Diazadioxacyclophanes

Richard A. Bartsch[a], Peter G. Jones[b], Piotr Kuś[c], and Ina Dix[d]

[a] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, USA
[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
[c] Department of Chemistry, Silesian University, 9 Szkolna Street, 40-006 Katowice, Poland
[d] Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany

Reprint requests to Dr. Piotr Kuś. E-mail: pkus@ich.us.edu.pl

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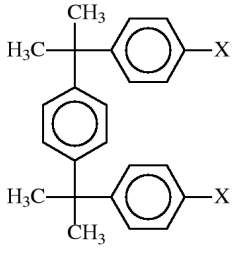
Six new cyclophane molecules (**5** – **10**) were synthesized from α,α'-bis(*N*-tosyl-4-aminophenyl)-1,4-diisopropylbenzene and α,α'-bis[4-(*n*-bromoalkyloxy)phenyl]-1,4-diisopropylbenzene. The crystal and molecular structures of α,α'-bis(4-aminophenyl)-1,4-diisopropylbenzene (**3**), α,α'-bis (*N*-tosyl-4-aminophenyl)-1,4-diisopropylbenzene **4** and the ditosyl derivative of the diazadioxacyclophane **6** were determined. The noncyclic compounds **3** and **4** display the *anti* conformation. Diazadioxacyclophane **6** possesses a central cavity that might be exploited to accommodate guest molecules, but some conformational change would probably be required.

Key words: Diazadioxacyclophane, Solid-state Structure, C–H$\cdots\pi$ Interactions

Introduction

In a search for new supramolecular "hosts", we have focused our attention on the triphenyldiisopropyl fragment **1**. According to the results of our preliminary model studies, it should prove much more useful than the diphenylmethane derivatives that were investigated earlier [1]. The dihydroxy derivative **2** was the starting point for a series of derivatives (called "corrals") that can form inclusion-type compounds with various aromatic molecules [2 – 5].

Compound **2** has also been used to obtain dioxacyclophanes and non-symmetric tetraoxacyclophanes, the other component of which is provided by aromatic dimethylene derivatives, for example: *ortho*-, *meta*- and *para*-xylenes [5], dimethylferrocene [6], 2,2″-dimethylterphenyl [7], and 4,4′-dihydroxybenzophenone [8, 9]. The presence of aromatic rings and polymethylene fragments means that all of the compounds thus obtained are very hydrophobic. Not all cyclic compounds obtained from the above-mentioned fragments form inclusion-type compounds with other molecules. Sometimes the geometry of the particular fragments making up the macrocycle does not permit the formation of a molecular cage capable of receiving the guest.



1 X = H
2 X = OH
3 X = NH_2
4 X = Tos-NH

The next compound that we decided to investigate in our search for suitable hosts was the diamine derivative **3**. This compound is known, but it is unavailable commercially; it can be obtained using a procedure slightly modified from that described in [10]. Compound **3** can be used in a manner similar to that known for 4,4′-di(aminophenyl)methane, the derivatives of which have often been used in the synthesis of cyclic, water-soluble polyparacyclophanes [11 – 13]. In our work we used synthetic methods reported for other cyclic compounds, with some modifications. Similarly to the dihydroxy derivative **2**, the diamine derivative **3** should force the molecule to create a suitable cavity capable of

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forming various inclusion-type compounds, especially with acidic compounds such as dicarboxylic acids.

The ditosyl derivative **4**, similarly to **2** and **3**, can occur in an *anti* conformation, which is not favorable for forming cyclic combinations, or in a *syn* conformation, which the molecule must adopt during cyclization. Our crystallographic studies of compound **2** [14] and compound **4** (see below) have confirmed the *anti* orientation in the solid, although the *syn* form must be present to a significant extent in solution.

Results and Discussion

Fig. 1 shows the crystal structure of the diamine derivative **3** as determined by single crystal X-ray diffraction analysis. The molecule displays no imposed symmetry. The outer ring orientations differ slightly, but the molecule displays approximate non-crystallographic inversion symmetry, as can be seen from the following pairs of equivalent torsion angles: C3–C4–C7–C10 27° *vs*. C14–C13–C16–C19 −31°, C4–C7–C10–C11 71° *vs*. C24–C19–C16–C13 −60°. The outer rings subtend interplanar angles of 85° and 75° to the central ring; intercentroid distances are 4.92 and 4.85 Å. The NH_2 groups are pyramidal, with the nitrogen atoms lying 0.28, 0.21 Å out of the plane of their substituents.

