# Self-Assembling [2]- and [3]Rotaxanes from Secondary Dialkylammonium Salts and Crown Ethers**

**Peter R. Ashton, Peter T. Glink, J. Fraser Stoddart,* Peter A. Tasker, Andrew J. P. White, and David J. Williams**

**Abstract**: The self-assembly of three new rotaxanes—two [2]rotaxanes and a [3]rotaxane—formed by a "threading followed by stoppering" approach is described. These template-directed syntheses rely on the formation of pseudorotaxane intermediates, which self-assemble in solution from functionalized secondary dialkylammonium hexafluorophosphate threads and macrocyclic polyether rings (either dibenzo-[24]crown-8 or its asymmetric constitutional isomer). The stoppers—substituted 1,2,3-triazoles—were created by thermally allowed 1,3-dipolar cycloadditions between azido groups, which terminate the threads, and di-*tert*-butyl acetylenedicarboxylate.

**Keywords**
interlocking molecules · molecular recognition · pseudorotaxanes · rotaxanes · template syntheses

## Introduction

Rotaxanes[1]—mechanically interlocked molecules, such as those depicted by the cartoons in Figure 1—have recently been elevated from the ranks of scientific curiosities to the level of chemically desirable and synthetically attainable[2] molecular compounds, primarily as a result of the burgeoning powers of supramolecular chemistry[3] and self-assembly[4] being brought together and made to act in unison. As a result of their "bead on a thread" structure and abacuslike properties, these molecules have considerable potential for applications (e.g., as shuttles[2a, 5] under chemical,[6] electrochemical,[7] or photochemical[8] control) in the fields of crystal engineering,[9] molecular sensors,[10] and polymer chemistry.[11] Recently, we have described novel supramolecular systems,[12–14] based upon the noncovalent bonding interactions that occur between secondary dialkylammonium ion centers and suitably sized crown ethers (24 ring atoms or more), which possess pseudorotaxane[15] structures in the solid state, in solution, and in the gas phase. Here, we wish to report[16] the results of our initial efforts in employing the information obtained from studying these pseudorotaxanes to self-assemble two new [2]rotaxanes and a new [3]rotaxane.

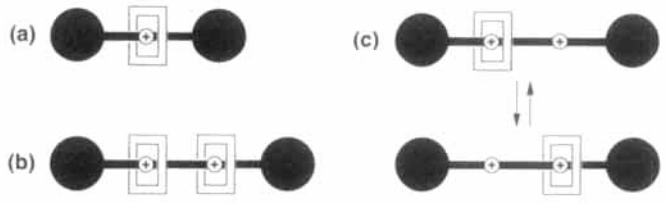


Fig. 1. Generic rotaxanes: a) a [2]rotaxane, b) a [3]rotaxane, and c) a two-station [2]rotaxane. These interlocked molecules comprise "beads" on "threads"—often containing recognition sites—terminated by sterically impassable "stoppers". The prefix of an [*n*]rotaxane indicates the number of interlocked components.

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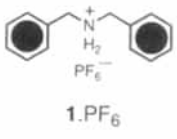
[**] Molecular Meccano, Part 7: for Part 6; see the preceding paper in this issue (ref. [14]).

## Results and Discussion

The 1:1 complex between dibenzylammonium hexafluorophosphate (**1**·$PF_6$) and dibenzo[24]crown-8 (**DB24C8**) exists as a [2]pseudorotaxane in the solid state[12, 14] in which the two benzyl groups of the disubstituted ammonium cation protrude from opposite faces of the macrocyclic polyether. If the phenyl rings of these two benzyl groups are now substituted with a functional group that can undergo reaction—without disrupting the hydrogen bonding and ion–dipole interactions which stabilize the pseudorotaxane in solution—with a suitably bulky molecule, then we will have all the elements necessary for a "threading followed by stoppering" rotaxane synthesis.[17] Not wishing to use reactions that require nucleophiles or bases—which would deprotonate the dialkylammonium ion center[18]—we chose a thermally allowed cycloaddition for the formation of the stoppers. The 1,3-dipolar cycloaddition between an azide and an electron-deficient alkyne[19] seemed a suitable choice since 1) azides are easily prepared, 2) bulky electron-deficient alkynes are commercially available or easily prepared, and 3) the cycloaddition is known to proceed very




**1**·$PF_6$

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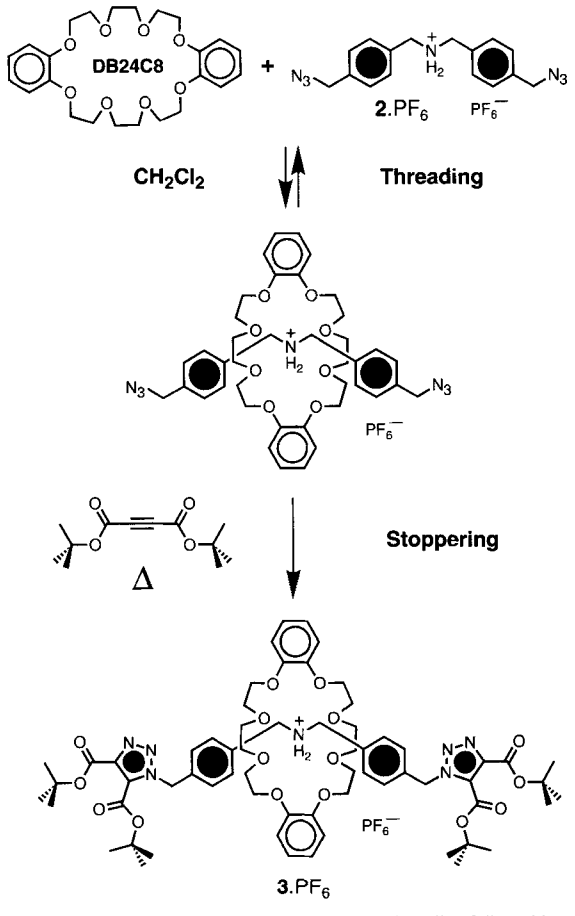
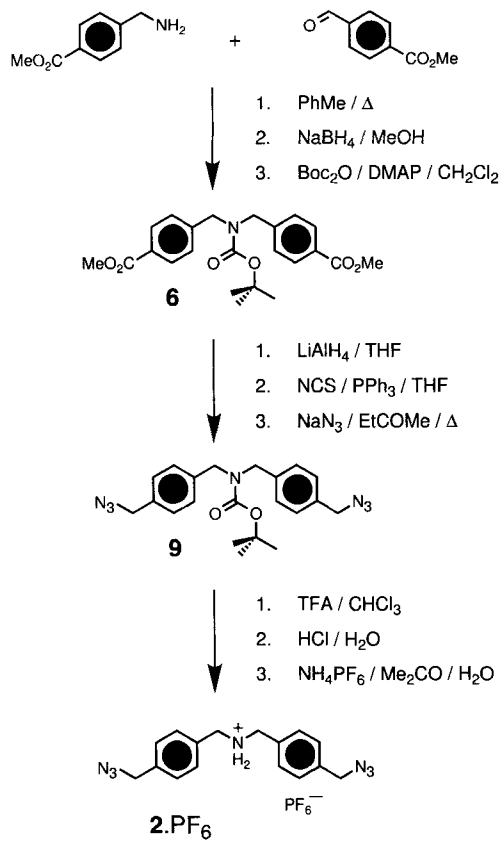
efficiently in a number of solvents. The proposed rotaxane-forming reaction between a bisazide $2\cdot PF_6$ and di-*tert*-butyl-acetylene dicarboxylate is depicted in Scheme 1. Inspection of CPK space-filling molecular models indicated that the triazole stoppers in the [2]rotaxane $3\cdot PF_6$, formed by the 1,3-dipolar cycloaddition between $2\cdot PF_6$ and the electron-deficient alkyne, are too large to allow dethreading of **DB24C8** from the dumbbell component of $3\cdot PF_6$.




Scheme 1. Synthesis of [2]rotaxane $3\cdot PF_6$ by a "threading followed by stoppering" approach.

