Post-Assembly Processing of [2]Rotaxanes**

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Abstract: The concept of using [2]rotaxanes that carry one or more surrogate stoppers which can subsequently be converted chemically into other structural units, resulting in the formation of new interlocked molecular compounds, is introduced and exemplified. Starting from simple NH_2^+-centered/crown-ether-based [2]rotaxanes, containing either one or two benzylic triphenylphosphonium stoppers, the well-known Wittig reaction has been employed to make, 1) other [2]rotaxanes, 2) higher order rotaxanes, 3) branched rotaxanes, and 4) molecular shuttles—all isolated as pure compounds, following catalytic hydrogenations of their carbon–carbon double bonds, obtained when aromatic aldehydes react with the ylides produced when the benzylic triphenylphosphonium derivatives are treated with strong base. The two starting [2]rotaxanes were characterized fully in solution and also in the solid state by X-ray crystallography. The new interlocked molecular compounds that result from carrying out post-assembly Wittig reactions on two [2]rotaxanes were characterized by (dynamic) ^{1}H NMR spectroscopy. In the case of a molecular shuttle in which the crown ether component is dibenzo[24]-crown-8 (DB24C8), shuttling is slow on the ^{1}H NMR timescale, even at high temperatures. However, when DB24C8 is replaced by benzometaphenylene[25]-crown-8 as the ring component in the molecular shuttle, the frequency of the shuttling is observed to be around 100 Hz in [D_4]methanol at 63 °C.

Keywords: mechanical bond · molecular recognition · molecular shuttle · template synthesis · Wittig reactions

Introduction

Mechanically interlocked molecules[1] are composed of two or more components between which there are *no* covalent bonds; only noncovalent bonds usually and at least one mechanical bond are present. Examples include the rotaxanes.[2] They are molecules in which one or more rings become trapped on a dumbbell-shaped component by two bulky terminal stoppers. They represent a major subset of interlocked molecular compounds[3] and have attracted much attention in recent years because of their potential shuttling[4] and switching[5] properties. On account of these properties, they provide a means[6] of constructing linear motor-molecules[7] and other forms of artificial molecular machinery[8] on the tiniest of scales, namely the nano one. Also, as a consequence of their mechanical characteristics and bistable hysteretic attributes, they are now being fine-tuned and fashioned for fabrication and incorporation[9] into molecular electronic devices.[10] So far, these devices have included electronically configurable[11] and reconfigurable[12] switches, which have made it possible[13] very recently to create[11, 12] both memory and logic circuits—two crucial milestones that must be reached if a finite-state molecular computer[14] is ever going to become a reality.

During the past 15 years, the exploitation of the fundamental aspects of molecular recognition,[15] together with the development of the concept of self-assembly,[16] also referred to as noncovalent (supramolecular) synthesis,[17] has led to the evolution of highly efficient template-directed procedures[18]—sometimes called supramolecular assistance to covalent synthesis[19]—for constructing interlocked molecular compounds.[1]

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[**] "Molecular Meccano", Part 65. For Part 64, see: S. J. Cantrill, G. J. Youn, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **2001**, *66*, 6857–6872.

0947-6539/02/0822-5170 $ 20.00+.50/0

Although a wide range of supramolecular synthons[20] have already been employed[1] as recognition motifs to bring together the separate components of catenanes and rotaxanes, our discovery[21] in the early 90s, that secondary dialkylammonium ions ($R_2NH_2^+$) will spontaneously thread through the cavities of appropriately sized crown ethers has led, in addition to our publishing more than 60 short communications and full papers, to an enormous amount of interest being shown by other research workers[22] in this simple and appealing way to assemble a whole new class of interlocked molecular compounds from inexpensive or readily available starting materials. It remains an attractive proposition to look for new synthetic protocols to aid and abet the further covalent modification and planned manipulation of interlocked molecules constructed originally using this particular recognition motif.

