R. R.; Wilcox, C. S. *J. Org. Chem.* **1988**, *53*, 463–470. (g) Cowart, M. D.; Sucholeiki, I.; Bukownik, R. R.; Wilcox, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 6204–6210.

(2) (a) Hosseini, M. W.; Lehn, J.-M.; *J. Am. Chem. Soc.* **1982**, *104*, 3525–3527. (b) Heyer, D.; Lehn, J.-M. *Tetrahedron Lett.* **1986**, *27*, 5869–5872. (c) Fujita, T.; Lehn, J.-M. *Tetrahedron Lett.* **1988**, *29*, 1709–1712. (d) Kimura, E.; Kuramoto, Y.; Koike, T.; Fujioka, H.; Kodama, M. *J. Org. Chem.* **1990**, *55*, 42–46.

(3) (a) Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504–2505. (b) Vögtle, F.; Müller, W. M.; Werner, U.; Losensky, H.-W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 901–903. (c) Koga, K.; Odashima, K. *J. Inclusion Phenomena* **1989**, *7*, 53–60.

(4) (a) Newkome, G. R.; Pappalardo, S.; Gupta, V. K.; Fronczek, F. R. *J. Org. Chem.* **1983**, *48*, 4848–4851. (b) Alpha, B.; Anklam, E.; Deschenaux, R.; Lehn, J.-M.; Pietraskiewicz, M. *Helv. Chim. Acta* **1988**, *71*, 1042–1052. (c) Takemura, H.; Shinmyozu, T.; Inazu, T. *Tetrahedron Lett.* **1988**, *29*, 1789–1792. (d) Kimura, E.; Yoshiyamo, Y.; Shionoya, M.; Shiro, M. *J. Org. Chem.* **1990**, *55*, 764–766.

(5) (a) Vinod, T. K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 6574–6575. (b) Vinod, T. K.; Hart, H. *J. Org. Chem.* **1990**, *55*, 881–890.

(6) (a) Vögtle, F.; Neumann, P. *Tetrahedron Lett.* **1970**, 115–118. (b) Vriesema, B. K.; Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1984**, *49*, 110–113. (c) Usui, M.; Nishiwaki, T.; Anda, K.; Hida, M. *Chem. Lett.* **1984**, 1561–1564. (d) Bottino, F.; DiGrazia, M.; Finocchiaro, P.; Fronczek, F. R.; Mamo, A.; Pappalardo, S. *J. Org. Chem.* **1988**, *53*, 3521–3529.

(7) Dijkstra, G.; Kruizinga, W. M.; Kellogg, R. M. *J. Org. Chem.* **1987**, *52*, 4230–4234.

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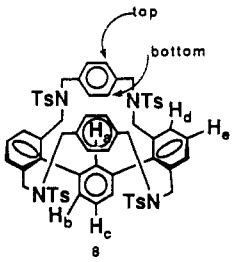
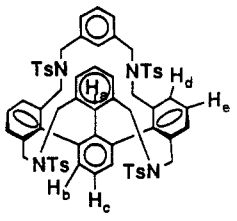
identical with that of the corresponding proton in the sulfur analogue of 8[4] (δ 6.26), thereby establishing the mode of linking of the *p*-xylylene units to the *m*-terphenyl moiety.



8

Rotation of the *p*-xylylene rings in 8 is restricted, so that the top and bottom aryl protons in those rings appear as two sets of broad singlets at δ 6.79 and 6.72.

Tetrakis-*N*-tosylamides **9** and **10** were similarly prepared in 74% and 60% yield, respectively. The internal protons H_a in **9** and **10** appeared at exceptionally high fields for aryl protons, at δ 4.56 and 4.76, respectively. The assignment was confirmed in the case of **9** by deuterium replacement (reaction of **4D**[5] with **6**). In the *S* analogue of **9**, this proton is also shielded, but not nearly as much (δ 6.39);[5] in the *S* analogue of **10** this proton is not shielded and lies in a complex multiplet (δ 7.09–7.50) that includes all the aryl protons. We believe a major factor responsible for this shielding is the need to accommodate the bulky tosyl groups below the large macrocyclic ring. This causes the two outer rings of the *m*-terphenyl moiety to tilt inward, thus placing H_a in their shielding zone. The effect is not observed in **8** because the para orientation of the linking units holds the outer *m*-terphenyl rings apart.



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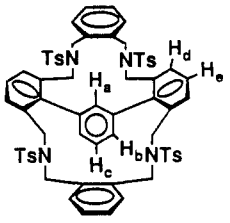


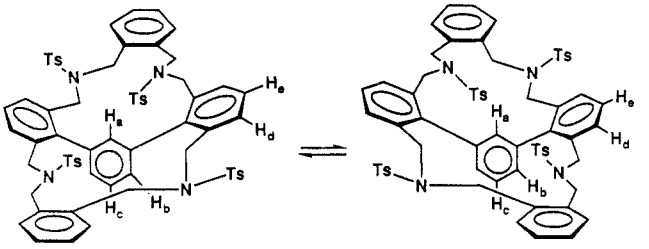
10

Neither **8** or **9** showed any significant change in NMR spectrum down to −70 °C. In particular, the signal due to the tosyl methyl group remained a sharp singlet. These are therefore rigid structures in which all four tosyl groups are equivalent. As seen in the following section, this was not the case with the ortho-bridged **10**.

Conformationl Features of Tetrakis-*N*-tosylamide 10. The room temperature ^{1}H NMR spectrum of **10** showed broad featureless signals for most of the aromatic and methylene protons. However a sharp doublet at δ 7.60 (7.7 Hz, 4 H) and triplet at δ 7.43 (J = 7.7 Hz, 2 H), shown by homonuclear decoupling to be mutually coupled, could be assigned to H_d and H_e, respectively, on the outer *m*-terphenyl rings. These were the lowest field protons in the spectrum (unlike the analogous protons in **8** and **9**), an indication of the steric compression on the outer *m*-terphenyl rings by the bulky tosyl groups, causing deshielding.[8]

The only other aromatic protons in the room temperature spectrum of **10** that could be uniquely assigned were those on the central ring of the *m*-terphenyl moiety. H_a and H_b were substantially shielded (a broad singlet at δ 4.76 and a doublet (J = 7.6 Hz) at δ 5.72, respectively), the former by the outer *m*-terphenyl rings and the latter by the tosyl rings that closely flank the central *m*-terphenyl ring. H_c, the remaining proton on the *m*-terphenyl ring, appeared as a triplet at δ 7.07 (J = 7.6 Hz). Arrayed decoupling of these three signals established their mutual coupling in a single homonuclear decoupling experiment.

