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# Pertosylated Polyaza[n](9,10)anthracenophanes

**Belén Altava, M. Isabel Burguete, Beatriz Escuder, and Santiago V. Luis***

Department of Inorganic and Organic Chemistry, University Jaume I, E-12080 Castellón, SPAIN

**Enrique García-España***

Department of Inorganic Chemistry, University of Valencia, 46100 Burjassot (Valencia), SPAIN

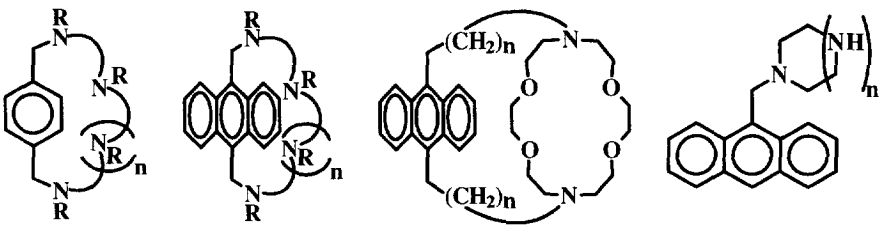
**M. Carmen Muñoz**

Department of Applied Physics, Polythecnic University of Valencia, 46071 Valencia, SPAIN

***Abstract***: Pertosylated polyaza[n](9,10)antracenophanes have been obtained in high yields by a modification of the Richman-Atkins methodology. Molecular Mechanics calculations as well as the crystal structure of the N,N´,N´´,N´´´-Tetratosyl-2,6,9,13-tetraaza[14](9,10)anthracenophane **4** derivative reveal the existence of a well defined cavity where both the aromatic moiety and the nitrogen donor atoms converge. Reduced mobility of the aliphatic chain is also observed as well as the presence of some strain at the benzylic positions. 

Polyazamacrocycles containing aromatic subunits as an integral part of the macrocycle represent an attractive class of synthetic receptors.[1,2] The presence of the aromatic moieties can impart some interesting properties to the resulting macrocycles. In this respect, polyammonium macrocycles containing several aromatic rings have been developed to build up water-soluble receptors having hydrophobic cavities.[3-5] Selective recognition of cationic, anionic and neutral molecules has been obtained with these hosts. Selectivity is accomplished, in most instances, not only through host-guest size complementarity but also by topological and functional complementarity, the aromatic subunits being able to interact with the guests by π-stacking and π-cation or π-H interactions.[3,4] In a number of cases, these receptors have found applications in catalytic processes and as enzyme mimics.[5] Recently, we have reported on the synthesis,[6] protonation behavior,[7] cation[8] and anion coordination chemistry[9] of a new family of macrocyclic receptors, polyaza[n]paracyclophanes (**1**), characterized by the presence of a *para*-phenylene spacer linking the ends of an aliphatic polyamine chain.[10] The presence of the aromatic ring favors the existence of definite protonation patterns for these compounds, which is of importance for their interaction with anions. On the other hand, the simultaneous involvement of both benzylic nitrogen atoms in the coordination to a metal center is precluded, giving a low symmetry coordination site which provides a simple way for developing catalytic applications.

One of the most interesting features of polyza[n]paracyclophanes is the convergence of the aromatic π-system and the nitrogen donor atoms in the cavity. This convergence has been evidenced in structural and photochemical studies.[9] Modification of the nature of the aromatic ring can be used in order to maximize the potential interaction of the π-system with the guests, and, in particular, with transition metal cations. Accordingly, polyaza[n](9,10)anthracenophanes **2** represent an interesting target.

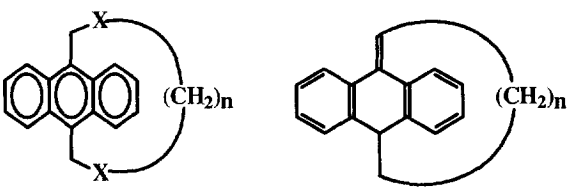



**1** **2** **3** **4**

Different synthetic receptors containing anthracene rings, such as **3** and **4**, have been recently reported as starting materials for the development of fluorescent chemosensors.[11-13] Polyaza[n](9,10)anthracenophanes **2** could provide, when compared with receptor **4** for instance, a higher degree of preorganization and a more direct interaction of the aromatic subunit and the transition metal. Here we report our first results on the synthesis and structural characterization of pertosylated polyaza[n](9,10)anthracenophanes **9-13**.