We can use [2]rotaxane **I** (Figure 1), which carries a surrogate stopper that can be chemically converted into another terminal group and results in a new interlocked molecule **II**, as a building block to construct infinitely more complex interlocked molecules. Here, we apply the well-known Wittig reaction, starting from simple [2]rotaxanes that contain either one or two benzylic triphenylphosphonium stoppers, to make other 1) [2]rotaxanes, 2) higher order rotaxanes, 3) branched rotaxanes, and 4) molecular shuttles. The results, which amount to an important and convincing proof of principle, have already been presented in skeleton format in a couple of short communications.[23]

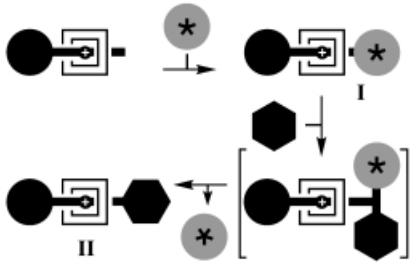


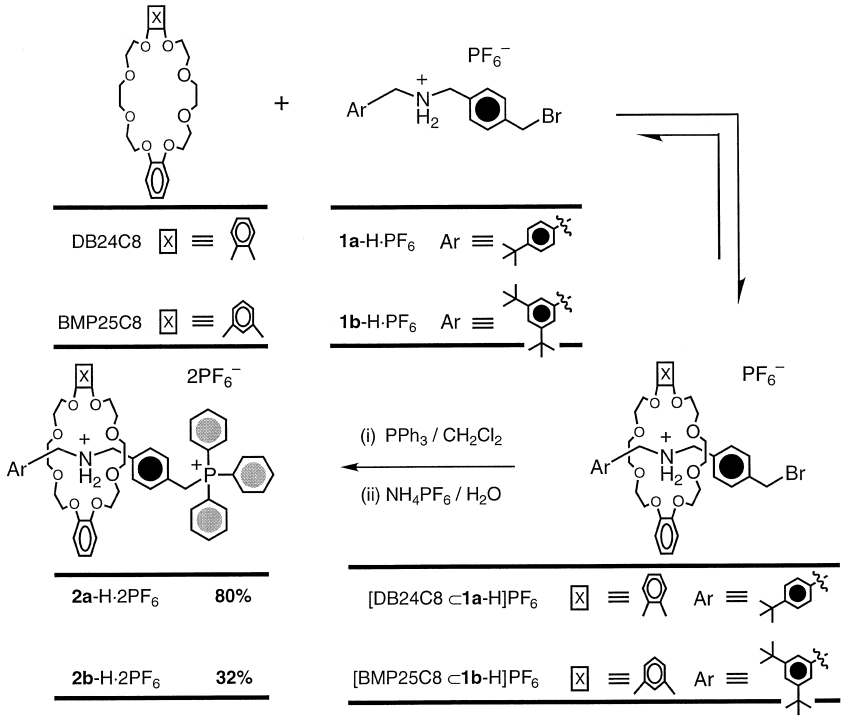
Figure 1. Graphical representation of the threading-followed-by-stoppering approach to [2]rotaxanes and the subsequent stopper-exchange concept.

Results and Discussion

The syntheses of two mono(triphenylphosphonium)-ion-stoppered [2]rotaxanes are shown in Scheme 1. On account of the fact that the free species and the pseudorotaxane are in slow exchange on the ^{1}H NMR timescale, the ability of the bromothread[23a] **1a**-H · PF_6 to form a [2]pseudorotaxane [DB24C8 ⊂ **1a**-H]PF_6 with DB24C8 was demonstrated by ^{1}H NMR spectroscopy. A K_a value of 400 M^{-1} was calculated, based on the single-point method[24] in CD_3CN. Building on this complexation, the template-directed synthesis of the [2]rotaxane **2a**-H · 2PF_6 was accomplished in 80 % yield, simply by adding PPh_3 to a mixture of **1a**-H · PF_6 and DB24C8 in CH_2Cl_2, followed by counterion exchange.

To demonstrate the generality of this new synthetic approach toward triphenylphosphonium-stoppered [2]rotaxanes, we decided to synthesize rotaxanes with the slightly larger crown ether, benzometaphenylene[25]crown-8 (BMP25C8). Since the *p-tert*-butylbenzyl group is not large enough to prevent dethreading of the BMP25C8 macrocycle,[25] we prepared **1b**-H · PF_6 (Scheme 1), a thread-like dialkylammonium salt,[26] containing a bromomethylphenyl group, and the sterically more demanding 3,5-di-*tert*-butylbenzyl group. Addition of PPh_3 to a solution of BMP25C8 and **1b**-H · PF_6 in CH_2Cl_2 yielded the [2]rotaxane **2b**-H · 2PF_6 in 32 % yield. This lower yield, when compared to the formation of the DB24C8-containing rotaxane **2a**-H · 2PF_6, is presumably a consequence of the much weaker binding[27] exhibited by BMP25C8 toward DBA^+ ions relative to that exhibited by DB24C8.