The broad signals due to most of the diastereotopic methylene protons and all of the remaining aryl protons suggested a slow conformational process involving wobbling of the bridges.[9] The magnetic equivalence of certain of the protons on the *m*-terphenyl moiety, as well as an analysis of the low-temperature spectrum, suggested that diagonally opposite bridges have identical spatial dispositions, and that the conformational process can be represented by the interconversion of **10A** and **10B**.



10A 10B

On heating a sample of **10** to 54 °C, lines for all the resonances sharpened as a consequence of rapid interconversion of **10A** and **10B**. For example, the aryl protons of the tosyl rings, formerly a multiplet at δ 7.20–7.32, now appeared as two sharp doublets at δ 7.36 and 7.21 (J = 8.2 Hz); the methylene protons now also appeared as sharp doublets (4 H each) at δ 4.19 and 3.33 (J = 15.5 Hz) and at δ 3.91 and 3.44 (J = 15.4 Hz).

By cooling a solution of **10** to −56 °C it was possible to observe the ^{1}H NMR spectrum of a single conformer. For example, the aryl protons of the tosyl rings now appeared as four four-proton doublets at δ 7.74 and 7.41 (J = 7.6 Hz) and at δ 7.03 and 6.75 (J = 7.9 Hz). The signal for the tosyl methyl group, which had been a singlet at δ 2.44, was now two singlets (6 H each) at δ 2.48 and 2.39. The methylene resonances, however, though relatively sharp at this temperature, were not fully resolved into the expected eight sets of two-proton signals. Significantly, the signal for H_b remained symmetric, ruling out a structure in which the two tosylamide groups at the left are equivalent, but different from two equivalent tosylamide groups at the "right", with the two sets equilibrating at elevated temperatures.

The free energy ($\Delta G_c^{\ddagger}$) for the interconversion of **10A** and **10B** was determined to be 12.3 kcal mol^{-1} by following the coalescence of the tosyl methyl singlets (T_c = 246 K).

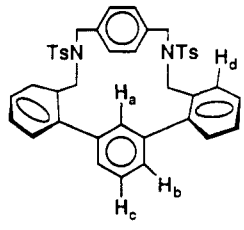
Synthesis and Conformatonal Aspects of Bis-*N*-tosylamides 11–13. The interesting conformational properties of **10** prompted us to synthesize and study the mono-linked analogues **11–13**. CPK models revealed that removal of one of the bridges allowed the outer rings of the *m*-terphenyl moiety to tilt in such a way as to bring these rings closer to the tosyl groups.

The *m*-terphenyl dibromide **16** required for the synthesis of **11–13** was readily prepared as outlined in Scheme I. Addition of 2,6-dichlorophenylmagnesium bromide (prepared from 2,6-dichloroiodobenzene **14** and vinylmagnesium bromide at −20 °C) to 2 equiv of *o*-tolylmagnesium bromide in refluxing THF gave, after aqueous

(8) Gschwend, H. W. *J. Am. Chem. Soc.* **1972**, *94*, 8430–8437.

(9) For a review on conformational aspects of thiacyclophanes, see: Lai, Y.-H. *Heterocycles* **1981**, *16*, 1739–1754.

(10) Calculation of $\Delta G_c^{\ddagger}$ was done making use of the equation $\Delta G_c^{\ddagger} = 2.303RT_c(10.319 + \log T_c - \log k_c)$.[9]



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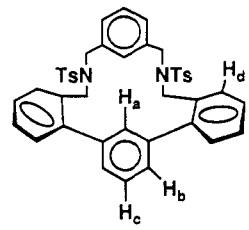

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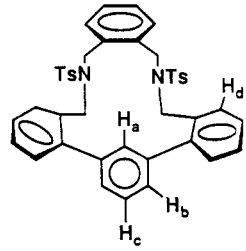


13

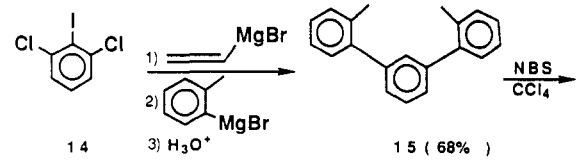
quench, *m*-terphenyl **15** in 68% yield. This reaction involves successive nucleophilic capture of two intermediate arynes.[11] Bromination (with *N*-bromosuccinimide, NBS) gave the required bis(bromomethyl)-*m*-terphenyl **16** in 62% yield. Treatment of **16** with **5**, **6**, or **7** in anhydrous DMF using cesium carbonate as the base gave respectively the bis-*N*-tosylamides **11** (80%), **12** (64%), and **13** (71%).

The room temperature ^{1}H NMR spectra of **11** and **12** showed broad resonances for the methylene protons and certain of the aromatic protons, indicating their conformational mobility, which is discussed in detail below. The poor solubility of **13** in common deuterated NMR solvents precluded recording a room-temperature spectrum. It was possible, however, to obtain a spectrum at 73 °C in DMSO-d_6, in which the most deshielded proton was H_d (δ 7.78, dd, J = 7.3, 1.3 Hz). The corresponding proton in **10** appeared at δ 7.62 (Table I). The additional deshielding of H_d in **13** vis-a-vis **10** is probably a consequence of H_d being closer to the tosyl groups, due to twisting of the outer *m*-terphenyl rings, when only one bridge is present. Unfortunately it was not possible to carry out VTNMR studies on **13**, due to its insolubility.

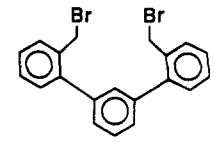
The most deshielded protons (at room temperature) in the *m*-terphenyl moiety of **12** were also H_d (δ 7.56, dd, J = 7.5, 1.4 Hz). This deshielding is less than in the ortho-bridged isomer **13** but greater than that in the doubly bridged meta isomer **9** (H_d at δ 7.30). These observations are consistent with the rationale that twisting of the outer *m*-terphenyl rings is greater in **13** than in **12** (shorter bridge) and greater in **12** than in **9**, where the outer rings must be orthogonal to the central *m*-terphenyl ring because of the double bridge.