## RESULTS AND DISCUSSION

Synthesis of [n](9,10)anthracenophanes has received much attention in the last years, and compounds containing aliphatic chains, as well as some thio and keto derivatives **5**, have been obtained, but no aza-derivatives of this class have been described.[14,15]



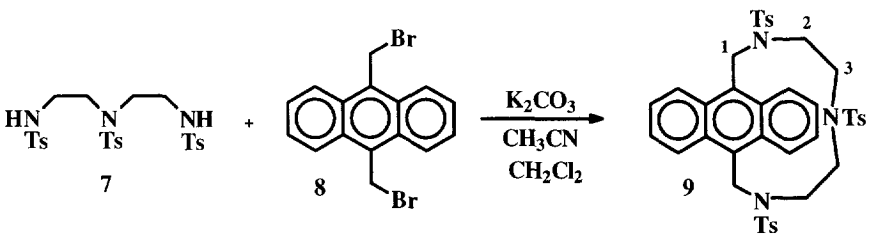

**X = $CH_2$, S, $CH_2CO$**

**5** **6**

Preparation of anthracenophanes seems to be more difficult than synthesis of other [n]paracyclophanes, in particular for those with smaller chain lenghts, and this has been partially ascribed to the relative stability of methylenedihydroanthracene (MDA) tautomers **6**. The [6](9,10)anthracenophane is the smallest compound of

this class that has been described, but the unsubstituted compound seems to be very unstable under a variety of conditions.[15]

Medium-size pertosylated polyaza[n](9,10)anthracenophanes **9-13** could be obtained, however, in high yields according to the general methodology developed for the preparation of N-tosylated polyaza[n]paracyclophanes[6] as illustrated in Scheme 1 for the synthesis of 2,5,8-tris(*p*-toluenesulfonyl)-2,5,8-triaza[9](9,10)anthracenophane **9**.




**Scheme 1**

The starting pertosylated polyamines were prepared as described[6] and 9,10-bis(bromomethyl)anthracene was obtained by direct bromomethylation of anthracene using aqueous hydrobromic acid, 1,3,5-trioxane and tetradecyltrimethylammonium bromide. Reaction of the corresponding pertosylated polyamine, i.e. **7**, with the bis(bromomethyl) derivative in $CH_3CN/CH_2Cl_2$, using anhydrous $K_2CO_3$ as the base, afforded the expected crude cyclophanes **9-13** which could be purified by column chromatography on silica using $CH_2Cl_2$/EtOAc mixtures for the elution. Yields obtained (see Table 1) are comparable to the ones previously obtained for related (1,4)naphthalenophanes[16] and are higher than those reported for simple polyaza[n]paracyclophanes,[6] and give further support to the idea that steric and conformational factors resulting from the presence of bulky tosyl groups play a key role in determining the efficiency of Richman-Atkins cyclizations.[17] In agreement with this, it can be noted that the higher yields are obtained for the smaller cyclophanes **9** and **10** which are prepared from polyamines having the lower conformational freedom.

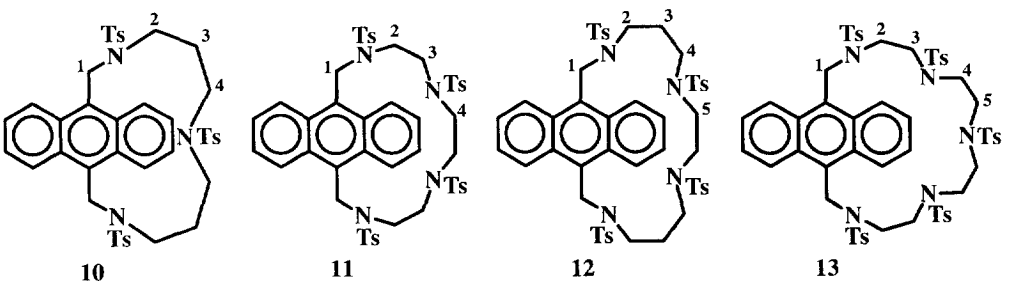
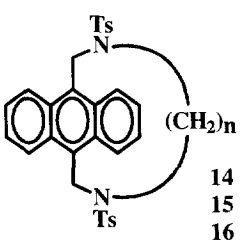