The molecule contains four H atoms (in the NH_2 groups) that are potential classical H bond donors, and two nitrogen atoms that are potential acceptors, but only one classical H bond is formed. Additionally, there are two N–H$\cdots\pi$ and one C–H$\cdots\pi$ interactions, all at short distances and acceptably linear angles (Fig. 2, Table 1). These interactions all lie in the regions $z \approx 0, 1/2, 1$, *etc*. One C–H$\cdots$N contact is listed in Table 1, but has a narrow angle; it is not included in Fig. 2.

The molecule of the ditosyl derivative **4** is shown in Fig. 3; it displays crystallographic inversion symmetry, and the *anti* conformation is clearly recogniz-

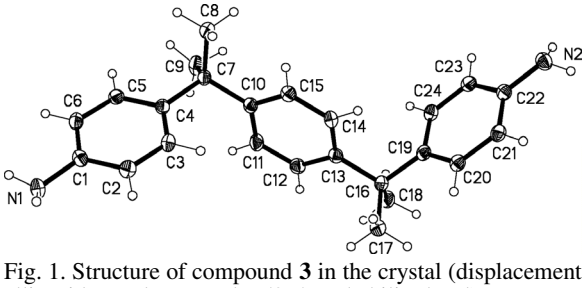


Fig. 1. Structure of compound **3** in the crystal (displacement ellipsoids are drawn at the 50 % probability level).

Table 1. Hydrogen bonds (Å and deg) for compound **3**[a].

D–H$\cdots$A	*d*(D–H)	*d*(H$\cdots$A)	*d*(D$\cdots$A)	∠(DHA)
N2–H03$\cdots$N1$^{\#1}$	0.95(3)	2.31(3)	3.231(3)	164(2)
N1–H01$\cdots$*C*(1 – 6)$^{\#2}$	0.93(3)	2.60	3.48	167
N2–H04$\cdots$*C*(19 – 24)$^{\#3}$	0.90(3)	2.71	3.60	176
C21–H21$\cdots$*C*(1 – 6)$^{\#1}$	1.08	2.46	3.44	150
C5–H5$\cdots$N(2)$^{\#4}$	1.08	2.52	3.300(3)	128

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, y+1/2, -z+1/2$; $^{\#2}$ $x+1/2, -y+3/2, -z+1$; $^{\#3}$ $x-1/2, -y+3/2, -z$; $^{\#4}$ $-x, -1/2+y, 1/2-z$. C–H bond lengths are normalized to 1.08 Å. Designations such as "*C*(1 – 6)" refer to the ring centroids.

Table 2. Hydrogen bonds (Å and deg) for compound **4**[a].

D–H$\cdots$A	*d*(D–H)	*d*(H$\cdots$A)	*d*(D$\cdots$A)	∠(DHA)
N–H01$\cdots$O1$^{\#1}$	0.808(14)	2.290(14)	3.0770(15)	164.6(17)
C12–H12$\cdots$O2$^{\#1}$	0.95	2.60	3.4312(16)	146
C25–H25$\cdots$O1$^{\#2}$	0.95	2.49	3.2331(17)	136
C16–H16$\cdots$O2$^{\#3}$	0.95	2.46	3.2621(17)	142

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1/2, y+1/2, -z+1/2$; $^{\#2}$ $x, y+1, z$; $^{\#3}$ $-x+1/2, y-1/2, -z+1/2$.

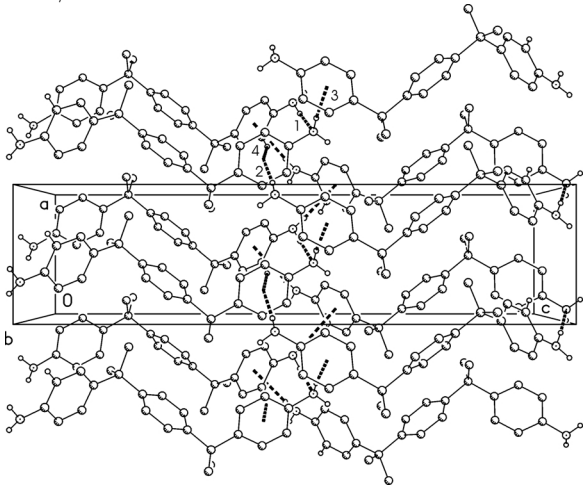


Fig. 2. Packing diagram of compound **3**. Thick dashed bonds in the region $z \approx 1/2$ represent hydrogen bonds (see text), and are numbered in the order in which they appear in Table 1.