The methylene and methyl signals in **12** provide the key to understanding its dynamic conformational changes. In the room-temperature spectrum, the two sets of methylene protons appear as a very broad resonance at δ 4.39 and a fairly sharp singlet at δ 4.14. At 56 °C both of these singlets are sharp. At −60 °C, however, the signal at δ 4.39 was resolved into two slightly broadened two-proton doublets at δ 4.67 and 3.67 (J = 15.3 Hz), whereas the other methylene signal was a broad four-proton singlet at δ 3.99. On the other hand, the tosyl methyl signal remained a sharp six-proton singlet throughout (δ 2.46 at 56 °C shifted to δ 2.34 at −60 °C). Clearly the dynamic process in **12** must be different from that in **10**, since the tosyl groups are not differentiated at low temperature.

Scheme I

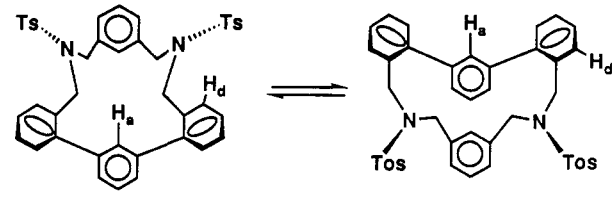


14 15 (68%)



16 (62%)

The dynamic process must be one which equilibrates the two methylene protons on each methylene carbon. This requires an inversion of the macrocyclic ring, as shown in **12A** and **12B**. The plane of symmetry insures that the



12A 12B

methyl signals remain sharp, but the "upper" and "lower" protons of each methylene group are equilibrated. The barrier for this process is 10.4 kcal mol^{-1}, determined from the coalescence of the two methylene doublets (T_c = 264 K). This type of process is, of course, not possible for the doubly bridged tosylamides. Finally, the proximity of the sulfonamide groups in **12** to H_d rationalizes their observed deshielding.

The ^{1}H NMR spectrum of **11** was also temperature dependent. At 72 °C the aryl protons of the *p*-xylylene ring appeared as a sharp singlet (δ 6.30, 4 H). At −51 °C, however, these protons appeared as two slightly broadened two-proton singlets at δ 6.49 and 6.11; thus the "top" and "bottom" protons were differentiated. A VTNMR study gave a barrier for the equilibration process of 14.1 kcal mol^{-1} (T_c = 296 K).

The methylene protons in **11** appeared as a broad multiplet around δ 4.6, but the signals sharpened somewhat on heating and at 130 °C were two singlets at δ 4.13 and 4.07. On cooling to −51 °C, the methylene protons resolved to two sets of two-proton doublets, at δ 4.79 and 3.29 (J = 16.1 Hz) and at δ 4.69 and 3.44 (J = 14.5 Hz). A VTNMR study gave a barrier of 14.0 kcal mol^{-1} (T_c = 313 K).

Throughout the temperature range, the tosyl methyl signal remained a sharp singlet (δ 2.46 at 72 °C, δ 2.48 at −51 °C).

The identical barriers for equilibration of the "top" and "bottom" *p*-xylylene protons and for the two protons attached to each methylene carbon suggests a single process, i.e. **11A** ⇌ **11B**. This is exactly analogous to the process suggested for **12**. The symmetry plane insures that the tosyl methyl signals remain unsplit.

An alternative mechanism could, of course, equilibrate the "top" and "bottom" *p*-xylylene protons, i.e. rotation of that aryl ring through the macrocyclic ring. Such a process was observed in the thia analogue of **8**,[5] where the barrier was 17.0 kcal mol^{-1}, but was not observed with **8**

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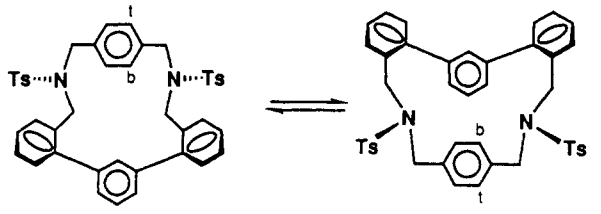
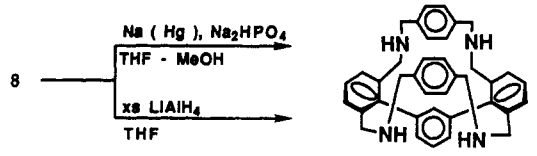


11A 11B

itself, where the barrier presumably would be higher due to the large tosyl groups and the shorter C–N vs C–S bonds. This process would not, of course, equilibrate the methylene protons, and the low observed barrier suggests that the *p*-xylylene ring maintains its orientation as the macrocyclic ring inverts.

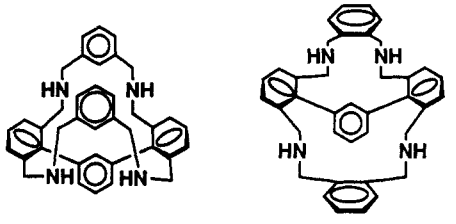
To summarize and compare the NMR behavior of the doubly and singly bridged tosylamides, the former are fairly rigid except for **10**, which undergoes a dynamic process in which two sets of oppositely disposed tosylamide groups equilibrate (**10A** ⇌ **10B**). In the latter, the macrocyclic ring undergoes a ring-inversion motion (**11A** ⇌ **11B**, **12A** ⇌ **12B**), a motion that is equivalent to rotation of the central aryl ring of the *m*-terphenyl moiety about both bonds that connect it to the "outer" *m*-terphenyl rings.

Tetraazacuppedophanes. The procedure developed by Trost[12] using sodium amalgam in a buffered medium was effective in detosylating **8–10**, but the solvent had to be modified to 9:1 v/v THF–MeOH because of the low solubility of our tosylamides, even in hot methanol. Thus **8** gave tetraamine **17** (mp >250 °C) in 79% yield; tetra-



17

amines **18** (mp 103 °C, 93%) and **19** (mp 158 °C, 93%) were similarly prepared from **9** and **10**, respectively. A recently reported detosylation procedure using excess lithium aluminum hydride in refluxing THF[13] was successful in nearly quantitative yield for **17** and **18**, but failed to give **19** from **10**, perhaps for steric reasons.