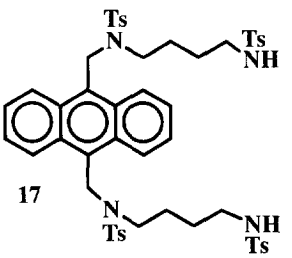
*Table1.- Isolated yields for Tosylated Polyaza[n](9,10)anthracenophanes.*

| Compound | Reaction time (h) | Yield (%)[a] |
|---|---|---|
| **9** | 42 | 99 |
| **10** | 48 | 95 |
| **11** | 48 | 84 |
| **12** | 46 | 70 |
| **13** | 72 | 79 |

As can be seen in Table 1, this procedure allows for the efficient preparation of a variety of cyclophanes having different chain lengths. However, the [9](9,10)anthracenophane **9** was the smallest cyclophane that could be prepared by this method. Attempts to obtain diaza[6], [7] or [8](9,10)anthracenophanes **14** to **16** by reaction of **8** with N-tosylated 1,2-ethylene, 1,3-propylene or 1,4-butylenediamine under basic conditions lead to the formation of complex mixtures of linear and cyclic oligomers even when high dilution conditions were used. Thus, pertosylated tetraamine **17** could be isolated as one of the major products when the synthesis of **16** was attempted using the standard methodology.



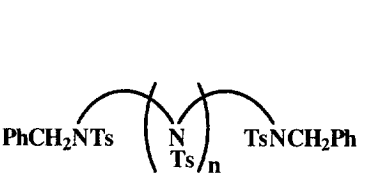

**14** n = 2
**15** n = 3
**16** n = 4



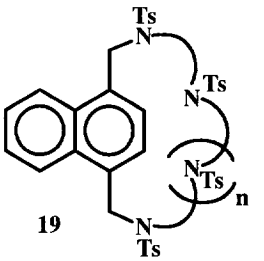

One important difference of compounds **9-13** with other polyaza[n]paracyclophanes is that internal rotation of the aromatic ring through the cavity is precluded except for very large aliphatic chains.[16] This reduces the conformational mobility of the compound and forces the polyamine strand to stay above the aromatic ring. The $^1$H NMR spectra of compounds **9-13** reflect this situation and the upfield shifts observed for the central protons of the chain are higher than those found for other related polyaza[n]paracyclophanes (see Table 2).

Thus for instance the singlet observed for the central ethylene group in **12** appears at 1.95 ppm, while it is found at 3.04 ($\Delta\delta$=-1.09) for the related dibenzylated polyamine **18** and at 2.74 ($\Delta\delta$=-0.79) and ca. 2.5 ($\Delta\delta$= -0.55) for related [14]paracyclophane **1** (R=Ts) and [14](1,4)naphthalenophane **19**.[6,16] As expected, shielding effects and chemical shift differences are smaller for the protons placed at both ends of the chain. Accordingly,

the central methylene group of the propylene subunit in compound **12** (δ=0.80 ppm) shows chemical shift differences of -0.82, -0.67 and -0.36 with respect to those found for related **1**, **18** and **19**.




**18**




**19**

*Table 2.- More relevant $^1H$ NMR data for anthracenophanes* ***9-12****.*

| Entry | Compound | Proton | δ (ppm)[a] | Δδ [b,f] (18) | Δδ [b, c, f] (1) | Δδ [b, c, g] (19) |
|---|---|---|---|---|---|---|
| *1* | **9** | *1* | 5.34 | 1.14 | 1.09 | -0.26[d] |
| *2* | **9** | *2* | 2.05 | -0.66 | -0.47 | -0.25[e] |
| *3* | **9** | *3* | 1.61 | -1.54 | -0.91 | -0.83[e] |
| *4* | **10** | *1* | 5.35 | 1.13 | 1.15 | -0.17[d] |
| *5* | **10** | *2* | 0.40 | -0.99 | -0.79 | 0.17[e] |
| *6* | **11** | *1* | 5.18 | 0.98 | 1.04 | -0.32[d] |
| *7* | **11** | *2* | 1.84 | -1.11 | -0.66 | -0.40[e] |
| *8* | **12** | *1* | 5.15 | 0.90 | 1.01 | 0.58 |
| *9* | **12** | *2* | 0.80 | -0.82 | -0.67 | -0.36 |
| *10* | **12** | *3* | 1.95 | -1.09 | -0.79 | -0.55 |