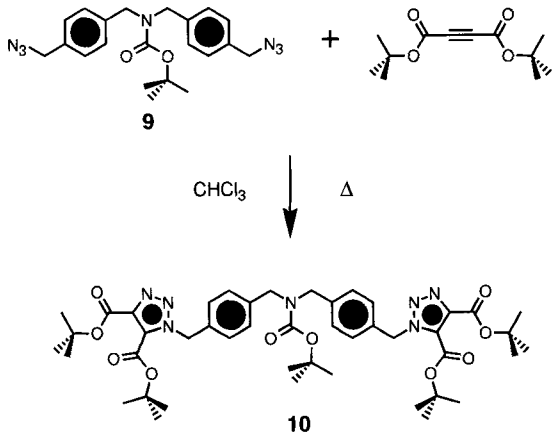
The synthesis of $2\cdot PF_6$ is outlined in Scheme 2. Methyl 4-aminomethylbenzoate[20] was condensed with methyl 4-formylbenzoate, and the imine (**4**) was reduced to the secondary amine (**5**), which was then Boc-protected to afford **6**. Reduction of the ester functionalities gave the expected diol (**7**), which was chlorinated[21] with the NCS/$PPh_3$ system before being converted to the bisazide **9** under Finkelstein conditions.[22] Removal of the Boc protecting group and subsequent counterion exchange gave the desired functionalized secondary dialkylammonium salt $2\cdot PF_6$. All the reactions in this sequence proceed efficiently and little or no chromatography is required: $2\cdot PF_6$ can be obtained readily in gram quantities in 34% overall yield from methyl 4-aminomethylbenzoate. Gratifyingly, $2\cdot PF_6$ is soluble[23] in $CHCl_3$ and $CH_2Cl_2$ solutions containing equimolar amounts of **DB24C8**. As in the case of the 1:1 complex formed between $1\cdot PF_6$ and **DB24C8** in a number of solvents,[12, 14] the $^1H$ NMR spectrum of an equimolar mixture of $2\cdot PF_6$ and **DB24C8** displays three sets of resonances—namely, signals for the 1:1 complex itself, for free $2\cdot PF_6$, and for free **DB24C8**—consistent with a recognition system that has high activation




Scheme 2. Synthesis of $2\cdot PF_6$ (Boc: *N*-*tert*-butoxycarbonyl, DMAP: 4-dimethylaminopyridine, NCS: *N*-chlorosuccinimide, TFA: trifluoroacetic acid).

barriers for both the complexation and decomplexation steps and consequently undergoes slow rates of threading and dethreading on the $^1H$ NMR timescale. The association constant ($K_a$) for this 1:1 complex[24] in $CDCl_3$ is approximately $4000\,M^{-1}$, that is, about seven times less than the $K_a$ value of $27000\,M^{-1}$ for the corresponding 1:1 complex involving $1\cdot PF_6$,[12, 14] a difference which presumably reflects the slightly higher solubility of $2\cdot PF_6$ in $CDCl_3$.

The stoppering reaction was investigated initially with the Boc-protected bisazide **9**. The reaction (Scheme 3), which was complete after three days of heating under reflux in $CHCl_3$ using 4.0 molar equivalents of di-*tert*-butyl acetylenedicarboxylate, gave the bistriazole **10** in excellent yield.




Scheme 3. Investigation of the stoppering reaction on model azide **9**.



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Having satisfied ourselves of the high association constants for the 1:1 complex between $2 \cdot PF_6$ and **DB24C8** in chlorinated solvents and of the success of the model reaction, we attempted our first rotaxane synthesis. The bisazide $2 \cdot PF_6$ was dissolved in $CH_2Cl_2$ in the presence of **DB24C8** (present in excess in order to drive the equilibrium in the direction of the 1:1 complex), and an excess of di-*tert*-butyl acetylenedicarboxylate was added. The reaction mixture was heated under reflux for seven days, before being subjected to chromatography on silica gel to afford the rotaxane $3 \cdot PF_6$ in 31% yield (Scheme 1). The fact that the [2]rotaxane survives chromatography indicates quite convincingly that the triazole stoppers are sufficiently large to ensure interlocking of the two components. Moreover, the $^1$H NMR spectrum shows that the dumbbell and ring components are present,[25] not only in equal stoichiometric quantities, but also interlocked with one another. The FAB mass spectrum of $3 \cdot PF_6$ provides evidence for the [2]rotaxane—with the loss of its $PF_6^-$ counterion—in the form of the base peak at *m/z* 1209. Smaller peaks (ca. 5% of the base peak's intensity) were present for fragmentations of the molecular ion involving a) the loss of a butyl group (*m/z* 1152), b) the loss of a triazole stopper (*m/z* 941), and c) the loss of a **DB24C8** ring (*m/z* 761). No signal was observed at *m/z* 448 for the free **DB24C8** ring.

Single crystals suitable for X-ray crystallography were grown by slow evaporation of a $CHCl_3/CH_2Cl_2/Et_2O$ solution of the [2]rotaxane $3 \cdot PF_6$ over a period of several months.[26] The X-ray crystal structure analysis of $3^+$ shows (Fig. 2) the **DB24C8** ring to have an extended open conformation through the center

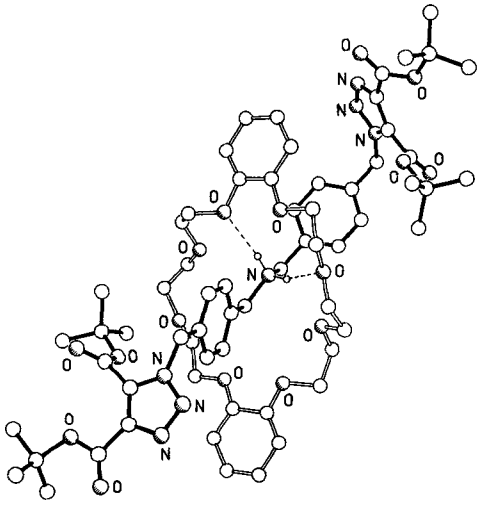
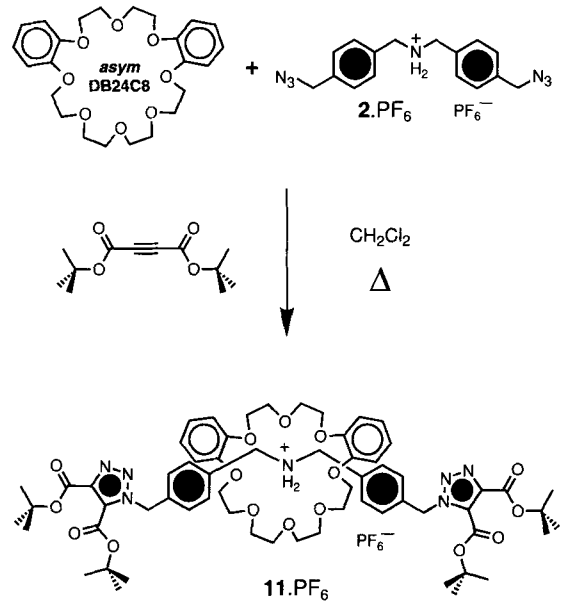


Fig. 2. The X-ray crystal structure of the [2]rotaxane $3 \cdot PF_6$.

of which is threaded the dumbbell-shaped cation. The [2]rotaxane is stabilized by a pair of [N–H···O] hydrogen bonds to one of the catechol oxygen atoms in one polyether linkage and to a dialkyl ether oxygen atom of the other. These hydrogen bonds are not particularly strong having [N···O] distances of 3.03 and 3.04 Å, respectively.[27] There are no significant intercomponent π–π stacking interactions, the centroid–centroid separation between the apparently overlapping catechol and paraxylyl rings being 4.34 Å. A study of the packing of the [2]rotaxane entities does not reveal any significant interrotaxane stabilizing effects, other than those arising from van der Waals interactions.

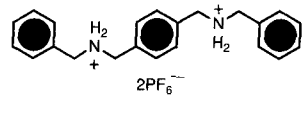
The formation of a [2]rotaxane $11 \cdot PF_6$, which is isomeric with $3 \cdot PF_6$, from asymmetric dibenzo[24]crown-8 (asym-**DB24C8**) as the ring component was investigated. We have shown recently that asym-**DB24C8** is an effective host for the complexation of secondary dialkylammonium ions.[14] Indeed, the superstructure formed in the solid state between $1 \cdot PF_6$ and asym-**DB24C8** has been established by X-ray crystallography to be that of a pseudorotaxane. Starting from this macrocycle, we were able to synthesize a [2]rotaxane, $11 \cdot PF_6$ (Scheme 4),

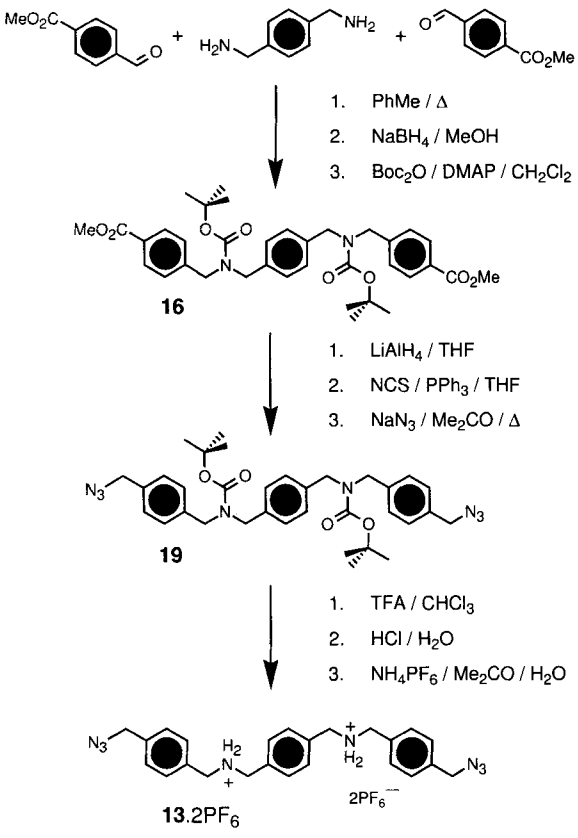



Scheme 4. Synthesis of $11 \cdot PF_6$ by a self-assembly protocol similar to that used for the isomeric rotaxane $3 \cdot PF_6$.

using a self-assembly protocol similar to that used in the synthesis of $3 \cdot PF_6$. A mixture of the bisazide ($2 \cdot PF_6$), asym-**DB24C8** (2.5 mol equiv) and di-*tert*-butyl acetylenedicarboxylate (4 mol equiv) were heated under reflux in $CH_2Cl_2$ for eight days. The [2]rotaxane $11 \cdot PF_6$ was isolated from the reaction mixture after chromatography in 24% yield. Once again, the ratio of the ring to dumbbell components was confirmed to be 1:1 by $^1$H NMR spectroscopy. The $^1$H NMR spectrum also established that the two components are indeed interlocked since the chemical shifts[28] for the resonances of protons of the bead and dumbbell components are shifted considerably from the δ values expected for the free components. The [2]rotaxane $11 \cdot PF_6$ gave a FAB mass spectrum very similar to that obtained for $3 \cdot PF_6$ in that there was a base peak in the spectrum at *m/z* 1209 for the molecular ion—having lost its $PF_6^-$ counterion—and fragmentations from this molecular ion were detected only as minor peaks (<5%).