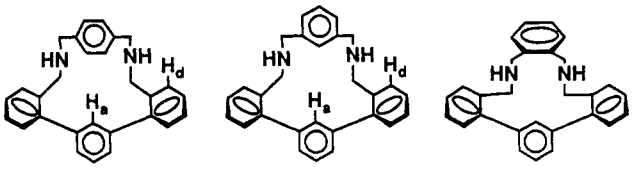
18 19

The cupped geometry of **17** and **18** was evident from the chemical shift of H_a, the internal proton on the central *m*-terphenyl ring. It was the most shielded aromatic resonance, at δ 6.27 (t, J = 1.5 Hz) in **17** and at δ 6.48 (t, J = 1.6 Hz) in **18**. These chemical shifts are very similar to those reported previously for the sulfur analogues[5] (δ 6.26, 6.39, respectively), and the shielding is undoubtedly caused by the bridging xylylene rings. The downfield shift of H_a in **18** (δ 6.48) vis-a-vis its tosylamide **9** (δ 4.56) is consistent with the proposal (vide supra) that in **9** the bulky tosyl groups force the outer *m*-terphenyl ring toward the central ring; detosylation removes this constraint.

As expected, rotation of the *p*-xylylene rings in **17** is restricted. Their aryl protons appeared as two sets of weakly (meta) coupled doublets; also the ^{13}C spectrum of **17** showed two different resonances for the "top" and "bottom" carbons of these rings.

All the aromatic protons in **19** appeared in the region δ 7.09–7.49. Lack of shielding of H_a in this case (and in its tetrathia analogue[5]) is consistent with the outward tilt of the *o*-xylylene rings, as drawn. Also, the lack of deshielding of H_d in **19** compared with that in **10** confirms that this deshielding in **10** was caused by the tosylamide groups.

Bis-*N*-tosylamides **11–13** were also reduced with sodium amalgam in high yield to give **20–22**, respectively. The ^1H NMR spectrum of **20** was temperature dependent. At 100



20 21 22

°C in DMSO-d_6 the four protons of the *p*-xylylene ring appeared as a sharp singlet at δ 6.76 and the methylene protons appeared as two sharp four-proton singlets at δ 3.57 and 3.28. At room temperature in $CDCl_3$, these peaks were broad and at −50 °C in CD_2Cl_2 the xylylene ring protons had separated into two two-proton singlets at δ 6.97 and 6.46, and the methylene protons had resolved to an AB quartet at δ 3.64 and 3.50 (4 H, J = 13.2 Hz) and two two-proton doublets at δ 3.54 and 3.03 (J = 14.0 Hz). A VT NMR study in CD_2Cl_2 gave a coalescence temperature of 276 K for the xylylene singlets and 279 K for the methylene doublets, or barriers of 12.8 and 12.9 kcal mol^{-1}, respectively. We conclude that the dynamic process for **20** is the same as that proposed for its bis-*N*-tosylamide precursor **11**. The lower barrier (by ~1.1 kcal/mol) is a consequence of replacing the bulky tosylamide groups by protons.

In the room-temperature ^1H NMR spectra of the meta- and ortho-bridged isomers **21** and **22** the methylene protons appear as sharp four-proton singlets, indicating that these diamines are conformationally more mobile than **20**. This was to be expected in view of the lower barriers in the corresponding tosylamides. At −50 °C the methylene protons in the *m*-isomer **21** separated into two AB quartets, but solubility problems precluded a barrier measurement. However, this barrier is probably about 9–10 kcal mol^{-1}, since the barriers for the corresponding bis-tosylamides (**11** and **12**) differ by nearly 4 kcal mol^{-1}.

In summary, we have demonstrated here the utility of the *m*-terphenyl framework (i.e. **4** and **16**) in constructing azacyclophanes and have described the interesting dynamic conformational features of their tosylamides. Further amplification of these structures and their potential as hosts and ligands for metal ions remains for future studies.

Experimental Section

General Procedures. ^1H NMR spectra was recorded at either 250 or 300 MHz in $CDCl_3$ unless otherwise stated. Mass spectra were measured at either 70 or 25 eV. High-resolution or FAB mass spectra were obtained at the Michigan State University Mass Spectrometry Facility, supported in part by a grant (DRR – 00480) from the Biotechnology Resources Branch, National Institutes of Health. Melting points are uncorrected. Anhydrous $MgSO_4$

(12) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477–3478.
(13) Fujita, T.; Lehn, J.-M. *Tetrahedron Lett.* **1988**, *29*, 1709–1712 and earlier references cited therein.

was the drying agent throughout, and the silica gel for chromatography was 230–400 mesh.

General Procedure for Bis-tosylamides 5 and 7.[6b] To a solution of 1.36 g (0.01 mol) of the appropriate xylylene diamine and 0.8 g (0.02 mol) of NaOH in 100 mL of water, under argon, was added a solution of 3.8 g (0.02 mol) of tosyl chloride in 100 mL of CH_2Cl_2. After the mixture was stirred at room temperature overnight, the organic layer was separated. The water layer was extracted twice with CH_2Cl_2 (50 mL), and the organic extracts were combined and dried. After filtration and evaporation, the crude product was recrystallized to obtain pure products with the properties listed below.

1,4-Bis[[(*p*-tolylsulfonyl)amino]methyl]benzene (5): yield 77%; mp 214 °C (recrystallized from THF); ^{1}H NMR (DMSO-d_6) δ 8.02 (t, J = 6.3 Hz, 2 H), 7.68 (d, J = 8.2 Hz, 4 H), 7.37 (d, J = 8.2 Hz, 4 H), 7.13 (s, 4 H), 3.89 (d, J = 6.3 Hz, 4 H), 2.37 (s, 6 H); mass spectrum (25 eV), m/e (relative intensity), 443 (0.3), 289 (39), 274 (8), 260 (9), 134 (10), 133 (71), 118 (38), 91 (100). Anal. Calcd for $C_{22}H_{24}N_2O_4S_2$: C, 59.44; H, 5.44; N, 6.30. Found: C, 59.54; H, 5.29; N, 6.22.