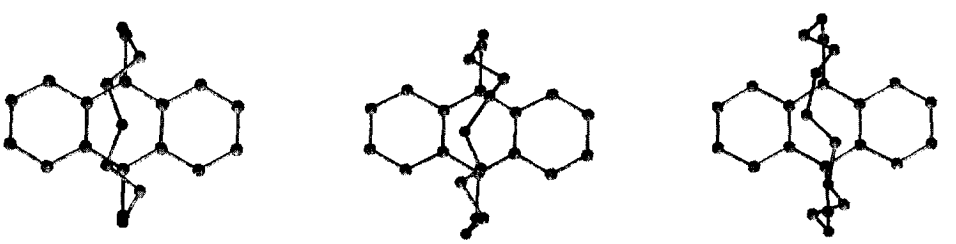
a) $CDCl_3$. b) Δδ calculated as the difference between the chemical shift for a given proton in compounds **9-12** and that of the analogous proton in related compounds **1**, **18** or **19**. c) Pertosylated derivative (R=Ts), containing the same polyamine subunit. d) For the most unshielded benzylic signal. e) For the most shielded signal of the two non-equivalent geminal protons. f) Data for **1** and **18** from ref. 6. g) Data for **19** from ref. 16.

Upfield shifts are larger for small cyclophanes, and chemical shift differences of ca. -0.9 are found when comparing the central protons of cyclophane **9** and the related compound **1** (R=Ts). Because of the restricted rotation for [9], [11] and [12](1,4)naphthalenophanes,[16] two different signals are observed for each pair of geminal protons. For those pairs, the upfield signals have been selected for comparison in Table 2, except for the benzylic protons where the downfield peaks have been considered. Those selected signals correspond to protons located in an environment comparable to that of protons in cyclophanes **9-12**, and, accordingly, no big differences in chemical shifts are observed in most cases.

For the benzylic protons, the limited conformational mobility is reflected in their location in the vicinity of the *peri* protons. Larger downfield shifts are observed in comparison with protons in related compounds, except when the internal benzylic protons of [9], [11] and [12](1,4)naphthalenophanes are considered.

Conformational analysis of polyaza[n](9,10)anthracenophanes **9-13** was carried out by means of molecular mechanics calculations. We applied the torsional Monte Carlo method exploited by the BATCHMIN V5.0 molecular mechanics program as a part of the MACROMODEL package.[18]

Results obtained using the MM2* and AMBER* force fields show, even for the larger cyclophanes, the prevalence of conformations in which the polyamine chain is arching above the central aromatic ring and are in good agreement with the general trends observed in the conformational analysis of other [n]paracyclophanes and with the results obtained for small non-functionalized [n](9,10)antracenophanes.[14b,19] According to Allinger,[19a] [n]paracyclophanes with an odd number of bridge methylene groups can have geometries with $C_s$ or $C_2$ symmetry while those with an even number of bridge methylene groups should have $C_2$ symmetry. For anthracenophanes **9-13** a high number of conformers were found within a few kJ $mol^{-1}$ of the minimum energy conformer; most of them have similar arrangements of the polyamine chains but differ in the tosyl group orientations. If the tosyl groups are not considered, the preferred geometry for the [9](9,10)anthracenophane **9** is $C_s$, the first conformer having a pseudo $C_2$ symmetry being located ca. 25 kJ $mol^{-1}$ above the minimum. On the contrary, the lowest energy structure found for the [11]anthracenophane **10** shows $C_2$ symmetry, but in this case the second conformer found, which has nearly the same energy ($\Delta E$=0.4 kJ $mol^{-1}$), presents $C_s$ geometry. For larger bridge lengths **11-13**, the lowest energy conformers found with the MM2* force field were neither $C_s$ nor $C_2$. The minimum energy conformers of [12] and [14]anthracenophanes (**11**, and **12**) have most of the chain ordered like in $C_s$ structures but the two central methylene groups are arranged so as to preclude the $C_s$ symmetry. For the [12]cyclophane **11** there is a conformer with a pseudo $C_2$ symmetry located just 0.44 kJ $mol^{-1}$ above the minimum. These results differ slightly when the AMBER* force field is used. It is noteworthy that, in this case, the minimum energy conformer calculated for **12** has $C_2$ symmetry.