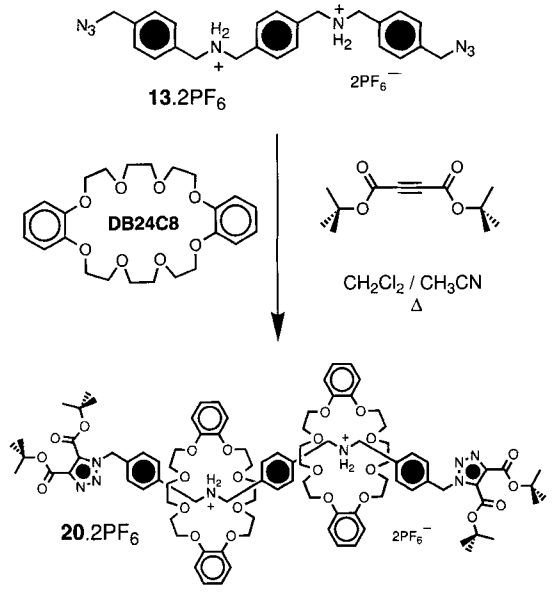
We have extended the template-directed methodology to the self-assembly of a rotaxane bearing two $NH_2^+$ ion centers. Recalling that $12 \cdot 2PF_6$ forms a 1:2 complex with **DB24C8** in both solution and solid states,[13, 14] we argued that we could obtain a [3]rotaxane by functionalizing the terminal phenyl rings with azidomethyl groups and then performing the 1,3-dipolar cycloaddition with di-*tert*-butyl acetylenedicarboxylate in the presence of an excess of **DB24C8**. This bisazide $13 \cdot 2PF_6$ was prepared in 50% yield over six steps (Scheme 5), via a route similar to that used to prepare $2 \cdot PF_6$. Evidence that a 1:2 complex is formed between $13 \cdot 2PF_6$ and **DB24C8** in solution was obtained by $^1$H NMR spectroscopy.[29] Reaction of $13 \cdot 2PF_6$ with di-*tert*-butyl






Scheme 5. Synthesis of bisazide **13**·$PF_6$ bearing two $NH_2^+$ centers.

acetylenedicarboxylate in the presence of an excess of **DB24C8** in $CH_2Cl_2/CH_3CN$ (ca. 20:1) for eight days (Scheme 6) led to the formation and subsequent isolation of the [3]rotaxane **20**·2$PF_6$ in 10% yield. The $^1$H NMR spectrum of **20**·2$PF_6$ (Fig. 3) is consistent with that expected on the basis of the palindromic symmetry of the dumbbell component and the asymmetry of the two faces of the crown ether—as well as with a 1:2 stoichiometry of the two components. The FAB mass spectrum of **20**·2$PF_6$ displays the molecular ion for the [3]rotaxane—having lost both $PF_6^-$ counterions—as the base peak at *m/z* 1777.




Scheme 6. Self-assembly of [3]rotaxane **20**·2$PF_6$.

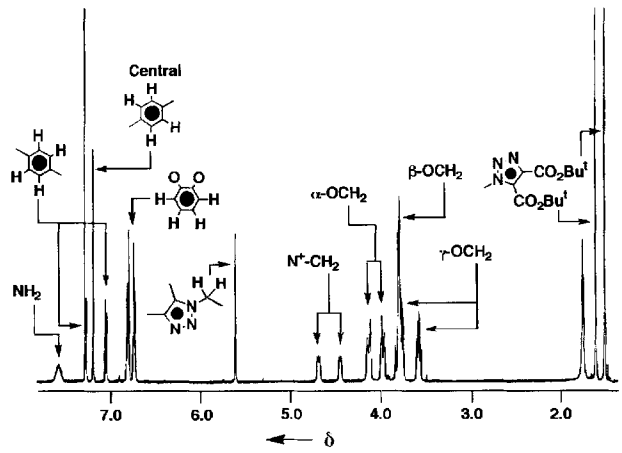



Fig. 3 . The $^1$H NMR spectrum of the [3]rotaxane **20**·2$PF_6$ recorded at 400 MHz in $CDCl_3$ at room temperature.

The major fragmentation of the [3]rotaxane **20**·2$PF_6$ is the extrusion of one **DB24C8** ring from the dumbbell component, presumably a result of the breaking of a covalent bond within the macrocyclic ring. Peaks corresponding to either the free dumbbell component or the free **DB24C8** macrocycle were not present in the spectrum.

So far, attempts to prepare "two-station" [2]rotaxanes from the dicationic threads and one equivalent of either **DB24C8** or asym-**DB24C8** have been unsuccessful. A probable explanation for this failure is that the intermediate cycloadduct is insoluble in $CH_2Cl_2$, $CHCl_3$, MeCN, and $Me_2CO$ in the presence of only one equivalent of either of the crown ethers and precipitates from the reaction mixture. The [3]rotaxane **20**·$PF_6$ can be synthesized successfully because the intermediate cycloadducts are soluble in $CH_2Cl_2$–MeCN mixtures in the presence of an *excess* of the crown ether. In fact, addition of the minimum of MeCN necessary to dissolve the bisammonium salt **13**·$PF_6$, followed by dilution with a solution of the crown ether in $CH_2Cl_2$, ensures that all of the intermediates are always complexed—and, consequently, do not precipitate—during the progress of the reaction.

We have shown that [2]- and [3]-rotaxanes may be prepared readily by sequences of simple reactions, given the self-assembling interactions that occur between secondary dialkylammonium cations and macrocyclic polyethers. These findings emphasize the potential of template-directed self-assembly as a new technique in organic synthesis and introduce a new family of rotaxanes to this ever-increasing class of fascinating interlocked molecular compounds.[1]

## Experimental Procedure

**General**: Chemicals were purchased from Aldrich and used without further purification. Solvents were either used as purchased or dried (THF from Na-benzophenone ketyl, MeCN from $CaH_2$) according to procedures described in the literature [30]. Methyl 4-formylbenzoate was prepared according to a published literature procedure [20]. Thin-layer chromatography was carried out using aluminum sheets precoated with silica gel 60 F (Merck 5554). The plates were inspected by UV light and developed with either a dilute solution of $I_2$ in $CHCl_3$ or a solution of 10% ammonium molybdate in dilute $H_2SO_4$ followed by development with heat. Column chromatography was carried out using silica gel 60 F (Merck 9385, 230–400 mesh). Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. $^1$H NMR spectra were recorded on either a Bruker AC 300 (300 MHz) spectrometer or a Bruker AMX 400 (400 MHz) spectrometer with either the solvent reference or TMS as the internal standard. $^{13}$C NMR spectra were recorded on a Bruker AC 300 (75.5 MHz) spectrometer or a Bruker AMX 400 (100.6 MHz) spectrometer using the JMOD pulse sequence. All chemical shifts are quoted on the $\delta$ scale. All coupling constants are expressed in Hertz (Hz). Low resolution electron impact mass spectra (EIMS) were obtained from either a Kratos Profile or VG



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Prospec mass spectrometers. Fast atom bombardment mass spectra (FABMS) were obtained from a Kratos MS80RF mass spectrometer coupled to an off-line Sun workstation for processing raw-data experiments. The atom gun was an adapted saddle-field source (Ion Tech) operating at 7 keV with a tube current of ca. 2 mA. Krypton was used to provide a primary beam of atoms, and samples of the molecules were dissolved in a small volume (ca. 1–2 μL) of *m*-nitrobenzyl alcohol and loaded on to a stainless steel probe tip. Spectra were recorded in the positive-ion mode at a scan speed of 10 s per decade. Liquid secondary-ion mass spectra (LSIMS) were obtained from a VG Zabspec mass spectrometer using a *m*-nitrobenzyl alcohol matrix and operating in the positive-ion mode at a scan speed of 5 s per decade. Accurate mass measurements were recorded in the VG Zabspec utilizing LSIMS with a *m*-nitrobenzyl alcohol matrix and employing narrow-range voltage scanning at a resolution of 6000 with either polyethyleneglycol or cesium iodide as reference compounds. Microanalyses were performed by the University of Sheffield Microanalytical Service.