1,2-Bis[[(*p*-tolylsulfonyl)amino]methyl]benzene (7): yield 82%; mp 111 °C (recrystallized from EtOH); ^{1}H NMR δ 7.73 (d, J = 8.1 Hz, 4 H), 7.31 (d, J = 8.1 Hz, 4 H), 7.19 (br s, 4 H), 5.09 (t, J = 5.9 Hz, 2 H), 4.11 (d, J = 5.9 Hz, 4 H), 2.45 (s, 6 H); mass spectrum, FAB (*m*-nitrobenzyl alcohol matrix), 445 (MH^+); high-resolution mass spectrum calcd for $C_{22}H_{25}S_2O_4N_2$ (MH^+) 445.1264, found 445.1257. Anal. Calcd for $C_{22}H_{24}S_2O_4N_2$: C, 59.44; H, 5.44; N, 6.30. Found: C, 59.46; H, 5.29; N, 6.22.

General Procedure for Tetrakis-*N*-tosylamides 8–10. A solution of tetrakis(bromomethyl) compound **4** (1 g, 1.7 mmol) and the required bis[[(*p*-tolylsulfonyl)amino]methyl]benzene (1.48 g, 3.4 mmol) in 100 mL of dry DMF was added dropwise over a period of 2–3 h to a well-stirred solution of Cs_2CO_3 (2.43 g, 7.46 mmol) in dry DMF (200 mL) under Ar. After the mixture was stirred at room temperature overnight, the solvent was removed under reduced pressure. The residue was taken up in $CHCl_3$ (150 mL), washed several times with water, and dried. Filtration and evaporation of the solvent (rotavap) gave the crude product, which was either recrystallized or chromatographed over silica gel to give pure product with the following spectral features.

1,4-Xylylene-Bridged Tetrakis-*N*-tosylamide 8. Chromatography over silica gel using $CHCl_3$ as the eluent gave 0.8 g (41%) of **8** as a white solid: mp 314–316 °C ($CHCl_3$–heptane); ^{1}H NMR δ 7.76 (d, J = 8.3 Hz, 8 H, tosyl ring protons), 7.39–7.43 (m, 2 H), 7.33 (d, J = 8.3 Hz, 8 H, tosyl ring protons), 6.98–7.19 (m, 7 H), 6.79 (br s, 4 H, top protons on the 1,4-xylylene ring), 6.72 (br s, 4 H, bottom protons on 1,4-xylylene ring), 6.25 (t, J = 1.5 Hz, 1 H, H_a), 4.98 (d, J = 14.0 Hz, 4 H, CH_2), 4.29 (d, J = 18.4 H, 4 H, CH_2), 3.92 (d, J = 14.0 Hz, 4 H, CH_2), 2.75 (d, J = 18.4 Hz, 4 H, CH_2), 2.50 (s, 12 H, CH_3); mass spectrum, FAB (*m*-nitrobenzyl alcohol matrix), 1167 (MH^+). Anal. Calcd for $C_{66}H_{62}N_4O_8S_4$: C, 67.89; H, 5.35; N, 4.80; S, 10.98. Found: C, 67.71; H, 5.38; N, 4.68; S, 11.02.

1,3-Xylylene-Bridged Tetrakis-*N*-tosylamide 9. Recrystallized from CH_2Cl_2–hexanes (1:1 v/v) to yield 1.44 g (74%) of **9** as a white solid: mp 158–160 °C; ^{1}H NMR δ 7.70 (d, J = 8.2 Hz, 8 H, tosyl ring protons), 7.34 (d, J = 8.2 Hz, 8 H, tosyl ring protons), 7.12–7.30 (m, 7 H), 6.79 (t, J = 7.6 Hz, 2 H), 6.77 (d, J = 7.7 Hz, 2 H, H_b), 6.57 (br d, J = 7.6 Hz, 4 H), 6.49 (br s, 2 H), 4.56 (br s, 1 H, H_a), 4.44 (d, J = 17.3 Hz, 4 H, CH_2), 4.42 and 4.04 (AB q, J = 14.4 Hz, 8 H, CH_2), 3.23 (d, J = 17.3 Hz, 4 H, CH_2), 2.46 (s, 12 H, CH_3); mass spectrum, FAB (*m*-nitrobenzyl alcohol matrix), 1167 (MH^+). Anal. Calcd for $C_{66}H_{62}N_4O_8S_4$: C, 67.89; H, 5.35; N, 4.80; S, 10.98. Found: C, 67.82; H, 5.40; N, 4.66; S, 11.00.

1,2-Xylylene-Bridged Tetrakis-*N*-tosylamide 10. Recrystallized from 1,4-dioxane to yield 1.16 g (60%) of **10** as a pale yellow solid: mp 310 °C; ^{1}H NMR (54 °C) δ 7.62 (d, J = 7.7 Hz, 4 H, H_d), 7.43 (t, J = 7.7 Hz, 2 H, H_e), 7.36 (d, J = 8.2 Hz, 8 H, tosyl ring protons), 7.21 (d, J = 8.2 Hz, 8 H, tosyl ring protons), 7.07 (t, J = 7.6 Hz, 1 H, H_c), 6.91 (m, 8 H), 5.72 (d, J = 7.6 Hz, 2 H, H_b), 4.76 (br s, 1 H, H_a), 4.19 (d, J = 15.5 Hz, 4 H, CH_2), 3.91 (d, J = 15.4 H, 4 H, CH_2), 3.44 (d, J = 15.4 Hz, 4 H, CH_2), 3.33 (d, J = 15.5 Hz, 4 H, CH_2), 2.44 (s, 12 H, CH_3); (room temperature) δ 7.60 (d, J = 7.8 Hz, 4 H, H_d), 7.41 (t, J = 7.8 Hz, 2 H, H_e), 7.20–7.32 (br m, 16 H), 7.03 (t, J = 7.3 Hz, 1 H), 6.85 (br m, 8 H), 5.46 (br d, J = 7.6 Hz, 2 H, H_b), 4.63 (br s, 1 H, H_a), 4.18 (d, J = 14.9 Hz, 4 H, CH_2), 3.82 (br m, 4 H, CH_2), 3.26 (br m, 8 H, CH_2), 2.44 (s, 12 H, CH_3); (−56 °C) δ 7.74 (d, J = 7.6 Hz, 4 H, tosyl ring protons), 7.65 (m, 2 H), 7.47–7.52 (m, 6 H), 7.41 (d, J = 7.6 Hz, 4 H, tosyl ring protons), 7.32 (m, 2 H), 7.03 (d, J = 7.9 Hz, 4 H, tosyl ring protons), 6.94 (t, J = 7.1 Hz, 1 H, H_c), 6.75 (d, J = 7.9 Hz, 4 H, tosyl ring protons), 6.27 (m, 4 H), 4.95 (d, J = 7.1 Hz, 2 H, H_b), 4.45 (br s, 1 H), 4.22 (br d, J = 14.9 Hz, 4 H, CH_2), 4.06 (m, 4 H, CH_2), 3.66 (br d, J = 13.2 Hz, 2 H, CH_2), 3.26 (br d, J = 14.9 Hz, 2 H, CH_2), 2.29 (m, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 2.38 (s, 6 H, CH_3); mass spectrum, FAB (*m*-nitrobenzyl alcohol matrix), 1167 (MH^+). Anal. Calcd for $C_{66}H_{62}N_4O_8S_4$: C, 67.89; H, 5.35; N, 4.80; S, 10.98. Found: C, 67.71; H, 5.24; N, 4.72; S, 10.94.