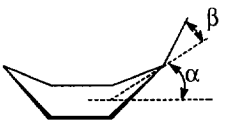
**9** **10** **11**

*Figure 1.- Minimum energy conformers calculated for compounds **9-11** (MM2* force field). Tosyl groups and hydrogen atoms have been omitted for clarity.*

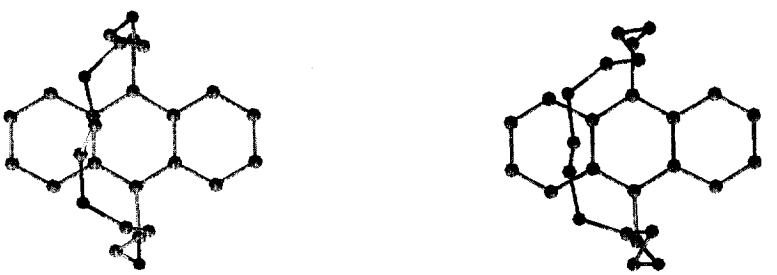
As for other polyaza[n]paracyclophanes some strain seems to be present in the calculated structures, strain being mainly located at the nitrogen atoms and at the benzylic positions. In this respect, deformation angles calculated for the minimum energy conformers found for compounds **9-13** were generally very low, except for the smaller cyclophane **9** for which values of $\alpha$=4.7 and $\beta$=9.0 were obtained.[14,15,19a] According to this, only minimum deformations of the aromatic anthracene rings are to be expected for **9-13**, in agreement with the absence of any remarkable effects on the UV-visible spectra.

*Table 3.- Calculated deformation angles.*

| Compound | $\alpha$ | $\beta$ | $\alpha + \beta$ |
|---|---|---|---|
| **9** ([9]anthracenophane) | 4.7 | 9.0 | 13.7 |
| **10** ([11]anthracenophane) | 0.4 | 2.1 | 2.5 |
| [9]paracyclophane[19b] | 4.3 | 3.5 | 7.8 |
| [10]paracyclophane[19b] | 2.6 | 0.9 | 3.5 |




Crystals suitable for X-ray analysis were obtained for **12**, making possible a direct comparison with results obtained from molecular mechanics calculations. The crystallographic structure (*Figure 2a*)[20] for **12** showed a very good agreement with the one for the minimum energy conformer calculated with the MM2* force field (*Figure 2b*) the same folding tendencies of the chain being observed in both cases. As in the calculated structure, although most of the polyamine chain is ordered as to form a $C_s$ geometry, the arrangement of the two central carbon atoms preclude such a geometry. These results seems to confirm that molecular mechanics calculations can be efficiently used to model polyaza[n](9,10)anthracenophanes and suggest that the MM2* force field could be slightly better, in this respect, than the AMBER* force field.



*(a)* *(b)*

*Figure 2.- X-Ray structure (a) and MM2* minimum energy conformer (b) calculated for* **12**. *Tosyl groups and hydrogen atoms have been omitted for clarity.*

Attempts to detosylate compounds **9-13** to obtain non-tosylated polyaza[n](9,10)anthracenophanes **2** (R=H) were carried out using the different methodologies described for deprotection of N-tosylated compounds such as HBr/AcOH/PhOH, $H_2SO_4$, Na(Hg), $LiAlH_4$, sodium naphthalenide, Na/BuOH, $NaBH_4$/hv, etc.[21,22] In all instances, the major products obtained were compounds produced by single or double benzylic C-N cleavage, the formation of compounds **2** (R=H) not being detected. Thus, for instance, treatment of compound **12** with Na(Hg) in a $Na_2HPO_4$ buffer, a method that has been successful for detosylation of other polyaza[n]paracyclophanes,[6] gave a 90% yield of 9,10-dimethylanthracene along with a mixture of 1,5,8,12-tetraazadocecane and partially detosylated derivatives of this polyamine. Similar results were also obtained when $LiAlH_4$ was used. The formation of these derivatives suggests that benzylic C-N cleavage does not occur after detosylation is complete, but competes efficiently with the detosylation process. Most likely, the stability of radical species that could be formed in the process or the participation of MDA like intermediates, along with the reactivity of the aromatic system under electron-transfer conditions, should be considered in order to explain those results.