Single crystals, suitable for X-ray crystallography, were grown by liquid diffusion of MeOH into a CH_2Cl_2 solution of the [2]rotaxane **2a**-H · 2PF_6. The solid-state structure of the [2]rotaxane **2a**-H · 2PF_6 shows (Figure 2) that the DB24C8 component has a conventional U-shaped conformation with the two catechol rings inclined by approximately 55° to each other. The dicationic dumbbell component is tethered to the



Scheme 1.

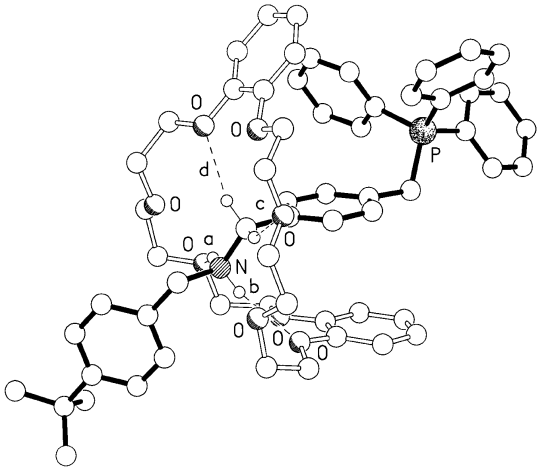
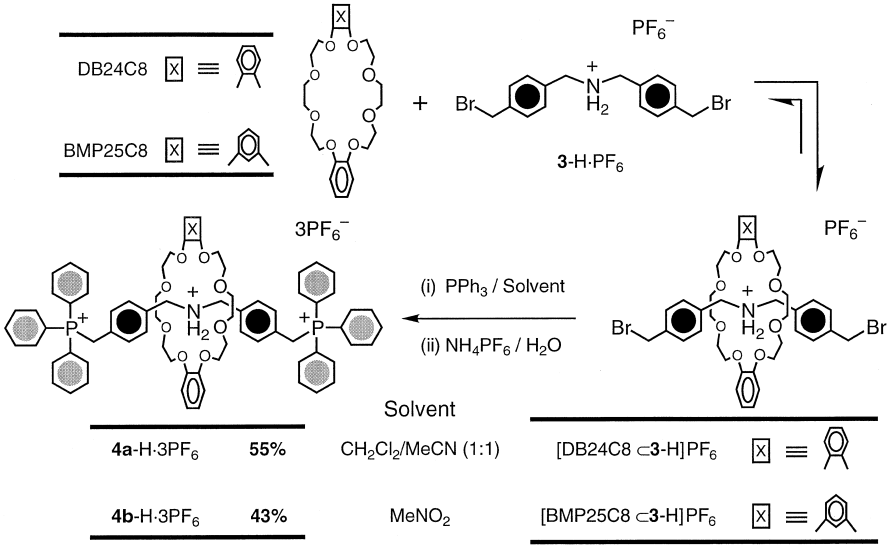


Figure 2. The cationic portion of the solid-state structure of the [2]rotaxane **2a**-H·2PF$_6$. The hydrogen bonding geometries, X···O, H···O [Å], and X–H···O [°]: a) 3.05, 2.21, 156; b) 3.14, 2.30, 154; c) 3.27, 2.40, 150; d) 3.23, 2.34, 153.

crown ether by weak N^+–H···O and C–H···O hydrogen bonds (a–d in Figure 2), a binding that is supplemented by π–π stacking between one of the catechol rings of the DB24C8 component and the central phenylene ring of the dumbbell component (centroid···centroid distance and mean interplanar separation: 3.74, 3.49 Å, respectively). There are no π–π interactions between the catechol rings and the phenyl rings of the Ph_3P^+ stopper. There are also no inter-[2]rotaxane interactions of note.