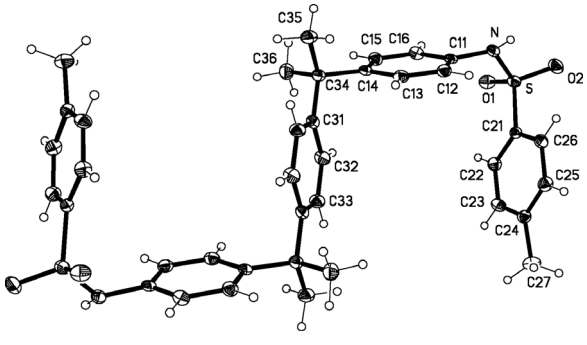


Fig. 3. Structure of compound **4** in the crystal (displacement ellipsoids at the 50 % probability level).

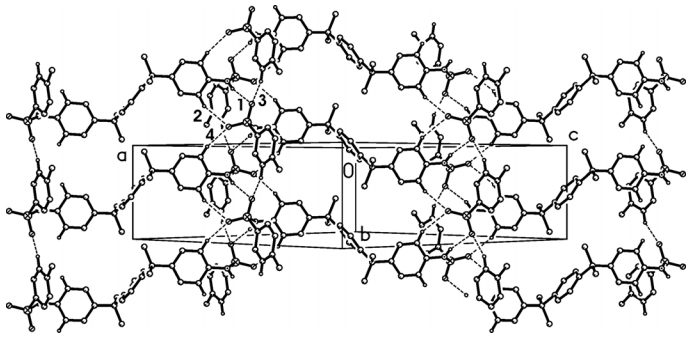
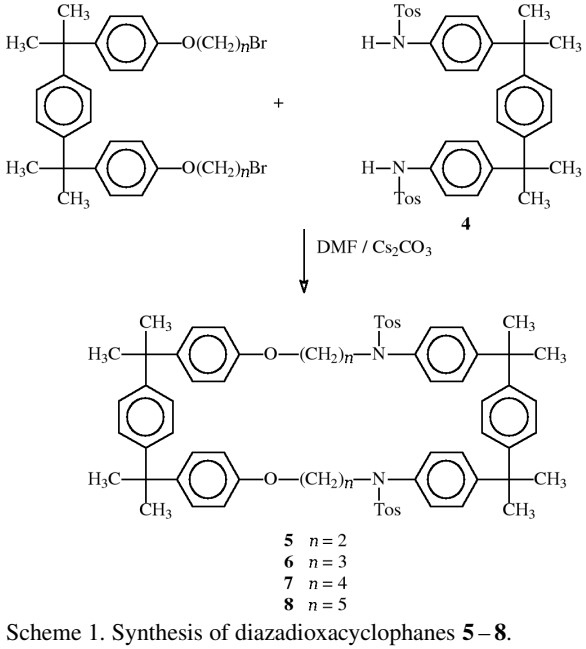


Fig. 4. Packing of compound **4** in the crystal. Thick dashed bonds represent hydrogen bonds (see text) and are numbered in the order in which they appear in Table 2.



Scheme 1. Synthesis of diazadioxacyclophanes **5** – **8**.

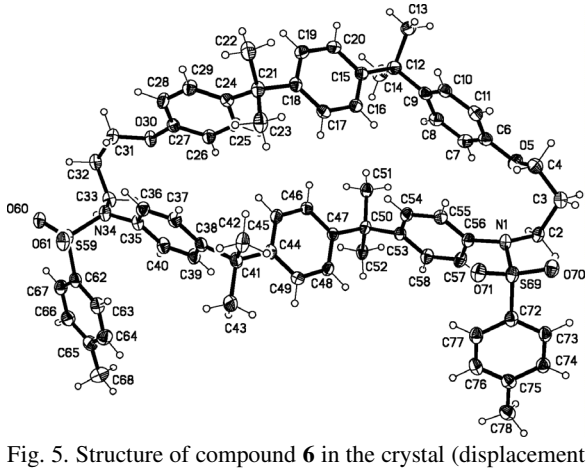
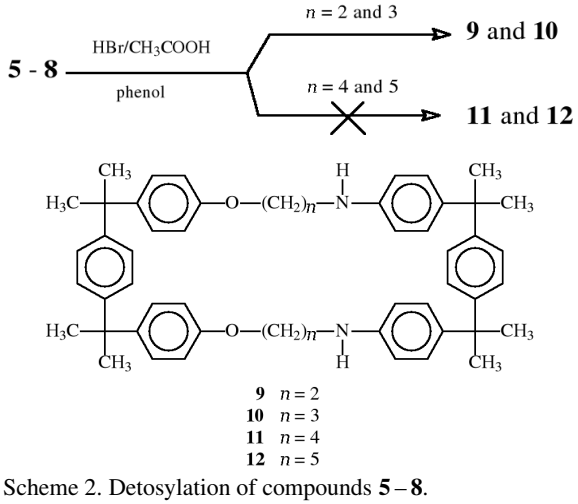