In conclusion, [n](9,10)anthracenophanes containing nitrogen atoms in the chain have been prepared by the first time. High yields (70-99%) have been obtained for medium-size compounds ([9] to [15] cyclophanes) but the Richman-Atkins methodology used does not seem to allow the preparation of smaller, highly strained systems. Molecular mechanics calculations suggest that conformational tendencies in these compounds follow similar patterns to those observed in related cyclophanes. Comparison with data obtained from the X-ray structure of **12** shows that molecular mechanics calculations can be used to accurately predict structural parameters for those macrocyclic systems. The lability of the benzylic C-N bond has precluded, up to now, the obtention of non-tosylated polyaza[n](9,10)anthracenophanes.

## EXPERIMENTAL SECTION

**General.** $^1H$ and $^{13}C$ NMR spectra were recorded at 200 and 50.3 MHz, respectively, in $CDCl_3$ and data are reported in ppm (δ). Molecular mechanics calculations with the MM2*[23] and AMBER*[24] force fields were performed with version 5.0 of MACROMODEL on an Indy Workstation of Silicon Graphics. The GB/SA solvation treatment was considered for chloroform.[25] These force fields were used as implemented in Macromodel without modification of any of the parameters. Starting geometries were drawn manually in the Input mode of the program and the torsional Monte Carlo method exploited by the BATCHMIN V5.0 molecular mechanics program was used for the conformational search. Structures were minimized using the conjugate gradient minimization with the Polak-Ribiere first derivative method and the convergence criterion was a value of of 0.05 kJ $mol^{-1}$ $Å^{-1}$ for the root-mean-square of the gradient. All structures were characterized as true minima. For each conformational search 500 to 1000 structures were generated and minimized to yield, in general a high number of unique conformers. The energy window was 25 kJ $mol^{-1}$.

**9,10-bis(bromomethyl)anthracene (8).** Anthracene (5 g, 28 mmol) was dissolved in a mixture of 48% aqueous hydrobromic acid (100 mL) and glacial acetic acid (25 mL) and then 1,3,5-trioxane (5 g, 56 mmol) and tetradecyltrimethylammonium bromide (0.2 g) were added. The mixture was stirred and refluxed for 24 h. After cooling, the green solid formed was filtered and washed with water and ethanol. The resulting crude product was recrystalized in toluene (7.66 g, 75%). mp >300 °C (dec.); IR (KBr) 3048, 1953, 1622, 1528, 1442, 1195 $cm^{-1}$; $^1H$ NMR: 5.50 (s, 4 H), 7.68 (dd, $J_1$= 3.4 Hz, $J_2$= 6.9 Hz, 4 H), 8.38 (dd, $J_1$= 3.4 Hz, $J_2$= 6.9 Hz, 4 H); $^{13}C$ NMR: 26.6, 124.4, 125.4, 126.7, 127.7; MS *m/z* (FAB): 364 ([M]$^+$). Anal. Calcd. for $C_{16}H_{12}Br_2$: C, 52.8; H, 3.3. Found: C, 52.4; H, 3.7.