**Bis(4-methoxycarbonylbenzyl)amine (5)**: A solution of methyl 4-aminomethylbenzoate (5.43 g, 32.9 mmol) and methyl 4-formylbenzoate (5.40 g, 32.9 mmol) was heated under reflux in PhMe (200 mL) and the liberated $H_2O$ was separated by means of a Dean–Stark apparatus. The organic phase was cooled and the PhMe was evaporated, yielding a white solid [**4**: $^1$H NMR ($CDCl_3$): $\delta$ = 3.92 (s, 3H; $CO_2CH_3$), 3.94 (s, 3H; $CO_2CH_3$), 4.90 (s, 2H; $CH_2N$), 7.43 (d, $J$ = 8.3 Hz, 2H; $CH$-C-$CH_2N$), 7.86 (d, $J$ = 8.0 Hz, 2H; $CH$-C-CH=N), 8.04 (d, $J$ = 8.3 Hz, 2H; $CH$-C-$CO_2$Me), 8.08 (d, $J$ = 8.0 Hz, 2H; $CH$-C-$CO_2$Me), 8.45 (s, 1H; CH=N); $^{13}$C NMR ($CHCl_3$): $\delta$ = 52.1 ($CO_2CH_3$), 52.3 ($CO_2CH_3$), 64.7 ($CH_2$-N), 127.8 (aromatic CH), 128.2 (aromatic CH), 129.0 (*C*-$CO_2CH_3$), 129.8 (aromatic CH), 129.9 (aromatic CH), 132.2 (*C*-$CO_2$Me), 139.8 (*C*-CH=N), 144.3 (*C*-$CH_2$-N), 161.6 (*C*H=N), 166.6 ($CO_2$Me), 167.4 ($CO_2$Me); MS (EI): *m/z* (%): 311 (62) $M^+$, 149 (100)].

The solid was taken up in warm MeOH (500 mL), and $NaBH_4$ (4 × 1.0 g, 4 × 26.4 mmol) was added portionwise to the warm solution over the following 2 h. The reaction mixture was stirred for 15 h at ambient temperature. Aqueous 2 M HCl solution (200 mL) was added carefully to the MeOH solution and then the solvents were evaporated in vacuo. The solid residue was suspended in aqueous 8 M NaOH (300 mL) and extracted with $CHCl_3$ (4 × 100 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated to yield the title compound as a thick oil, which eventually solidified (9.0 g, 90%); m.p. 55–58 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.68 (br, 1H; NH), 3.84 (s, 4H; $CH_2N$), 3.90 (s, 6H; $CH_3$), 7.41 (d, $J$ = 7.5 Hz, 4H; aromatic CH), 7.99 (d, $J$ = 7.5 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 52.1 ($CO_2CH_3$), 52.8 ($CH_2N$), 128.0 (aromatic CH), 129.0 (*C*-$CO_2$Me), 129.8 (aromatic CH), 145.4 (*C*-$CH_2N$), 167.0 ($CO_2$Me); MS (EI): *m/z* (%): 312 (20) $[M - H]^+$, 164 (93), 149 (100). A small portion of **5** was converted to its HCl salt for analytical purposes: $C_{18}H_{20}ClNO_4$ (349.8): calcd C 61.80, H 5.76, N 4.00; found C 61.80, H 5.79, N 3.98.

***N*-(*tert*-Butoxycarbonyl)bis(4-carbomethoxybenzyl)amine (6)**: Amine **5** (5.5 g, 17.6 mmol) was dissolved in $CHCl_3$ (150 mL), and then di-*tert*-butyl dicarbonate (3.83 g, 17.6 mol) and DMAP (22 mg, 0.18 mmol) were added. The reaction mixture was stirred overnight, before being washed with aqueous 2 M HCl solution (2 × 100 mL) and $H_2O$ (1 × 100 mL). The organic phase was dried ($MgSO_4$) and the solvent evaporated to yield the title compound as a thick colorless oil (6.89 g, 95%). A portion of this oil was chromatographed ($SiO_2$: EtOAc/hexane, 30:70) in order to yield a purer sample; m.p. 93–94 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.45 (s, 9H; C($CH_3$)$_3$), 3.90 (s, 6H; $CO_2CH_3$), 4.38 and 4.48 (2 brs, 2H each; $CH_2$-N-$CH_2$), 7.25 (br, 4H; aromatic CH), 7.98 (d, $J$ = 8.5 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.4 [C($CH_3$)$_3$], 49.7 ($CH_2N$), 52.1 ($CO_2CH_3$), 80.7 [*C*($CH_3$)$_3$], 127.1 and 127.7 (2 brs, aromatic CH), 129.3 (*C*-$CO_2CH_3$), 129.9 (aromatic CH), 143.1 (*C*-$CH_2N$), 155.8 ($CO_2$Bu), 166.8 ($CO_2$Me); MS (EI): *m/z* (%): 382 (14) $[M - OMe]^+$, 357 (88) $[M - Bu]^+$, 164 (94), 149 (100); $C_{23}H_{27}NO_6$ (413.5): calcd C 66.81, H 6.58, N 3.39; found C 66.85, H 6.72, N 3.32.

***N*-(*tert*-Butoxycarbonyl)bis(4-hydroxymethylbenzyl)amine (7)**: A THF solution (200 mL) of **6** (6.7 g, 16.2 mmol) was heated under reflux. Portions of $LiAlH_4$ (4 × 0.61 g, 4 × 16.2 mmol) were added at regular intervals over 30 min, and the mixture was heated for a further 30 min. The gray suspension was cooled to room temperature. Water was added until a white suspension had formed, and then the mixture was acidified with 2 M HCl solution until a pH of 3–4 was reached. After the solvents had been evaporated and the residue partitioned between $H_2O$ (100 mL) and $CHCl_3$ (100 mL), the aqueous phase was extracted with $CHCl_3$ (3 × 100 mL). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated to yield a thick, colorless oil (5.03 g, 87%). A small portion of this oil was purified by column chromatography ($SiO_2$: EtOAc/hexane, 1:1) yielding a pure sample of the title compound, which eventually solidified; m.p. 65–68 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.48 (s, 9H; C($CH_3$)$_3$), 2.52 (br, 2H; OH), 4.29 and 4.33 (2 brs, 2H each; $CH_2$-N-$CH_2$), 4.60 (s, 4H; $CH_2$OH), 7.13 (br, 4H; aromatic CH), 7.35 (d, $J$ = 7.5 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.5 [C($CH_3$)$_3$], 48.9 (br, $CH_2N$), 64.8 ($CH_2$OH), 80.3 [C($CH_3$)$_3$], 127.2 (aromatic CH), 127.6 and 128.1 (2 brs, aromatic *CH*), 137.1 and 140.1 (quaternary aromatics), 156.1 (C=O); MS (FAB): *m/z* (%): 380 (8) $[M + Na]^+$, 358 (14) $[M + H]^+$, 302 (100) $[M - C_4H_8]^+$; $C_{21}H_{27}NO_4$ (357.4): calcd C 70.56, H 7.61, N 3.92; found C 70.60, H 7.59, N 3.76.

***N*-(*tert*-Butoxycarbonyl)bis(4-chloromethylbenzyl)amine (8)**: Triphenylphosphine (12.3 g, 47.0 mmol) in THF (250 mL) and *N*-chlorosuccinimide (7.2 g, 53.7 mmol) in THF (250 mL) were mixed at ambient temperature, producing a white precipitate. Diol **7** (4.80 g, 13.4 mmol) was added as a THF solution (ca. 20 mL), and the reaction mixture stirred overnight. A brown solution containing a white suspension formed. The solvent was evaporated and the residue purified by chromatography ($SiO_2$: EtOAc/hexane, 1:9). The product was isolated as a colorless oil, which eventually solidified (4.80 g, 91%); m.p. 90–92 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.50 (s, 9H; C($CH_3$)$_3$), 4.33 and 4.42 (2 brs, 2H each; $CH_2$-N-$CH_2$), 4.59 (s, 4H; $CH_2$Cl), 7.19 (br, 4H; aromatic CH), 7.35 (d, $J$ = 8.0 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.5 [C($CH_3$)$_3$], 46.0 ($CH_2$Cl), 49.1 (br, $CH_2$N), 80.3 [*C*($CH_3$)$_3$], 127.8 and 128.3 (2 brs, aromatic CH), 128.8 (aromatic CH), 136.6 and 138.3 (quaternary aromatics), 155.9 (C=O); MS (EI): *m/z* (%): 394 (7) $[M + H]^+$, 337 (70) $[M - Bu]^+$, 198 (100); $C_{21}H_{25}NO_2Cl_2$ (394.3): calcd. C 63.96, H 6.39, N 3.55; found C 63.86, H 6.44, N 3.49.

***N*-(*tert*-Butoxycarbonyl)bis(4-azidomethylbenzyl)amine (9)**: A mixture of dichloride **8** (4.20 g, 10.7 mmol) and sodium azide (3.46 g, 53.3 mmol) was heated under reflux in 2-butanone (200 mL) for 5 d. The solvent was evaporated, and the residues were taken up into $CHCl_3$ and filtered. Evaporation of the solvent yielded the title compound as a pale yellow oil (4.30 g, 99%). A small portion was purified by column chromatography ($SiO_2$: EtOAc/hexane, 1:9) yielding a colorless thick oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.49 (s, 9H; C($CH_3$)$_3$), 4.35 and 4.43 (2 brs, 2H each; $CH_2$-N-$CH_2$), 4.33 (s, 4H; $CH_2N_3$), 7.22 (br, 4H; aromatic CH), 7.27 (d, $J$ = 8.0 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.4 [C($CH_3$)$_3$], 49.2 (br, $CH_2$N), 54.5 ($CH_2N_3$), 80.3 [*C*($CH_3$)$_3$], 128.0 (br, aromatic CH), 128.5 (aromatic CH), 134.4 and 138.2 (quaternary aromatics), 155.9 (C=O); MS (FAB): *m/z* (%): 408 (12) $[M + H]^+$, 380 (28) $[M + H - N_2]^+$, 352 (100); $C_{21}H_{25}N_7O_2$ (407.5): calcd C 61.90, H 6.18, N 24.06; found C 61.93, H 6.35, N 24.06.