Fig. 5. Structure of compound **6** in the crystal (displacement ellipsoids at the 50 % probability level).

able. The ring C11–16 subtends interplanar angles of 72° to C21–26 and 87° to the central ring. The asymmetric unit contains one classical H bond donor (the NH group) and two classical acceptors (the O atoms of the SO_2 group). As would be expected, "weak" C–H···O interactions supplement the classical N–H···O hydrogen bonds. Each O atom acts as acceptor to two H bonds (Table 2), in such a way as to form a layer structure parallel to (101) (Fig. 4).

Compounds **5** – **8** were obtained from the ditosyl derivative **4** and appropriate di(ω-bromoalkyl) derivatives of compound **2**, as shown in Scheme 1. The yields of cyclic compounds were: **5** 35 %, **6** 55 %, **7** 42 % and **8** 52 %.

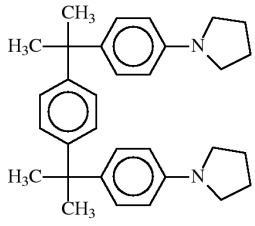
The tosyl derivatives are easily soluble in organic solvents. Single crystals of compound **6** were obtained and its structure determined (Fig. 5). The molecule has very approximate mirror symmetry (torsion angles in the sequences C56–N1–C2–C3–C4–O5–C6 and C35–N34–C33–C32–C31–O30–C27 are equal and opposite), but the central rings in particular (C15–20 and C44–48) depart considerably from the ideal symmetry. The molecule possesses a central cavity, but it is not clear how this should be defined. The centroids of the rings C6–11, 24–29, 35–40, and 53–58 define a rectangular box with approximate dimensions 9.5 × 4.5 Å, but this is effectively blocked by the contacts H25···H45, H23C···H42A and H16···H51A, which are all *ca*. 2.5 Å. A more realistic box is that defined by the atoms C12, C21, C41, and C50, with all sides *ca*. 6 Å. To utilize this box for host-guest interactions, the central rings (with an interplanar angle of 6° and an intercentroid distance of 6 Å) would have to rotate considerably. Other conformational changes would also be needed, even more so if the larger box was to be utilized. The packing involves four C–H···O and two C–H···π interactions, but we do not present the over-



Scheme 2. Detosylation of compounds **5**–**8**.

all picture because of its complexity. The remaining cyclic compounds do not crystallize easily and, so far, we have not succeeded in obtaining crystals suitable for crystallographic studies.

The detosylation of compounds **5**–**8** proved to be difficult (Scheme 2). After trying several methods, we found that the best was that described in lit. [15], based on the use of hydrogen bromide solution in acetic acid with small amounts of phenol. In this way we were able to detosylate all of compounds **5**–**8**. In the case of compounds **5** and **6**, the expected cyclic compounds **9** and **10** were obtained, and their structure was confirmed using elemental analysis and spectroscopic methods. With compounds **7** and **8**, a mixture of compounds was obtained from which we were in each case able to isolate one main product, **13** from **7** and **14** from **8**. These compounds were characteristized by the lack of an NH vibrational band in their IR spectra, and by the presence of only two signals originating from aliphatic methylene protons for **13** and three for **14**, whereas there should be four signals for **11** and five for **12** (two triplets from the outlying methylene groups in both compounds, similar to compounds **9** and **10**) in their ^{1}H NMR spectra. No ions with a mass corresponding to the detosylated cyclic compounds **11** and **12** could be detected by mass spectrometry of the mixtures. These compounds (**13** and **14**) were extremely unstable in solution. Spectroscopic data and mass spectra were in agreement with structures **13** and **14**. These are not cyclic compounds with a large cavity, but instead are aromatic heterocyclic derivatives unsuitable for 'host-guest'-type systems. The formation of these compounds can be explained by the promotion of ether



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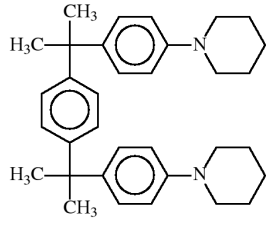

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bond breakage by hydrogen bromide. The question remains unsettled, however, why such products were only obtained in these cases. We surmise that the stability of five- and six-membered rings may be the deciding factor.