**N,N´,N´´-Tristosyl-2,6,10-triaza[11](9,10)anthracenophane (10).** Pertosylated 1,5,9-triazanonane (4.9 g, 8.2 mmol) and $K_2CO_3$ were suspended in refluxing $CH_3CN$ (300 mL). To this mixture, a solution of 9,10-bis(bromomethyl)anthracene (3 g, 8.2 mmol) in $CH_2Cl_2$ (100 mL) was added dropwise. After the addition was complete, the suspension was refluxed for 48 h and then filtered. The solution was vacuum evaporated to dryness to give the crude product which was purified by elution column chromatography on silica gel ($CH_2Cl_2$/AcOEt 97/3) to afford pure **10** as a dark yellow solid (6.2 g, 95%). mp >300 °C (dec.); IR (KBr) 3061, 2924, 1654, 1630, 1598, 1399, 1337, 1158 $cm^{-1}$; $^1H$ NMR: 0.4 (m, 4 H), 2.0 (t, 4 H), 2.36 (s, 3H), 2.54 (s, 6H), 5.35 (s, 4 H), 7.0-7.8 (m, 16H), 8.48 (dd, $J_1$= 3.1 Hz, $J_2$= 6.9 Hz, 4 H); $^{13}C$ NMR: 21.5, 21.7, 29.9, 45.8, 46.1, 46.3, 124.7, 126.8, 127.6, 129.6, 130.1, 130.8, 143.9; MS *m/z* (FAB): 796 ([M+H$^+$]). Anal. Calcd. for $C_{43}H_{45}N_3S_3O_6$: C, 64.9; H, 5.7; N, 5.3; S, 12.1. Found: C, 64.4; H, 5.8; N, 5.6; S, 12.5.

**N,N´,N´´-Tristosyl-2,5,8-triaza[9](9,10)anthracenophane (9).** 98% yield; mp 269-273 °C; $^1H$ NMR: 1.61 (m, 4 H), 2.05 (m, 5H), 2.39 (s, 3 H), 2.50 (s, 6 H), 5.34 (s, 4 H), 7.19 (d, J = 8.3 Hz, 2 H), 7.42 (d+d, J = 8.1, J' = 7.9 Hz, 6 H), 7.58 (dd, $J_1$ = 3.0 Hz, $J_2$ = 6.8 Hz, 4 H), 7.76 (d, J = 7.8 Hz, 4 H), 8.28 (dd, $J_1$=3.0 Hz, $J_2$= 6.8 Hz, 4 H); $^{13}C$ NMR: 21.5, 21.6, 43.7, 45.9, 46.5, 124.6, 126.8, 127.0, 127.3, 127.4, 129.6, 130.0, 131.4, 134.6, 143.1, 143.9; MS *m/z* (FAB): 763 ([M+H]$^+$). Anal. Calcd. for $C_{41}H_{41}N_3S_3O_6$: C, 64.1; H, 5.4; N, 5.5; S, 12.5. Found: C, 64.1; H, 5.5; N, 5.8; S, 13.0.

**N,N´,N´´,N´´´-Tetrakistosyl-2,5,8,11-tetraaza[12](9,10) anthracenophane (11).** 84% yield; mp >300 °C (dec.); $^1H$ NMR: 1.84 (s, 4 H), 2.30 (m, 4 H), 2.40 (s, 6 H), 2.55 (s, 6H), 2.94 (m, 4H), 5.18 (s, 4H), 7.23 (d, J = 8.4 Hz, 4 H), 7.45-7.60 (m, 12 H), 8.00 (d, J = 8.2 Hz, 4 H), 8.28 (dd, $J_1$=3.0 Hz, $J_2$= 6.8 Hz, 4 H); $^{13}C$ NMR: 21.5, 21.7, 45.5, 45.9, 47.8, 50.3, 124.6, 127.2, 127.3, 127.5, 127.9, 128.8, 129.7, 130.0, 130.2, 130.7, 130.9, 143.6, 144.2; MS *m/z* (FAB): 965 ([M+H]$^+$). Anal. Calcd. for $C_{50}H_{52}N_4S_4O_8$: C, 62.2; H, 5.4; N, 5.8; S, 13.3. Found: C, 62.1; H, 5.5; N, 6.1; S, 13.6.

**N,N´,N´´,N´´´-Tetrakistosyl-2,6,9,13-tetraaza[14](9,10)anthracenophane (12).** 70% yield; mp 177-178 °C; $^1H$ NMR: 0.80 (m, 4 H), 1.95 (s, 4H), 2.40 (s, 6 H), 2.50 (s, 6 H), 2.70 (t, 4 H ), 3.15 (t, 4 H), 5.15 (s, 4 H ),7.20 (d, 4 H), 7.50 (m, 8 H + 4 H), 7.90 (d, 4 H), 8.50 (dd, 2 H); $^{13}C$ NMR: 21.5, 21.7, 29.2, 46.4, 46.5, 46.8, 47.6, 124.7, 126.8, 127.3, 127.7, 129.6, 130.2, 130.8, 134.2, 135.3, 143.3, 144.0; MS *m/z* (FAB): 993 ([M+H] $^+$). Anal. Calcd. for $C_{52}H_{56}N_4S_4O_8$: C, 62.9; H, 5.7; N, 5.6; S, 12.9. Found: C, 62.6; H, 5.7; N, 5.9; S, 13.3.