**Bis(4-azidomethylbenzyl)ammonium Hexafluorophosphate (2·$PF_6$)**: Trifluoroacetic acid (ca. 5 mL, excess) was added to a solution of Boc-protected amine **9** (4.0 g, 9.8 mmol) in $CHCl_3$ (150 mL), and the reaction mixture stirred at ambient temperature overnight. The solvent was evaporated, and the residue taken up into aqueous 6 M NaOH (200 mL) and extracted with $CHCl_3$ (4 × 100 mL). The organic phase was dried ($MgSO_4$) and the solvent evaporated to yield an oil, which was dissolved in 5 M HCl solution (100 mL). Evaporation of the solvents produced a white solid, which was dissolved in $H_2O$. A saturated solution of $NH_4PF_6$ in $H_2O$ was added dropwise until no further precipitate was detected. The aqueous phase was extracted with $CHCl_3$ (4 × 100 mL). The organic phase was dried ($MgSO_4$), and the solvent evaporated to yield an off-white solid (2.2 g, 50%); m.p. 159–160 °C; $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ = 4.26 (s, 4H; $CH_2N_3$), 4.45 (s, 4H; $CH_2NH_2$), 7.35 (d of AB quartet, 4H), 7.47 (d of AB quartet, 4H); $^{13}$C NMR (75 MHz, $CH_3CN$): $\delta$ = 52.0 and 54.5 ($CH_2$Cl and $CH_2$N), 129.7 (aromatic CH), 131.0 (quaternary aromatic), 131.5 (aromatic CH), 138.5 (quaternary aromatic); MS (FAB): *m/z* (%): 308 $[M - PF_6]^+$; $C_{16}H_{18}N_7PF_6$ (453.3): calcd C 42.39, H 4.00, N 21.63; found C 42.38, H 4.02, N 21.45.

***N*-(*tert*-Butoxycarbonyl)bis[4-{[4,5-bis(*tert*-butoxycarbonyl)-1,2,3-triazo-1-yl]methyl}benzyl]amine (10)**: A solution of bisazide **9** (20.0 mg, 49 μmol) and di-*tert*-butyl acetylenedicarboxylate (42 mg, 186 μmol) was heated under reflux in $CHCl_3$ (5 mL) for 3 d. The reaction mixture was cooled down to room temperature, and the solvent evaporated in vacuo. The residue was chromatographed ($SiO_2$: EtOAc/hexane, 1:4), yielding the title compound as a colorless oil (36 mg, 84%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.45 (s, 27H; C($CH_3$)$_3$), 1.58 (s, 18H; C($CH_3$)$_3$), 4.23 and 4.31 (2 brs, 2H each; $CH_2$-N-$CH_2$), 5.74 (s, 4H; $CH_2$-triazole), 7.05–7.30 (m, 8H; aromatic CH's); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 27.8 (C-$CO_2$C($CH_3$)$_3$), 28.1 (C-$CO_2$C(*C*H$_3$)$_3$), 28.4 (N-$CO_2$C(*C*H$_3$)$_3$), 48.9 (br, $CH_2$N), 53.1 ($CH_2$-triazole), 80.4 (N-$CO_2$*C*(CH$_3$)$_3$), 82.9 (C-$CO_2$*C*(CH$_3$)$_3$), 84.8 (C-$CO_2$*C*(CH$_3$)$_3$), 127.8 (br, aromatic CH), 128.2 (aromatic CH), 130.5 (quaternary aromatic), 133.5 (quaternary aromatic), 138.4 (quaternary aromatic), 141.7 (quaternary aromatic), 155.8 (N-$CO_2$Bu), 157.6 (C-$CO_2$Bu), 159.4 (C-$CO_2$Bu); MS (FAB): *m/z* (%): 860 (10) $[M]^+$, 580 (87), 423 (100); HRMS (LSIMS): $C_{45}H_{62}N_7O_{10}$ requires 860.4558; found 860.4537.

**{[2]-Bis[4-{[4,5-bis(*t*-butoxycarbonyl)-1,2,3-triazo-1-yl]methyl}benzyl]ammonium}-[DB24C8]rotaxane}[$PF_6$] (3·$PF_6$)**: **2**·$PF_6$ (100 mg, 0.221 mmol) was dissolved in a $CH_2Cl_2$ (10 mL) solution of **DB24C8** (297 mg, 0.662 mmol), and then di-*tert*-butyl acetylenedicarboxylate (200 mg, 0.882 mmol) was added. The reaction mixture was heated under reflux for 9 d. The solution was cooled to room temperature and the solvent evaporated. The residue was purified by chromatography ($SiO_2$: gradient elution with $CH_2Cl_2$/MeOH, 100:0 to 90:10) to yield the title compound as a colorless oil, which eventually solidified (92 mg, 31%); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.43 (s, 18H; C($CH_3$)$_3$), 1.52 (s, 18H; C($CH_3$)$_3$), 3.40 (s, 8H; γ-$OCH_2$), 3.68 (m, 8H; β-$OCH_2$), 3.97 (m, 8H; α-$OCH_2$), 4.52 (m, 4H; $CH_2NH_2$), 5.57 (s, 4H; $CH_2$-triazole), 6.64 (m, 4H; catechol CH), 6.78 (m, 4H; catechol CH), 7.01 (d, $J$ = 8.0 Hz, 4H; *p*-phenylene CH), 7.18 (d, $J$ = 8.0 Hz, 4H; *p*-phenylene CH), 7.52 (br, 2H; $NH_2$); $^{13}$C NMR (100 MHz, $CHCl_3$): $\delta$ = 27.8 (C($CH_3$)$_3$), 28.0 (C($CH_3$)$_3$), 52.0 ($CH_2NH_2$), 52.6 ($CH_2$-triazole), 68.0 (α-$OCH_2$), 70.1 (β-$OCH_2$), 70.6 (γ-$OCH_2$), 83.0 (*C*($CH_3$)$_3$), 85.1 (*C*($CH_3$)$_3$), 112.6 (catechol CH), 121.7 (catechol CH), 128.0 (*p*-phenylene CH), 129.5 (*p*-phenylene CH), 130.3 (quaternary

aromatic), 131.8 (quaternary aromatic), 135.5 (quaternary aromatic), 141.6 (quaternary aromatic), 147.1 (catechol *C*–O), 157.2 (C=O), 159.3 (C=O); MS (LSIMS): *m/z* (%): 1209 (100) $[M - PF_6]^+$, 1153 (4) $[M - PF_6 - Bu]^+$, 941 (4) [*M* – $PF_6$ – triazole stopper]$^+$, 760 (3) [*M* – $PF_6$ – **DB24C8**]$^+$; HRMS (LSIMS): $C_{64}H_{86}N_7O_{16}$ [*M* – $PF_6$]$^+$ requires 1208.6131; found 1208.6101.

**{[2]-[Bis[4-{[4,5-bis(*tert*-butoxycarbonyl)-1,2,3-triazo-1-yl]methyl}benzyl]ammonium][asym-DB24C8]rotaxane}[$PF_6$]$_2$** (**11**·$PF_6$)$_2$·$PF_6$ (119 mg, 0.263 mmol) was dissolved in a $CH_2Cl_2$ (10 mL) solution of asym-**DB24C8** (294 mg, 0.656 mmol), then di-*tert*-butyl acetylenedicarboxylate (238 mg, 1.05 mmol) was added. The reaction mixture was heated under reflux for 8 d. The solution was cooled down to room temperature and the solvent evaporated. The residue was chromatographed ($SiO_2$: gradient elution with $CH_2Cl_2$/MeOH, 99:1 to 95:5) to yield the title compound as a foam (84 mg, 24%); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.52 (s, 18H; C($CH_3$)$_3$), 1.61 (s, 18H; C($CH_3$)$_3$), 3.45 (m, 4H; $\gamma$- or $\delta$-$OCH_2$), 3.50 (m, 4H; $\delta$- or $\gamma$-$OCH_2$), 3.76 (m, 4H; $\beta$- or $\beta'$-$OCH_2$), 3.80 (m, 4H; $\beta'$- or $\beta$-$OCH_2$), 4.04 (m, 4H; $\alpha$- or $\alpha'$-$OCH_2$), 4.14 (m, 4H; $\alpha'$- or $\alpha$-$OCH_2$), 4.60 (m, 4H; $CH_2NH_2$), 5.67 (s, 4H; $CH_2$–triazole), 6.75 (m, 2H; catechol CH), 6.83 (m, 2H; catechol CH), 6.86–6.93 (m, 4H; catechol CH's), 7.12 (d, *J* = 8.0 Hz, 4H; *p*-phenylene CH), 7.32 (d, *J* = 8.0 Hz, 4H; *p*-phenylene CH), 7.63 (br, 2H; $NH_2$); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 27.7 ($CH_3$), 27.9 ($CH_3$), 51.9 ($CH_2NH_2$), 52.6 ($CH_2$–triazole), 67.9 ($\alpha$- or $\alpha'$-$OCH_2$), 68.3 ($\alpha'$- or $\alpha$-$OCH_2$), 70.2 ($\beta$- and $\beta'$-$OCH_2$), 70.5 ($\gamma$- or $\delta$-$OCH_2$), 70.7 ($\delta$- or $\gamma$-$OCH_2$), 83.1 (*C*($CH_3$)$_3$), 85.1 (*C*($CH_3$)$_3$), 112.5 (catechol *CH*-C-O), 112.6 (catechol *CH*-C-O), 121.5 (catechol *CH*-CH-C-O), 121.7 (catechol *CH*-CH-C-O), 128.0 (*p*-phenylene CH), 129.7 (*p*-phenylene CH), 130.3 (quaternary aromatic), 131.8 (quaternary aromatic), 135.6 (quaternary aromatic), 141.5 (quaternary aromatic), 147.2 (both catechol C–O), 157.1 (C=O), 159.3 (C=O); MS (LSIMS): *m/z* (%): 1209 (100%) $[M - PF_6]^+$, 1153 (4) $[M - PF_6 - Bu]^+$, 941 (4) [*M* – $PF_6$ – triazole stopper]$^+$, 760 (3) [*M* – $PF_6$ – asym-**DB24C8**]$^+$; HRMS (LSIMS): $C_{64}H_{86}N_7O_{16}$ [*M* – $PF_6$]$^+$ requires 1208.6131; found 1208.6104.