2,2″-Dimethyl-1,1′:3′,1″-terphenyl (15). Vinylmagnesium bromide (1.92 g, 14.6 mmol as a 1.0 M solution in THF) was added to a stirred solution of 2,6-dichloroiodobenzene (3.97 g, 14.6 mmol) in THF (50 mL) maintained at −22 °C under Ar. After 2 h the mixture was added over a period of 20 min under Ar to a solution of (2-methylphenyl)magnesium bromide (prepared from 5 g, 29.2 mmol of 2-bromotoluene and 0.78 g, 32.0 mmol of magnesium in 80 mL of anhydrous THF maintained at reflux). The resulting mixture was stirred at reflux for an additional 2 h, cooled, quenched with 40 mL of cold 10% HCl, extracted with ether (2 × 100 mL), and dried. The crude product obtained after removal of the ether (rotavap) was chromatographed over silica gel using petroleum ether (30–60 °C) as the eluent to give 2.5 g (68%) of **15** as a viscous oil: ^{1}H NMR δ 7.27–7.51 (m, 12 H), 2.38 (s, 6 H); mass spectrum, m/e (relative intensity) 258 (100), 243(8), 228 (6), 165 (11). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.52; H, 7.19.

2,2″-Bis(bromomethyl)-1,1′:3′,1″-terphenyl (16). *N*-Bromosuccinimide (3.04 g, 17.1 mmol) was added in two equal portions 6 h apart to a solution of **15** (2.1 g, 8.2 mmol) in 100 mL of CCl_4 heated at reflux. After each addition, a few milligrams of benzoyl peroxide were also added. After 24 h total reaction time at reflux, the mixture was cooled, and the precipitated succinimide was removed by filtration. The solvent was removed (rotavap), and the residue was chromatographed over silica gel using CH_2Cl_2–hexanes (1:5 v/v) as the eluent to give 2.1 g (62%) of **16**: mp 89–90 °C (CH_2Cl_2–hexanes, 1:4, v/v); ^{1}H NMR δ 7.36–7.58 (m, 12 H), 4.55 (s, 4 H); mass spectrum, m/e (relative intensity) 416 (1), 335 (1), 255 (100), 240 (15), 238 (18). Anal. Calcd for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88. Found: C, 57.56; H, 3.92.

General Procedure for Bis-*N*-tosylamides 11–13. A solution of bis(bromomethyl) compound **16** (0.6 g, 1.44 mmol) and the required bis[[(*p*-tolylsulfonyl)amino]methyl]benzene (0.64 g, 1.44 mmol) in 60 mL of dry DMF was added dropwise over a period of 2–3 h to a well-stirred suspension of Cs_2CO_3 (1.41 g, 4.33 mmol) in dry DMF (100 mL). The mixture was stirred at room temperature overnight, the solvent was removed under reduced pressure, and the residue was taken up in $CHCl_3$ (100 mL), washed several times with water, and dried. Filtration and evaporation of the solvent (rotavap) gave the crude product, which on chromatography over silica gel using $CHCl_3$ as the eluent gave pure products with the following spectral features.

1,4-Xylylene-Bridged Bis-*N*-tosylamide 11: yield 0.81 g (80%); mp 290 °C; ^{1}H NMR (DMSO-d_6, 72 °C) δ 7.87 (d, J = 8.2 Hz, 4 H, tosyl ring protons), 7.48 (d, J = 8.2 Hz, 4 H, tosyl ring protons), 7.13–7.40 (m, 9 H), 7.01 (dd, J = 7.6, 1.6 Hz, 2 H, H_b), 6.62 (t, J = 1.6 Hz, 1 H, H_a), 6.30 (s, 4 H, *p*-xylylene ring protons), 3.95–4.11 (m, 8 H, CH_2), 2.46 (s, 6 H, CH_3); ($CDCl_3$, room temperature) the peak at δ 6.30 due to the *p*-xylylene ring protons was very broad; the peak due to the methylene protons was broad, centered at δ 4.60; ($CDCl_3$, −51 °C) δ 7.82 (d, J = 8.0 Hz, 4 H, tosyl ring protons), 7.38 (d, J = 8.0 Hz, 4 H, tosyl ring protons), 7.09–7.32 (m, 9 H), 6.88 (dd, J = 7.6, 1.6 Hz, 2 H, H_b), 6.70 (br s, 1 H, H_a), 6.49 (br s, 2 H, "top" protons on *p*-xylylene ring), 6.11 (br s, 2 H, "bottom" protons on *p*-xylylene ring), 4.79 (d, J = 16.1 Hz, 2 H, CH_2), 4.69 (d, J = 14.5 Hz, 2 H, CH_2), 3.44 (d, J = 14.5 Hz, 2 H, CH_2), 3.29 (d, J = 16.1 Hz, 2 H, CH_2), 2.48 (s, 6 H, CH_3); mass spectrum, FAB (*m*-nitrobenzyl alcohol matrix), 699 (MH^+); high-resolution mass spectrum calcd for $C_{24}H_{39}N_2O_4S_2$ (MH^+) 699.2352, found 699.2357. Anal. Calcd for $C_{42}H_{38}N_2O_4S_2$: C, 72.18; H, 5.48; N, 4.00; S, 9.18. Found: C, 71.97; H, 5.40; N, 4.05; S, 9.15.