So far, we have not been able to obtain inclusion-type compounds from these cyclophanes and other organic molecules; diazadioxacyclophanes do not co-crystallize readily. Some interesting information concerning their ability to form complexes is provided by mass spectrometric data. ESI MS can often provide evidence for adducts of macrocycles with alkali metal cations [16, 17]. For this reason, we studied the relative cation affinity of our diazadioxacyclophanes; an electrospray ionization source without any separation columns (flow injection system) was used. A stock solution of the diazadioxacyclophane was mixed with excess solution of the following cations: Li^+, Na^+, K^+, Rb^+ and Cs^+. The cesiated molecules $[M+Cs]^+$ dominated in all mass spectra. The absence of any protonated peak indicates the very low affinity of diazadioxacyclophanes for protons and their high affinity for cations. Especially at high concentrations of added ions, clathrates were obtained; for example when using Li^+ ions from LiI for ionization, we obtained various ions $[M+n\text{LiI}+\text{Li}]^+$ (where n = 0–5) with differing intensities. It is noteworthy that in our experiment no clathrate formation between Li^+ and LiI is observed (in contrast to observations for other alkali metal salts [18]) leading to a mass smaller than that of the $[M+Li]^+$ ion.

Experimental Section

NMR spectra were obtained with a 400 MHz Bruker spectrometer. Spectra were taken in $CDCl_3$ or $[D_6]$DMSO, and chemical shifts are reported in ppm downfield from TMS. Reagent-grade reactants and solvents were used as received from chemical suppliers. The IR spectra were recorded with a Nicolet Magna 560 FT-IR spectrometer using KBr pellets. ESI mass spectra were recorded on a LCQ DUO Finni-

Table 3. Crystallographic data for compounds **3**, **4** and **6**.

	3	**4**	**6**
Formula	$C_{24}H_{28}N_2$	$C_{38}H_{40}N_2O_4S_2$	$C_{68}H_{74}N_2O_6S_2$
M_r	344.48	652.84	1079.41
Temperature, K	100(2)	108(2)	100(2)
Crystal size, mm^3	$0.20 \times 0.20 \times 0.05$	$0.40 \times 0.16 \times 0.10$	$0.055 \times 0.05 \times 0.012$
Crystal habit	colorless tablet	colorless prism	colorless plate
Radiation; λ, Å	CuK_α; 1.54184	MoK_α; 0.71073	CuK_α; 1.54184
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P2_1/c$
a, Å	6.4840(4)	22.2229(6)	11.3775(3)
b, Å	11.1766(8)	7.1134(3)	45.8875(12)
c, Å	26.1072(14)	21.4621(6)	12.3443(3)
β, deg	90	98.021(3)	116.091(3)
Volume, Å^3	1892.0(2)	3359.55(19)	5788.0(3)
Z	4	4	4
$D_{calcd.}$, g cm^{-3}	1.209	1.291	1.239
$F(000)$, e	744	1384	2304
$2\theta_{max}$, deg	142	61.4	133
Refl. collected/independ.	6569/2010	35832/4872	38663/10088
R_{int}	0.030	0.040	0.055
Completeness	99 % to 135°	98 % to 60°	99 % to 132°
Ref. parameters	255	215	713
$R1$ [$I > 2\sigma(I)$]	0.032	0.037	0.039
$wR2$ (all refl.)	0.077	0.105	0.096
Goodness-of-fit on F^2	1.07	1.06	1.01
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.15/−0.20	0.39/−0.29	0.32/−0.36

gan Thermoquest instrument for methanol/dichloromethane solutions in the presence of Li^+, Na^+, K^+, Rb^+ and Cs^+ salts.

Crystal structure determinations

Colorless single crystals were obtained from dichloromethane/methanol (**3**, **4**) and ethanol/dichloromethane (**6**) solutions by slow evaporation. Data were recorded on an Oxford Diffraction Nova diffractometer (CuK_α, microsource) for **3**, an Oxford Diffraction Xcalibur S diffractometer (MoK_α) for **4**, and a Bruker SMART 6000 diffractometer (CuK_α, rotating anode) for **6**. Absorption corrections were performed using the multi-scan method. Structures were refined using the program SHELXL-97 [19]. Hydrogen atoms were included as follows: NH refined freely, riding methyl groups, all other hydrogen atoms riding. Numerical details are given in Table 3.

Special features and exceptions

For compound **3**, the anomalous scattering of nitrogen was insufficient to determine the absolute structure; Friedel opposites were therefore merged. For compound **4**, the NH hydrogen was refined subject to a distance restraint.

Complete crystallographic data have been deposited at The Cambridge Crystallographic Data Centre under the numbers CCDC 690142 (**3**), 690143 (**4**), and 690144 (**6**). Copies can be obtained free of charge *via* www.ccdc.ac.uk/data.request/cif.