***N,N'*-Bis(4-carbomethoxybenzyl)-*p*-xylenediamine (15)**: A mixture of *p*-xylenediamine (1.0 g, 7.3 mmol) and methyl 4-formylbenzoate (2.41 g, 14.7 mmol) in PhMe (100 mL) was heated under reflux for 30 min, and the $H_2O$ which evolved was collected in a Dean–Stark apparatus. The reaction mixture was cooled down to room temperature and the solvent evaporated to yield a white solid [**14**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.93 (s, 6H; $CO_2CH_3$), 4.85 (s, 4H; $CH_2N$), 7.33 (s, 4H; $CH_2C_6H_4CH_2$), 7.33 (d, *J* = 8.0 Hz, 4H), 8.08 (d, *J* = 8.0 Hz, 4H), 8.43 (s, 2H; CH=N); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 52.3 ($CH_3$), 64.9 ($CH_2N$), 128.1 (CH aromatic), 128.3 (CH aromatic), 129.9 (CH aromatic), 131.9 (quaternary aromatic), 137.8 (quaternary aromatic), 140.0 (quaternary aromatic), 160.9 (CH=N), 166.7 ($CO_2Me$)].

The solid was suspended in MeOH (150 mL) and the mixture heated under reflux. $NaBH_4$ (5 × 0.4 g, 5 × 10.6 mmol) was added portionwise over 1 h—dissolution of the solid occurred after the addition of the third portion. The reaction mixture was cooled down to room temperature, and a 2 M HCl solution (100 mL) was added cautiously. The solvents were evaporated and the residue was partitioned between 3 M NaOH (100 mL) and $CHCl_3$ (100 mL), and the aqueous phase extracted with $CHCl_3$ (3 × 100 mL). The combined extracts were dried ($MgSO_4$) and the solvent evaporated to yield the title compound as a white solid (2.97 g, 94%); m.p. 113–115 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.66 (br, 2H; NH); 3.79 (s, 4H; $CH_2N$); 3.86 (s, 4H; $CH_2N$), 3.90 (s, 6H; $CO_2CH_3$), 7.31 (s, 4H; $CH_2C_6H_4CH_2$), 7.42 (d, *J* = 8.0 Hz, 4H), 8.00 (d, *J* = 8.0 Hz, 4H); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 52.0 ($CH_3$), 52.8 and 53.0 ($CH_2$-N-$CH_2$), 128.0 (CH aromatic), 128.3 (CH aromatic), 128.9 (quaternary aromatic), 129.7 (CH aromatic), 138.9 (quaternary aromatic), 145.8 (quaternary aromatic), 167.1 ($CO_2Me$)]; MS (FAB): *m/z* (%): 433 (35) $[M+H]^+$, 268 (89), 149 (100); $C_{26}H_{28}N_2O_4$ (432.5): calcd C 72.20, H 6.52, N 6.48; found C 72.12, H 6.57, N 6.52.

***N,N'*-Bis(*tert*-butoxycarbonyl)-*N,N'*-(4-carbomethoxybenzyl)-*p*-xylenediamine (16)**: A solution of diamine **15** (2.95 g, 6.84 mmol), di-*tert*-butyl dicarbonate (3.14 g, 14.4 mmol), and DMAP (42 mg, 0.34 mmol) was stirred at ambient temperature in $CHCl_3$ (100 mL) for 3 h. The solution was washed successively with 10% HCl solution (1 × 75 mL) and saturated $NaHCO_3$ solution (1 × 75 mL) and dried. The solvent was evaporated, and the residue chromatographed ($SiO_2$: EtOAc/hexane, 1:10 to 3:10) to yield the title compound as a thick oil which eventually solidified (3.95 g, 91%); m.p. 130–132 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.48 (br, 18H; C($CH_3$)$_3$), 3.39 (s, 6H; $CO_2CH_3$), 4.25–4.50 (br m, 8H; $CH_2$-N-$CH_2$), 7.15 (br, 4H; aromatic CH), 7.25 (br, 4H; $CH_2C_6H_4CH_2$), 7.98 (d, *J* = 8.5 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.4 [C($CH_3$)$_3$], 49.5 (br, $CH_2$-N-$CH_2$), 52.1 ($CO_2CH_3$), 80.4 [*C*($CH_3$)$_3$], 127.2 (aromatic CH), 127.7 (aromatic CH), 129.2 (quaternary aromatic), 129.9 (aromatic CH), 136.9 (quaternary aromatic), 143.4 (br, quaternary aromatic), 155.9 (N-*C*=O), 166.9 ($CO_2Me$); MS (FAB): *m/z* (%): 631 (5) $[M - H]^+$, 531 (25) $[M - CO_2Bu]^+$, 477 (64), 298 (100); $C_{36}H_{44}N_2O_8$ (632.8): calcd C 68.34, H 7.01, N 4.43; found C 68.24, H 7.11, N 4.30.

***N,N'*-Bis(*tert*-butoxycarbonyl)-*N,N'*-(4-hydroxymethylbenzyl)-*p*-xylenediamine (17)**: $LiAlH_4$ (0.23 g, 6.10 mmol) was added to a solution of **16** (3.86 g, 6.10 mmol) in THF (150 mL), and the mixture was heated under reflux. Further portions of $LiAlH_4$ (2 × 0.30 g, 2 × 7.91 mmol) were added during the following 60 min. The mixture was cooled down to room temperature, 2 M HCl was added until the pH was less than 2, and the solvents were evaporated. The residue was partitioned between $H_2O$ (100 mL) and $CHCl_3$ (100 mL), and the aqueous phase extracted with $CHCl_3$ (3 × 100 mL). The combined extracts were dried ($MgSO_4$), and the solvents evaporated to yield the title compound as a thick oil (3.08 g, 88%), which eventually solidified; m.p. 155–157 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.50 (s, 18H; C($CH_3$)$_3$), 2.18 (br, 2H; OH), 4.25–4.45 (br m, 8H; $CH_2$-N-$CH_2$), 4.66 (s, 4H; $CH_2OH$), 7.10–7.25 (br m, 8H; aromatic CH's), 7.32 (d, *J* = 8.0 Hz, 4H; aromatic CH); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.5 [C($CH_3$)$_3$], 49.0 (br, $CH_2$-N-$CH_2$), 65.0 ($CH_2OH$), 80.2 [*C*($CH_3$)$_3$], 127.2 (*CH*-C-$CH_2OH$), 127.7 (br, N-$CH_2$-C-*CH*'s), 137.0 (quaternary aromatic), 137.3 (quaternary aromatic), 140.1 (quaternary aromatic), 156.0 (C=O); MS (FAB): *m/z* (%): 575 (13) $[M - H]^+$, 403 (100); $C_{34}H_{44}N_2O_6$ (576.7): calcd C 70.81, H 7.69, N 4.86; found C 70.90, H 7.69, N 4.74.