1,3-Xylylene-Bridged Bis-*N*-tosylamide 12: yield 0.64 g (64%); mp 138 °C; ^{1}H NMR (56 °C) δ 7.75 (d, J = 8.2 Hz, 4 H, tosyl ring protons), 7.56 (dd, J = 7.5, 1.4 Hz, 2 H, H_d), 7.17–7.37 (m, 5 H), 7.32 (d, J = 8.2 Hz, 4 H, tosyl ring protons), 7.06 (dd, J = 7.4, 1.2 Hz, 2 H), 6.99 (dd, J = 7.6, 1.5 Hz, 2 H), 6.70 (t, J = 7.5 Hz, 1 H, H_c), 6.53 (d, J = 7.5 Hz, 2 H, H_b), 6.38 (br s, 1 H), 6.34 (br s, 1 H, H_a), 4.39 (s, 4 H, CH_2), 4.14 (s, 4 H, CH_2), 2.46 (s, 6 H, CH_3); (−60 °C) δ 7.63 (d, J = 8.0 Hz, 4 H, tosyl ring protons), 7.25 (d, J = 8.0 Hz, 4 H, tosyl ring protons), 7.04–7.20 (m, 7 H), 6.88 (d, J = 7.3 Hz, 2 H), 6.79 (d, J = 7.4 Hz, 2 H), 6.46 (br t, J = 7.8 Hz, 1 H), 6.36 (m, 2 H), 6.25 (br s, 1 H), 6.08 (br s, 1 H), 4.67 (br d, J = 15.3 Hz, 2 H, CH_2), 3.99 (br s, 4 H, CH_2), 3.67 (br d, J = 15.3 Hz, 2 H, CH_2), 2.34 (s, 6 H, CH_3); mass spectrum, FAB (m-nitrobenzyl alcohol matrix), 699 (MH^+); high-resolution mass spectrum calcd for $C_{42}H_{39}N_2O_4S_2$ (MH^+) 699.2352, found 699.2357. Anal. Calcd for $C_{42}H_{38}N_2O_4S_2$: C, 72.18; H, 5.48; N, 4.00; S, 9.18. Found: C, 71.44; H, 5.57; N, 4.04; S, 9.10.

1,2-Xylylene-Bridged Bis-*N*-tosylamide 13: yield 0.72 g (71%); mp >280 °C dec; ^{1}H NMR (DMSO-d_6, 73 °C) δ 7.78 (dd, J = 7.3, 1.3 Hz, 2 H, H_d), 7.74 (d, J = 8.1 Hz, 4 H, tosyl ring protons), 7.39 (d, J = 8.1 Hz, 4 H, tosyl ring protons), 6.96–7.46 (m, 9 H), 6.54–6.68 (m, 4 H, 1,2-xylylene ring protons), 5.69 (br s, 1 H, H_a), 4.42 (br s, 4 H, CH_2), 3.75 (br s, 4 H, CH_2), 2.42 (s, 6 H, CH_3); mass spectrum, FAB (m-nitrobenzyl alcohol matrix), 699 (MH^+). Anal. Calcd for $C_{42}H_{38}N_2O_4S_2$: C, 72.18; H, 5.48; N, 4.00; S, 9.18. Found: C, 71.68; H, 5.50; N, 4.08; S, 9.31.

General Procedure for Tetraamines 17–19 Using Sodium Amalgam. A mixture of the required tetrakis-*N*-tosylamide (1.0 g, 0.86 mmol), Na_2HPO_4 (1.2 g, 8 mmol), and finely ground 6% sodium amalgam (10 g) in THF–MeOH (40 mL, 9:1 v/v) was stirred rapidly and heated at gentle reflux overnight. The cooled mixture was poured into water, extracted with $CHCl_3$ (3 × 75 mL), and dried. Filtration and evaporation (rotavap) gave practically pure tetraamines with the following physical data.

1,4-Xylylene-Bridged Tetramine 17: yield 0.38 g (79%); mp >250 °C; ^{1}H NMR δ 7.26–7.46 (m, 7 H), 7.10 (dd, J = 7.6, 1.5 Hz, 2 H, H_b), 6.95 (d, J = 1.5 Hz, 4 H, 1,4-xylylene "top" protons), 6.93 (d, J = 1.5 Hz, 4 H, 1,4-xylylene "bottom" protons), 6.27 (t, J = 1.5 Hz, 1 H, H_a), 3.97 (d, J = 13.4 Hz, 4 H, CH_2), 3.62 (d, J = 13.4 Hz, 4 H, CH_2), 2.71 (d, J = 12.1 Hz, 4 H, CH_2), 2.51 (d, J = 12.1 Hz, 4 H, CH_2), 1.63 (br s, 4 H, NH); ^{13}C NMR (DMSO-d_6) 140.2, 138.2, 138.0, 137.7, 129.4, 129.3, 129.0, 128.9, 128.3, 127.6, 127.2 (aromatic), 51.7, 47.4 (methylenes); mass spectrum, FAB (m-nitrobenzyl alcohol matrix), 551 (MH^+); high-resolution mass spectrum calcd for $C_{38}H_{39}N_4$ (MH^+) 551.3174, found 551.3162.

1,3-Xylylene-Bridged Tetraamine 18: yield 0.44 g (93%); mp 163–166 °C; ^{1}H NMR δ 7.03–7.47 (m, 13 H), 6.83 (dd, J = 7.6, 1.6 Hz, 2 H, H_b), 6.75 (br s, 2 H), 6.48 (t, J = 1.6 Hz, 1 H, H_a), 3.77 (s, 8 H, CH_2), 3.26 (s, 8 H, CH_2), 2.0 (br s, 4 H, NH); ^{13}C NMR ($CDCl_3$) δ 139.9, 138.5, 137.6, 129.4, 129.3, 128.4, 127.9, 127.6, 127.5, 127.4, 126.5 (aromatic), 53.8, 49.3 (methylenes); mass spectrum, FAB (m-nitrobenzyl alcohol matrix), 551 (MH^+); high-resolution mass spectrum calcd for $C_{38}H_{39}N_4$ (MH^+) 551.3174, found 551.3173.