*α,α′-Bis(4-aminophenyl)-1,4-diisopropylbenzene (**3**)*

M. p. 173 – 175 °C (lit. 162 – 164 °C [10]). – ^{1}H NMR ([D$_6$]DMSO): δ = 7.05 (s, 4H), 6.86, 6.46 (dd, 8H, J = 8.4 Hz), 4.81 (bs, 4H), 1.52 (s, 12H). – ^{13}C NMR ([D$_6$]DMSO): δ = 30.7, 41.1, 113.7, 125.8, 126.8, 137.6, 146.1, 147.9.

*α,α′-Bis(N-tosyl-4-aminophenyl)-1,4-diisopropylbenzene (**4**)*

Compound **4** was obtained according to the described method [20]. Yield 60 %. – M. p. 271 – 272 °C. – ^{1}H NMR ([D$_6$]DMSO + $CDCl_3$): δ = 9.15 (s, 2H), 7.46 (m, 4H), 7.00 (m, 4H), 6.77 – 6.83 (m, 12H), 2.16 (bs, 6H), 1.36 (bs, 12H). – ^{13}C NMR ([D$_6$]DMSO + $CDCl_3$): δ = 21.0, 30.2, 41.5, 120.1, 125.6, 126.6, 126.9, 128.9, 134.7, 136.7, 142.6, 146.1, 147.1.

*Synthesis of compounds **5** – **8** (general procedure)*

A solution of α,α′-bis[4-(*n*-bromoalkyloxy)phenyl]-1,4-diisopropylbenzene (1 mmol) in 40 mL of dry DMF was added dropwise to the stirred mixture of α,α′-bis[4-(*N*-tosylamino)phenyl]-1,4-diisopropylbenzene (1 mmol) and

1.0 g of Cs_2CO_3 in 100 mL of dry DMF over 3 – 4 h at r. t. The resulting mixture was stirred for 48 h at r. t. and evaporated *in vacuo*. A CH_2Cl_2/water mixture was added to the residue, the organic layer was separated, washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography with dichloromethane and crystallized from a mixture of ethanol/dichloromethane (10 : 1, v/v).

*N,N′-Ditosyl-11²,18²,35²,42²-octamethyl-1,28-diaza-4,25-dioxa[4.1.1.4.1.1]paracyclophane (**5**)*

Yield 35 %. – M. p. > 260 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.54 (d, 4H, *J* = 8.4 Hz), 7.25 (d, 4H, *J* = 8.8 Hz), 7.10 (d, 4H, *J* = 8.4 Hz), 7.08 (s, 4H), 7.04 (d, 4H, *J* = 8.8 Hz), 7.04 (s, 4H), 6.94 (d, 4H, *J* = 8.8 Hz), 6.56 (d, 4H, *J* = 8.8 Hz), 3.95 (t, 4H), 3.89 (t, 4H), 2.42 (s, 6H), 1.62, (s, 12H), 1.61 (s, 12H). – ^{13}C NMR ($CDCl_3$): δ = 21.7, 30.9, 41.9, 42.6, 50.3, 65.9, 113.7, 126.3, 126.5, 127.6, 127.8, 127.9, 128.5, 129.5, 136.0, 137.0, 143.3, 143.5, 147.4, 147.9, 150.9, 156.2. – IR (KBr): ν = 3045, 2967, 2932, 2872, 1608, 1506, 1463, 1403, 1349, 1248, 1184, 1164, 1088, 1017, 833, 737, 711 cm^{-1}. – (+) ESI MS: *m/z* = 1058 $[M+Li]^+$. – Anal. for $C_{66}H_{70}N_2O_6S_2$: calcd. C 75.39, H 6.71, N 2.66; found C 75.30, H 6.88, N 2.56.

*N,N′-Ditosyl-12²,19²,37²,44²-octamethyl-1,30-diaza-5,26-dioxa[5.1.1.5.1.1]paracyclophane (**6**)*