***N,N'*-Bis(*tert*-butoxycarbonyl)-*N,N'*-(4-chloromethylbenzyl)-*p*-xylenediamine (18)**: *N*-Chlorosuccinimide (2.78 g, 20.8 mmol) and triphenylphosphine (4.78 g 18.2 mmol) were stirred in dry, distilled THF (100 mL) for 15 min, forming a white precipitate. A solution of **17** (3.0 g, 5.20 mmol) in THF (20 mL) was added, and the reaction mixture was stirred at ambient temperature overnight. A clear, dark brown solution containing a white suspension was formed. The solvent was evaporated, and the residue chromatographed ($SiO_2$: EtOAc/hexane, 1:9) to yield the title compound as a thick colorless oil which eventually solidified (2.76 g, 86%); m.p. 94–97 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.49 (s, 18H; C($CH_3$)$_3$), 4.33 and 4.41 (both brs, 4H each; $CH_2$-N-$CH_2$), 4.58 (s, 4H; $CH_2Cl$), 7.17 (br, 8H), 7.35 (d, *J* = 8.5 Hz, 4H; *CH*-C-$CH_2OH$); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.5 [C($CH_3$)$_3$], 46.0 ($CH_2Cl$), 49.1 (both $CH_2$-N-$CH_2$), 80.3 [*C*($CH_3$)$_3$], 127.7 (br, N-$CH_2$-C-*CH*'s), 128.8 (CH-C-$CH_2Cl$), 136.5 (quaternary aromatic), 137.0 (quaternary aromatic), 138.4 (quaternary aromatic), 156.0 (C=O); MS (FAB): *m/z* (%): 635 (10) $[M+Na]^+$, 613 (12) $[M+H]^+$, 501 (62) $[M - 2(C_4H_8)]^+$, 421 (100); $C_{34}H_{42}Cl_2N_2O_4$ (613.6): calcd C 66.55, H 6.90, N 4.57; found C 66.61, H 7.00, N 4.48.

***N,N'*-Bis(*tert*-butoxycarbonyl)-*N,N'*-(4-azidomethylbenzyl)-*p*-xylenediamine (19)**: A mixture of **18** (2.24 g, 6.65 mmol) and sodium azide (0.71 g, 11.0 mmol) was heated under reflux in $Me_2CO$ (100 mL) for 20 h, and then a further portion of sodium azide (1.0 g, 15.4 mmol) was added and the refluxing continued for a further 24 h. The reaction mixture was cooled down to room temperature and filtered. The salts were washed with $CHCl_3$ (100 mL) and the combined organic phases evaporated to yield the title compound as a colorless oil (2.24 g, 98%); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.50 (s, 18H; C($CH_3$)$_3$), 4.32 (s, 4H; $CH_2N_3$), 4.35 and 4.42 (both br, 4H each; $CH_2$-N-$CH_2$), 7.18 (br, 4H; aromatic CH's), 7.10–7.25 (br, 4H; aromatic CH's), 7.28 (d, *J* = 8.0 Hz, 4H; *CH*-C-$CH_2N_3$); $^{13}$C NMR (75 MHz, $CHCl_3$): $\delta$ = 28.4 [C($CH_3$)$_3$], 49.2 (br, both $CH_2$-N-$CH_2$), 54.5 ($CH_2N_3$), 80.3 [*C*($CH_3$)$_3$], 127.8 (br, aromatic CH), 128.4 (br, overlapping CH's), 134.3 (quaternary aromatic), 138.1 (br, quaternary aromatics), 155.9 (C=O); MS (FAB): *m/z* (%): 649 (12) $[M+Na]^+$, 633 (19) $[M+Li]^+$, 625 (12) $[M - H]^+$, 599 (14) $[M+H - N_2]^+$, 525 (33) $[M+H - CO_2Bu]^+$, 471 (53), 281 (100); $C_{34}H_{42}N_8O_4$ (626.8): calcd C 65.16, H 6.75, N 17.88; found C 65.07, H 6.86, N 17.67.

***N,N'*-Bis(4-azidomethylbenzyl)-*p*-xylenediammonium Hexafluorophosphate (13**·$2PF_6$): Trifluoroacetic acid (5 mL, excess) was added to a solution of **19** (2.0 g, 3.2 mmol) in $CHCl_3$ (100 mL), and the reaction mixture stirred at ambient temperature for 20 h. The solvents were evaporated and the residue was partitioned between 3 N NaOH (100 mL) and $CHCl_3$ (100 mL), and the aqueous phase extracted with $CHCl_3$ (3 × 100 mL). The combined organic extracts were dried and the solvent evaporated. The residue was dissolved in 10% HCl solution (200 mL) and the solvents were evaporated. The solid obtained was suspended in $Me_2CO$ (50 mL) and aqueous $NH_4PF_6$ solution (ca. 2.0 g in 5 mL) was added. $H_2O$ was added until dissolution occurred and the mixture filtered. $H_2O$ was added to the filtrate, and an off-white solid precipitated, which was collected by filtration (1.81 g, 79%); m.p. > 290 °C; $^1$H NMR (300 MHz, $CD_3CN$): $\delta$ = 4.27 and 4.29 (2s, 4H each; $CH_2$-N-$CH_2$), 4.45 (s, 4H; $CH_2N_3$), 7.45 (AA' part of AA'BB' spin system, 4H), 7.52 (BB' part of AA'BB' spin system, 4H), 7.56 (s, 4H; central $C_6H_4$); $^{13}$C NMR (75 MHz, $CD_3CN$): $\delta$ = 51.9 and 52.3 (both $CH_2$-N-$CH_2$), 54.6 ($CH_2N_3$), 130.0 (aromatic CH), 131.1 (quaternary aromatic), 131.7 and 131.8 (aromatic CH's), 132.9 (quaternary aromatic), 138.8 (quaternary aromatic); MS (FAB): *m/z* (%): 573 (26) $[M - PF_6]^+$, 427 (100) $[M - PF_6 - HPF_6]^+$; $C_{24}H_{28}N_8P_2F_{12}$ (718.5): calcd C 40.12, H 3.93, N 15.60; found C 40.02, H 3.97, N 15.52.

**{[3]-[DB24C8]-[*N,N'*-Bis[4-{[4,5-bis(*tert*-butoxycarbonyl)-1,2,3-triazo-1-yl]methyl}benzyl]-*p*-xylenediammonium]-[DB24C8]rotaxane}[$PF_6$]$_2$** (**20**·$2PF_6$): **13**·$2PF_6$ (155 mg, 0.216 mmol) was dissolved in MeCN (ca. 100 μL), and then a solution of **DB24C8** (387 mg, 0.863 mmol) in $CH_2Cl_2$ (5 mL) was added, followed by di-*tert*-butyl acetylenedicarboxylate (195 mg, 0.863 mmol). The reaction mixture was heated under reflux for 8 d. The solvent was evaporated and the residue chromatographed ($SiO_2$: gradient elution with $CH_2Cl_2$:MeOH, 100:0 to 70:30) to yield the title compound as a thick colorless oil (45 mg, 10%); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.50 (s, 18H; C($CH_3$)$_3$), 1.60 (s, 18H; C($CH_3$)$_3$), 3.57 (m, 8H; $\gamma$-$OCH_aH_b$), 3.75 (m, 8H; $\gamma$-$OCH_aH_b$), 3.78 (m, 16H; $\beta$-$OCH_2$), 3.97 (m, 8H; $\alpha$-$OCH_aH_b$), 4.13 (m, 8H; $\alpha$-$OCH_aH_b$), 4.44 (m, 4H; $CH_2NH_2$), 4.68 (m, 4H; $NH_2CH_2$), 5.62 (s, 4H; $CH_2$–triazole), 6.72 (m, 8H; catechol CH), 6.87 (m, 8H;



0947-6539/96/0206-0734 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 6

catechol CH), 7.03 (d, $J = 8.0$ Hz, 4H; terminal $C_6H_4$), 7.16 (s, 4H; central $C_6H_4$), 7.25 (d, $J = 8.0$ Hz, 4H; terminal $C_6H_4$), 7.56 (br, 4H; $NH_2$); $^{13}C$ NMR (100 MHz, $CHCl_3$): $\delta = 27.9$ ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$), 52.1 ($CH_2NH_2$), 52.7 ($NH_2CH_2$), 53.4 ($CH_2$–triazole), 68.0 ($\alpha$-$OCH_2$), 70.4 ($\beta$-$OCH_2$), 71.0 ($\gamma$-$OCH_2$), 83.2 ($C(CH_3)_3$), 85.0 ($C(CH_3)_3$), 112.6 (catechol CH), 121.4 (catechol CH), 128.0 (terminal phenylene CH), 129.9 (terminal phenylene CH), 130.1 (central phenylene CH), 130.2 (quaternary aromatic), 132.3 (quaternary aromatic), 132.4 (quaternary aromatic), 135.4 (quaternary aromatic), 141.9 (quaternary aromatic), 147.3 (catechol C–O), 157.2 (C=O), 159.4 (C=O); MS (FAB): *m/z* (%): 1777 (100) $[M - 2PF_6]^+$, 1721 (5) $[M - 2PF_6 - Bu]^+$, 1328 (41) $[M - 2PF_6 -$ **DB24C8**$]^+$, 1209 (14), 1060 (5) $[M - 2PF_6 -$ triazole stopper $-$ **DB24C8**$]^+$, 889 (7) $[M - 2PF_6]^{2+}$; HRMS (LSIMS): $C_{96}H_{127}N_8O_{24}$ $[M - 2PF_6]^+$ requires 1775.8963; found 1775.8987.