1,2-Xylylene-Bridged Tetraamine 19: yield 0.44 g (93%); mp 158 °C; ^{1}H NMR δ 7.04–7.50 (m, 18 H), 3.76 and 3.64 (AB q, J = 11.9 Hz, 8 H, CH_2), 3.65 and 3.49 (AB q, J = 11.3 Hz, 8 H, CH_2), 1.72 (br s, 4 H, NH); ^{13}C NMR (CD_2Cl_2) δ 142.3, 139.8, 139.4, 132.3, 130.9, 129.4, 128.5, 128.4, 127.9, 127.8 (aromatic, one overlapped), 53.3 (methylenes overlapped); mass spectrum, FAB (m-nitrobenzyl alcohol matrix), 551 (MH^+); high-resolution mass spectrum calcd for $C_{38}H_{39}N_4$ (MH^+) 551.3174, found 551.3184.

General Procedure for Tetraamines 17 and 18 Using Excess Lithium Aluminum Hydride. A mixture of the required tetrakis-*N*-tosylamide (0.25 g, 0.22 mmol) and lithium aluminum hydride (0.5 g, 13.2 mmol) was heated at reflux in dry THF (50 mL) for 24 h. After cooling to room temperature, the excess lithium aluminum hydride was very cautiously destroyed using 1 mL of water followed by 1 mL of 15% NaOH. The inorganic precipitate was filtered, and to the filtrate was added a mixture of ether and water (100 mL, 1:1 v/v). The organic layer was separated, dried, and evaporated (rotavap) to give quantitative yields of tetraamines **17** and **18** with physical properties identical with those described above.

General Procedure for Diamines 20–22. The procedure was similar to that described for **17–19** except that the following amounts of reagents were used: bis-*N*-tosylamides **11–13** (0.5 g, 0.72 mmol), Na_2HPO_4 (0.8 g, 5.3 mmol), and sodium amalgam (6 g) and the product was extracted with $CHCl_3$ (2 × 50 mL).

1,4-Xylylene-Bridged Diamine 20: yield 0.25 g (89%); mp 165–167 °C; ^{1}H NMR (DMSO-d_6, 100 °C) δ 7.67 (dd, J = 7.4, 1.8 Hz, 2 H, H_d), 7.21–7.39 (m, 5 H), 7.13 (br d, J = 7.5 H, 2 H), 6.97 (br d, J = 7.5 Hz, 2 H), 6.76 (s, 4 H, 1,4-xylylene ring protons), 6.74 (br s, 1 H, H_a), 3.57 (s, 4 H, CH_2), 3.28 (s, 4 H, CH_2), 2.90 (br s, 2 H, NH); ($CDCl_3$, room temperature) δ 7.65 (dd, J = 7.3, 1.7 Hz, 2 H, H_d), 7.20–7.44 (m, 7 H), 7.04 (dd, J = 7.4, 1.8 Hz, 2 H), 6.89 (t, J = 1.7 Hz, 1 H, H_a), 6.85 (br s, 4 H, 1,4-xylylene ring protons), 3.72 (s, 4 H, CH_2), 3.38 (br s, 4 H, CH_2), 1.89 (br s, 2 H, NH); (CD_2Cl_2, −50 °C) δ 7.64 (br d, J = 7.5 Hz, 2 H, H_d), 7.19–7.42 (m, 7 H), 7.00 (m, 2 H), 6.97 (s, 2 H, 1,4-xylylene ring "top" protons), 6.87 (br s, 1 H, H_a), 6.46 (s, 2 H, 1,4-xylylene ring "bottom" protons), 3.64 and 3.50 (AB q, J = 13.2 Hz, 4 H, CH_2), 3.54 (d, J = 14.0 Hz, 2 H, CH_2), 3.03 (d, J = 14.0 Hz, 2 H, CH_2), 1.80 (br s, 2 H, NH); ^{13}C NMR ($CDCl_3$, room temperature) δ 141.7, 140.8, 137.8, 136.8, 129.5, 128.6, 128.4, 128.1, 127.9, 127.5, 126.3, 126.2 (aromatic), 51.3, 46.9 (methylenes); mass spectrum, FAB (m-nitrobenzyl alcohol matrix), 391 (MH^+); high-resolution mass spectrum calcd for $C_{28}H_{27}N_2$ (MH^+) 391.2172, found 391.2183.

1,3-Xylylene-Bridged Diamine 21: yield 0.25 g (89%); mp >220 °C; ^{1}H NMR δ 7.59 (dd, J = 7.0, 1.8 Hz, 2 H, H_d), 7.06–7.40 (m, 13 H), 6.67 (br s, 1 H, H_a), 3.78 (s, 4 H, CH_2), 3.65 (s, 4 H, CH_2), 1.91 (br s, 2 H, NH); ^{13}C NMR (CD_2Cl_2) δ 142.4, 142.1, 140.6, 138.4, 130.7, 130.1, 129.8, 129.2, 128.9, 128.3, 128.2, 127.8, 127.4 (aromatic, one overlapped), 52.9, 49.7 (methylenes); mass spectrum, FAB (m-nitrobenzyl alcohol matrix) 391 (MH^+); high-resolution mass spectrum calcd for $C_{28}H_{27}N_2$ (MH^+) 391.2172, found 391.2190.

1,2-Xylylene-Bridged Diamine 22: yield 0.26 g (92%); mp 111–114 °C; ^{1}H NMR δ 7.18–7.47 (m, 16 H), 3.80 (s, 4 H, CH_2), 3.73 (s, 4 H, CH_2); ^{13}C NMR δ 142.4, 141.4, 138.9, 138.1, 130.6, 130.5, 130.3, 128.1, 127.9, 127.8, 127.6, 127.3 (aromatic, one overlapped), 52.5, 52.4 (methylenes); mass spectrum, FAB (m-nitrobenzyl alcohol matrix) 391 (MH^+); high-resolution mass spectrum calcd for $C_{28}H_{27}N_2$ (MH^+) 391.2172, found 391.2188.

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Registry No. **4**, 116129-61-4; **5**, 5011-10-9; **5** (amine), 539-48-0; **7**, 128926-56-7; **7** (amine), 17300-02-6; **8**, 128926-57-8; **9**, 128926-58-9; **10**, 128926-59-0; **11**, 128926-60-3; **12**, 128926-61-4; **13**, 128926-62-5; **15**, 22058-35-1; **16**, 22058-37-3; **17**, 128926-63-6; **18**, 128926-64-7; **19**, 128926-65-8; **20**, 128926-66-9; **21**, 128926-67-0; **22**, 128926-68-1; H_2C=CHMgBr, 1826-67-1; 2,6-dichloroiodobenzene, 19230-28-5; (2-methylphenyl)magnesium bromide, 932-31-0.