Yield 55 %. – M. p. 237 – 241 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.47 (d, 4H, *J* = 8.0 Hz), 7.20 (d, 4H, *J* = 8.0 Hz), 7.12 (d, 4H, *J* = 8.8 Hz), 7.10 (s, 8H), 7.04 (d, 4H, *J* = 8.8 Hz), 6.93 (d, 4H), (d, 4H, *J* = 8.4 Hz), 6.64 (d, 4H, *J* = 8.8 Hz), 3.89 (t, 4H), 3.67 (t, 4H), 2.39 (s, 6H), 1.88 (q, 4H), 1.64 (s, 12H), 1.62 (s, 12H). – ^{13}C NMR ($CDCl_3$): δ = 21.6, 28.4, 30.8, 30.9, 41.9, 42.6, 47.8, 65.1, 113.9, 126.4, 126.5, 127.6, 127.7, 127.8, 128.1, 129.5, 135.4, 136.7, 143.3, 143.4, 147.4, 147.9, 150.7, 156.6. – IR (KBr): ν = 3051, 2967, 2930, 2872, 1608, 1506, 1463, 1402, 1349, 1247, 1184, 1164, 1088, 1017, 832, 737, 711 cm^{-1}. – (+) ESI MS: *m/z* = 1086 $[M+Li]^+$. – Anal. for $C_{68}H_{74}N_2O_6S_2$: calcd. C 75.66, H 6.91, N 2.59; found C 75.67, H 6.94, N 2.52.

*N,N′-Ditosyl-13²,20²,39²,46²-octamethyl-1,32-diaza-6,27-dioxa[6.1.1.6.1.1]paracyclophane (**7**)*

Yield 42 %. – M. p. 133 – 136 °C (as the monohydrate). – ^{1}H NMR ($CDCl_3$): δ = 7.47 (d, 4H, *J* = 8.4 Hz), 7.22 (d, 4H, *J* = 8.4 Hz), 7.10 (d, 4H, *J* = 8.4 Hz), 7.08 (s, 4H), 7.06 (s, 4H), 7.05 (d, 4H, *J* = 8.8 Hz), 6.89 (d, 4H, *J* = 8.4 Hz), 6.61 (d, 4H, *J* = 8.8 Hz), 3.83 (t, 4H), 3.53 (t, 4H), 2.41 (s, 6H), 1.62 (bs, 24H), 1.4 – 1.8 (m, 8H). – ^{13}C NMR ($CDCl_3$): δ = 21.7, 25.1, 26.4, 30.9, 41.9, 42.6, 50.4, 67.3, 113.8, 126.3, 126.5, 127.5, 127.8, 127.9, 128.2, 129.4, 135.6, 136.4, 143.0, 143.3, 147.5, 148.0, 150.6, 156.7. – IR (KBr): ν = 3035, 2966, 2935, 2871, 1608, 1506, 1471, 1402, 1384, 1348, 1248, 1183, 1164, 1089, 1017, 832, 736, 710 cm^{-1}. – (+) ESI MS: *m/z* = 1114 $[M+Li]^+$. – Anal. for $C_{70}H_{78}N_2O_6S_2 \cdot H_2O$: calcd. C 74.70, H 7.16, N 2.49; found C 75.01, H 6.96, N 2.37.

*N,N′-Ditosyl-14²,21²,41²,48²-octamethyl-1,34-diaza-7,28-dioxa[7.1.1.7.1.1]paracyclophane (**8**)*

Yield 52 %. – M. p. 201 – 205 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.46 (d, 4H, *J* = 8.0 Hz), 7.21 (d, 4H, *J* = 8.0 Hz), 7.12 (d, 4H, *J* = 8.8 Hz), 7.08 (s, 4H), 7.07 (s, 4H), 7.07 (d, 4H, *J* = 8.4 Hz), 6.90 (d, 4H, *J* = 8.4 Hz), 6.69 (d, 4H, *J* = 8.8 Hz), 3.80 (t, 4H), 3.48 (t, 4H), 2.39 (s, 6H), 1.68 (q, 4H), 1.63 (s, 12H), 1.61 (s, 12H), 1.42 – 1.48 (m, 8H). – ^{13}C NMR ($CDCl_3$): δ = 21.6, 22.9, 27.9, 28.7, 30.9, 30.9, 41.9, 42.5, 50.4, 67.5, 113.8, 126.3, 126.5, 127.5, 127.8, 127.8, 128.3, 129.4, 135.7, 136.7, 142.9, 143.3, 147.5, 148.0, 150.5, 156.8. – IR (KBr): ν = 3035, 2964, 2940, 2869, 1609, 1509, 1467, 1402, 1384, 1349, 1248, 1182, 1164, 1089, 1017, 831, 735, 711 cm^{-1}. (+) ESI MS: *m/z* = 1142 $[M+Li]^+$. – Anal. for $C_{72}H_{82}N_2O_6S_2$: calcd. C 76.15, H 7.28, N 2.47; found C 76.26, H 7.39, N 2.34.

*Detosylation of compounds **5** – **8** (general procedure)*

100 mg of ditosyl derivative (**5**, **6**, **7** or **8**) and 1 g of phenol were dissolved in 30 mL of a solution of HBr (33 %) in glacial acetic acid at r. t. The mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled, and 60 mL of ether was added, after which the mixture was refrigerated for 1 – 2 d. The white solid that precipitated was filtered off, washed with ether and dissolved in water. The solution was rendered alkaline with 30 % NaOH solution and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous $MgSO_4$ and evaporated; the residue was purified by chromatography on silica with dichloromethane.