**N,N´,N´´,N´´´,N´´´´-Pentakistosyl-2,5,8,11,14-pentaaza[15](9,10)anthracenophane (13).** 79% yield. mp >300 °C (dec.); $^1H$ NMR: 2.1-2.6 (m, 21 H), 2.70 (m, 4 H), 3.0 (m, 4 H), 5.1 (s, 4 H), 7.20-8.0 (m, 24 H), 8.27 (m, 4 H); $^{13}C$ NMR: 22.5, 45.4, 46.1, 46.7, 48.5, 49.5, 124.6, 126.8, 127.4, 127.7, 128.3, 129.7, 130.1,

131.0, 134.9, 143.6, 144.1; MS *m/z* (FAB): 1162 ([M+H] $^+$). Anal. Calcd. for $C_{59}H_{63}N_5S_5O_{10}$: C, 60.96; H, 5.5; N, 6.0; S, 13.8. Found: C, 60.6; H, 5.7; N, 6.1; S, 14.0.

**Bis(N,N´-ditosyl-2,7-diazaheptyl)(9,10)anthracene (17).** 15% yield. mp 108-110 °C; $^1$H NMR: 0.6 (m, 4 H), 0.8 (m, 4 H), 2.3 (m, 4 H), 2.4 (s, 6 H), 2.9 (t, 4 H), 3.7 (t, 2 H), 5.3 (s, 4 H), 7.2 (d, 4 H), 7.3-7.6 (m, 12 H), 7.9 (d, 4 H), 8.5 (dd, 4 H); $^{13}$C NMR: 21.5, 21.6, 25.7, 26.2, 42.0, 45.8, 47.2, 124.9, 126.4, 126.9, 127.7, 129.6, 130.0, 130.8, 134.3, 136.5, 143.2, 143.9.

**Crystal Structure Determination for 12.**

**Crystal Data.** $C_{52}N_4S_4O_8H_{55}.CH_3CN$; Fwt. 1033.32; Prismatic, space group $P\bar{1}$; a=14.450(4) Å; b=14.998(6) Å; c=15.717(6) Å; $\alpha$=94.31(3)°; $\beta$= 114.75(2)°; $\gamma$=116.15(3)°; V=2632(2); Z=2; $D_{calc}$ 1.305 g cm$^{-3}$; crystal size: 0.2 x 0.1 x 0.1 mm; $\mu(MoK_\alpha)$=2.279 cm$^{-1}$.

**Data Collection.** Diffraction data on a prismatic crystal were collected at 293 K with an Enraf-Nonius CAD-4 Diffractometer using graphite-monochromated $MoK_\alpha$ radiation ($\lambda$=0.71703 Å). The cell parameters were determined by least-square refinement of 25 well-centered reflections in the range $12<\theta>20°$. A total of 8849 reflections were collected in the range $0<2\theta>50°$. Three reference reflections monitored throughout data collection showed no significant signs of crystal deterioration. The usual correction for Lorentz and polarisation effects were carried out but not for absorption correction (the absorption correction was $\mu$=2.279 cm$^{-1}$).

**Structure solution and refinement.** The structure was resolved by Patterson methods and refined by the full-matrix least-square methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter. The final full-matrix least-square refinement, minimizing $\sum[\omega(F_o-F_c)^2]$ and including 5584 reflections with $I \geq 4\sigma(I)$, each reflection being assigned a unity weight, converged at R and R$\omega$ 5.6 and 8.1, respectively. ($R=\sum(|F_o|-|F_c|)/\sum|F_o|$, $R\omega=\sum[\omega(F_o-F_c)^2]/\sum\omega|F_o|^2$, $\omega=4F_o^2/[\gamma^2(|F_o|) - (0.00000043|F_o|^2])$. f, f' and f'' were taken from ref. 20a. All calculations were performed by using SHELX 86,[20b] SHELX 76,[20c] and SCHAKAL[20d] programs.

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