**Crystallographic Data for the [2]Rotaxane $3\cdot0.75NO_3\cdot0.25Cl\cdot CH_2Cl_2\cdot Et_2O$:** $M_r = 1423.8$, Monoclinic, space group $P2_1/n$, $a = 9.777(1)$, $b = 43.455(8)$, $c = 18.361(1)$ Å, $\beta = 101.13(1)°$, $V = 7654(2)$ Å$^3$, $Z = 4$, $D_c = 1.236$ g cm$^{-3}$, $\mu(CuK_\alpha) = 14.4$ cm$^{-1}$, $F(000) = 3034$, $T = 193$ K. Data for a clear rhombic plate of dimensions $0.10 \times 0.33 \times 0.40$ mm were measured on a Siemens P4 rotating anode diffractometer with graphite monochromated $Cu_{K\alpha}$ radiation at reduced temperature using $\omega$ scans. 7576 Independent reflections were measured ($2\theta \leq 114°$), and of these 5376 had $|F_0| > 4\sigma(|F_0|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors, but not for absorption. The structure was solved by direct methods and the major occupancy non-hydrogen atoms of the [2]rotaxane were refined anisotropically; the carbon atoms of the included, disordered $CH_2Cl_2$ molecule and the carbon and oxygen atoms of the disordered $Et_2O$ molecules were refined isotropically. The analysis also revealed the presence of partial disorder (70:30) within one of the polyether linkages in the **DB24C8**. The positions of the hydrogen atoms in the $NH_2^+$ center were determined from a $\Delta F$ map; the position of these hydrogen atoms and those of the other hydrogen atoms within the structure were subsequently idealized, assigned isotropic thermal parameters and allowed to ride on their parent C/N atoms. Refinement was by full-matrix least-squares based on $F^2$ (925 refined parameters) and converged to give $R_1 = 0.089$, $wR_2 = 0.221$. The maximum and minimum residual electron densities in the final $\Delta F$ map were 0.52 and $-0.30$ e Å$^{-3}$. The mean and maximum $\Delta/\sigma$ in the final refinement cycle were 0.006 and 0.155, respectively. Computations were carried out using the SHELXTL program system [31]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-8. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

**Acknowledgements:** This research, which was sponsored in the UK by the ZENECA Strategic Research Fund, was supported additionally by the Engineering and Physical Sciences Research Council. We thank Drs. Andrew Collins and Ewan Chrystal of ZENECA Specialties (Blackley) and ZENECA Agrochemicals (Jealott's Hill), respectively, for helpful discussions.

Received: December 5, 1995 [F261]

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[15] A rotaxane is a molecule that contains a linear component (the axle) encircled by one, or more, macrocyclic component (the wheel). In order to prevent the wheel from slipping off the axle, the linear component must be terminated at both ends by large blocking groups or stoppers. The addition of the prefix pseudo to the term rotaxane indicates that in a pseudorotaxane the wheel is free to dissociate from the axle in the same way as ligands may in a more conventional type of complex. The molecular components of a pseudorotaxane are held together only by their mutual noncovalent bonding interactions. See P. R. Ashton, D. Philp, N. Spencer, J. F. Stoddart, *J. Chem. Soc. Chem. Commun.* **1991**, 1677–1679.

[16] After our research had been completed, Busch et al. (A. G. Kolchinski, D. H. Busch, N. W. Alcock, *J. Chem. Soc. Chem. Commun.* **1995**, 1289–1291) reported the synthesis of a [2]rotaxane incorporating a secondary dialkylammonium ion on the dumbbell and a **DB24C8** ring. This [2]rotaxane was self-assembled by the acylation of a primary amine—possibly at the $CHCl_3$–water interface—of a molecule which also contained a secondary amino group, in the presence of **DB24C8**.

[17] D. B. Amabilino, J. F. Stoddart, *Pure Appl. Chem.* **1993**, *65*, 2351–2359.

[18] Although the addition of a weak nitrogenous base, such as 2,6-lutidine, does not affect the association constant of the interaction between dibenzylammonium hexafluorophosphate ($\mathbf{1}\cdot PF_6$) and **DB24C8** to any significant extent, a

stronger base, benzylamine, was found to destroy this 1:1 complex almost totally.

[19] T. Sheradsky in *The Chemistry of the Azido Group* (Ed.: S. Patai), Interscience, London, **1971**, pp. 331–395.

[20] M. G. Nair, P. C. O'Neal, C. M. Baugh, *J. Med. Chem.* **1978**, *21*, 673–677.

[21] A. K. Bose, B. Lal, *Tetrahedron Lett.* **1973**, 3937–3940; b) S. Trippett, *J. Chem. Soc.* **1962**, 2337–2340.

[22] M. E. C. Biffin, J. Miller, D. B. Paul in *The Chemistry of the Azido Group*, (Ed.: S. Patai), Interscience, London, **1971**, pp. 57–190.

[23] The ammonium salt **2**·$PF_6$ is only sparingly soluble in these chlorinated solvents in the absence of **DB24C8**.

[24] The association constant may be determined readily from a single $^1$H NMR spectrum because the absolute concentrations of the uncomplexed **DB24C8**, uncomplexed ammonium salt (**2**·$PF_6$), and the 1:1 complex formed between the two can be calculated from the relative mole fractions of these three species in solution and the total concentrations of the host and guest. See refs. [12] and [14].

[25] The $^1$H NMR spectrum of **3**·$PF_6$ recorded in $CDCl_3$ shows resonances for the dumbbell component and **DB24C8** in a 1:1 molar ratio as determined by integration. Resonances for both these components indicate that they are mutually interlocked. Particular signals of interest are those for the macrocyclic polyether α-, β-, and γ-$OCH_2$ protons which resonate at $\delta$ = 3.97, 3.68, and 3.40, respectively, in the [2]rotaxane **3**·$PF_6$ compared with $\delta$ = 4.15, 3.92 and 3.84, respectively, in the free macrocycle (i.e., corresponding to $\Delta\delta$ values of −0.18, −0.24 and −0.44 ppm). On the dumbbell, the signal for the $N^+CH_2$ protons appears at $\delta$ = 4.52 as a second-order multiplet resulting from coupling of these protons to the adjacent $NH_2^+$ protons. By way of comparison, a singlet at $\delta$ = 4.28 is observed for the resonance of the $N^+CH_2$ protons of the uncomplexed bisazidomethyl dibenzylammonium salt **2**·$PF_6$ in $CDCl_3$. These types of signals (i.e., a second order multiplet when complexed and a singlet when uncomplexed) are also observed for the $N^+CH_2$ protons in the $^1$H NMR spectra of dibenzylammonium hexafluorophosphate **1**·$PF_6$ in the presence of **DB24C8** in a number of different solvents (see refs. [12] and [14]).

[26] The X-ray analysis shows that over the extended period during which crystallization occurred anion exchange took place with replacement of the $PF_6^-$ anion with a mixture of $NO_3^-$ (confirmed by negative ion FAB mass spectrometry) and $Cl^-$ anions in the ratio 3:1.

[27] The associated [H···O] distances and [N–H···O] angles are 2.14 and 2.15 Å, and 165 and 159°, respectively. The only other intercomponent contact is one of 2.51 Å from one of the -$C_6H_4CH_2NH_2^+$- methylene hydrogen atoms to the diammetrically opposite oxygen atom to that involved in [N–H···O] bonding within the **DB24C8** component.

[28] The $^1$H NMR chemical shift values of the resonances for the $OCH_2$ protons in the [2]rotaxane **11**·$PF_6$ are considerably different from the values for the corresponding protons in the free asym-**DB24C8** macrocycle in $CDCl_3$: α and α′-$OCH_2$ (cf. $\delta$ = 4.04 and 4.14 in the rotaxane with $\delta$ = 4.19 and 4.14 in the free macrocycle), β and β′-$OCH_2$ (cf. $\delta$ = 3.76 and 3.80 with $\delta$ = 3.98 and 3.87), γ and δ-$OCH_2$ (cf. $\delta$ = 3.45 and 3.50 with $\delta$ = 3.76 and 3.70). The signal for the $N^+CH_2$ protons on the dumbbell component of **11**·$PF_6$ resonates as a second-order multiplet—as a result of coupling to the $NH_2^+$ protons—at $\delta$ = 4.60 in $CDCl_3$, compared with a singlet with a $\delta$ value of 4.28 for the corresponding protons in the uncomplexed bis(azidomethylbenzyl)ammonium salt **2**·$PF_6$ in the same solvent.

[29] A 1:2 molar ratio of bisammonium salt **13**·2$PF_6$ and **DB24C8** in $CD_3CN$ gives a complicated $^1$H NMR spectrum which relates to four discrete species—uncomplexed **13**·2$PF_6$, uncomplexed **DB24C8**, and two complexes (with 1:1 and 1:2 stoichiometries) formed between **13**·2$PF_6$ and **DB24C8**. These discrete species arise, rather than a time-averaged set of resonances, because of the slow rates of complexation and decomplexation on the $^1$H NMR timescale at 300 MHz, together with the modest association constants for complexation in $CD_3CN$ between the salt and crown (ca. $10^2$ $L mol^{-1}$). In order to reduce the number of species in the system, the spectrum of **13**·2$PF_6$ was recorded in $CD_3CN/CDCl_3$ (1:1 v/v) (since reducing the hydrogen-bond accepting ability of the solvent encourages complexation) in the presence of 10 molequiv of **DB24C8** to drive the equilibria toward the 1:2 complex. In this case, two species were observed in solution—the 1:2 complex and uncomplexed excess of the crown ether.

[30] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals* (3rd ed.), Pergamon Press, Oxford, **1988**.

[31] SHELXTL (Version 5.03), Siemens Analytical X-Ray Instruments, Madison, WI, 1994.



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