*11²,18²,35²,42²-Octamethyl-1,28-diaza-4,25-dioxa-[4.1.1.4.1.1]paracyclophane (**9**)*

Yield 41 %. – M. p. *ca.* 290 °C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 7.11 (s, 4H), 7.06 (s, 4H), 6.75, 7.06 (dd, 8H, *J* = 8.6 Hz), 6.51, 6.96 (dd, 8H, *J* = 8.6 Hz), 4.08 (t, 4H), 3.96 (bs, 2H), 3.48 (t, 4H), 1.65 (s, 12H), 1.63 (s, 12H). – ^{13}C NMR ($CDCl_3$): δ = 30.8, 30.9, 41.8, 41.9, 43.6, 66.3, 112.9, 114.0, 126.4, 127.7, 127.8, 140.8, 143.6, 145.2, 147.9, 148.0, 156.5. – IR (KBr): ν = 3420, 3048, 2964, 2925, 2866, 1612, 1509, 1459, 1400, 1382, 1360, 1302, 1248, 1184, 1054, 1017, 911, 829, 731 cm^{-1}. – (+) ESI MS: *m/z* = 744 $[M+H]^+$, 750 $[M+Li]^+$, 884 $[M+LiI+Li]^+$. – Anal. for $C_{52}H_{58}O_2N_2$: calcd. C 84.05, H 7.87, N 3.77; found C 83.65, H 7.85, N 3.60.

*$12^2,19^2,37^2,44^2$-Octamethyl-1,30-diaza-5,26-dioxa-[5.1.1.5.1.1]paracyclophane (**10**)*

Yield 43 %. – M. p. 274 – 276 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.12 (s, 8H), 6.76, 7.09 (dd, 8H, J = 8.6 Hz), 6.50, 7.00 (dd, 8H, J = 8.6 Hz), 4.03 (t, 4H), 3.78 (bs, 2H), 3.29 (t, 4H), 1.65 (s, 12H), 1.62 (s, 12H). – ^{13}C NMR ($CDCl_3$): δ = 29.1, 30.9, 30.9, 41.7, 41.8, 41.9, 66.2, 112.6, 113.9, 126.3, 126.4, 127.7, 127.8, 140.2, 143.4, 145.8, 147.9, 148.1, 156.7. – IR (KBr): ν = 3419, 3401, 3053, 2968, 2931, 2869, 1615, 1516, 1507, 1473, 1458, 1404, 1363, 1299, 1244, 1185, 1151, 1065, 1021, 830, 668 cm^{-1}. – (+) ESI MS: m/z = 772 $[M+H]^+$, 778 $[M+Li]^+$, 912 $[M+LiI+Li]^+$. – Anal. for $C_{54}H_{62}O_2N_2$: calcd. C 84.11, H 8.10, N 3.63; found C 84.01, H 8.07, N 3.68.

*Compound **13***

^{1}H NMR ($CDCl_3$): δ = 7.11 (s, 4H), 6.48, 7.10 (dd, 8H, J = 8.8 Hz), 3.25 (m, 8H), 1.96 (m, 8H), 1.62 (s, 12H). – IR (KBr): ν = 3088, 2959, 2930, 2889, 2865, 2824, 1614, 1557, 1520, 1492, 1459, 1375, 1358, 1283, 1242, 1200, 1180, 1158, 1084, 1020, 906, 830, 810, 731 cm^{-1}. – MS (EI 70 eV): m/z = 452 $[M]^+$. – Anal. for $C_{32}H_{40}N_2 \cdot H_2O$: calcd. C 81.66, H 8.99, N 5.95; found C 81.76, H 8.54, N 5.66.

*Compound **14***

^{1}H NMR ($CDCl_3$): δ = 7.08 (s, 4H), 6.83, 7.10 (dd, 8H, J = 8.8 Hz), 3.11 (m, 8H), 1.50 – 1.70 (m, 12H), 1.62 (s, 12H). – IR (KBr): ν = 3089, 3031, 2960, 2931, 2854, 2807, 1617, 1560, 1516, 1450, 1383, 1357, 1335, 1243, 1130, 919, 819 cm^{-1}. – MS (EI 70 eV): m/z = 480 $[M]^+$. – Anal. for $C_{34}H_{44}N_2$: calcd. C 84.95, H 9.23, N 5.83; found C 84.22, H 8.85, N 4.96.

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