After having made and characterized two different mono(triphenylphosphonium)-stoppered [2]rotaxanes, **2a**-H·2PF$_6$ and **2b**-H·2PF$_6$, we became interested in synthesizing bis(triphenylphosphonium)-stoppered [2]rotaxanes, which are not only more highly symmetrical, but also carry functionality at both termini of their dumbbell components. Again, since the free species and the pseudorotaxane [DB24C8⊂**3**-H]PF$_6$ are in slow exchange on the ^{1}H NMR timescale, the single-point method[24] was used to obtain K_a values of 350 M^{-1} and 1800 M^{-1} for the 1:1 complex formed in CD_3CN and CD_2Cl_2/CD_3CN (1:1), respectively. The binding constant in CD_2Cl_2/CD_3CN of this bis(4-bromomethyl)-substituted thread **3**-H·PF$_6$ with DB24C8 is slightly smaller than that (K_a = 2000 M^{-1}) of the bis(4-bromo)-substituted dibenzylammonium salt,[24b] but larger than that (K_a = 960 M^{-1}) of the bis(4-methyl)-substituted one.[24b]

The [2]rotaxane **4a**-H·3PF$_6$ was assembled (Scheme 2) by adding PPh_3 to a mixture of **3**-H·PF$_6$ (100 mM) and DB24C8 (174 mM) in CH_2Cl_2/CH_3CN (1:1). A CH_2Cl_2/MeCN mixed-solvent system was utilized because of the poor solubility of **3**-H·PF$_6$ in CH_2Cl_2 alone. After counterion exchange, **4a**-H·3PF$_6$ was isolated in 55% yield. Based on the moderately high K_a for the formation of the [2]pseudorotaxane precursor [DB24C8⊂**3**-H]PF$_6$ in the reaction solvent, as well as the relatively high concentration of the host and guest in solution, >99% of the total amount of **3**-H·PF$_6$ is expected to be complexed as the [2]pseudorotaxane. Nonetheless, we observed a large amount of unthreaded dumbbell being formed at the expense of a higher yield of the corresponding [2]rotaxane **4a**-H·3PF$_6$. The mixture of counterions present after PPh_3 displaces bromide ions from **3**-H·PF$_6$ results presumably in the formation of a tight ion-pair between the Br^- and the NH_2^+ center of both the **3**-H^+ and the intermediate mono(triphenylphosphonium)-substituted ions, a situation which reduces the strength of the binding between them and DB24C8 and, consequently, hinders the formation of the [2]rotaxane **4a**-H·3X and encourages the production of the free dumbbell-shaped compound (see Experimental Section).



Scheme 2.

By using a similar protocol to that employed in the synthesis of **4a**-H·3PF$_6$, the [2]rotaxane **4b**-H·3PF$_6$, in which the crown ether BMP25C8 is the macrocyclic component, was assembled in 43% yield. Again, we believe that the slightly lower yield of **4b**-H·3PF$_6$, relative to that of the [2]rotaxane **4a**-H·3PF$_6$, is a consequence of the weaker binding between the dialkylammonium thread **3**-H·X and the larger BMP25C8 macrocycle relative to that of DB24C8.[28]

Single crystals, suitable for X-ray crystallography, were grown by slow evaporation of a CH_2Cl_2/MeOH solution of the [2]rotaxane **4a**-H·3PF$_6$. The solid-state structure of the [2]rotaxane **4a**-H·3PF$_6$ shows (Figure 3) that the DB24C8 component adopts a U-shaped conformation, very similar to that observed in **2a**-H·2PF$_6$, with the two catechol rings subtending an angle of about 54°. The tricationic dumbbell component is threaded approximately centrally through the crown ether and is held in position by a combination of weak N^+–H···O and C–H···O hydrogen bonds (a–e in Figure 3).

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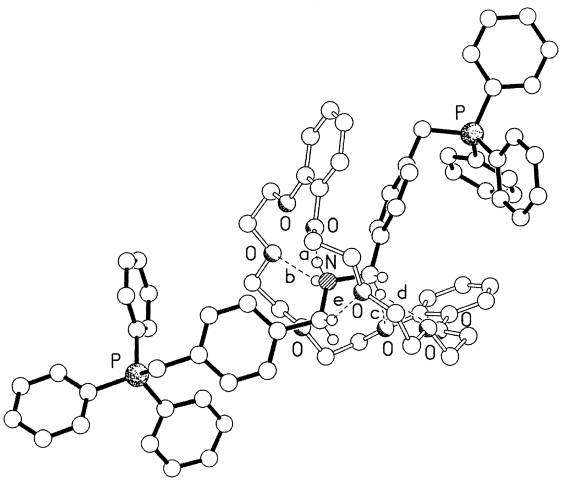
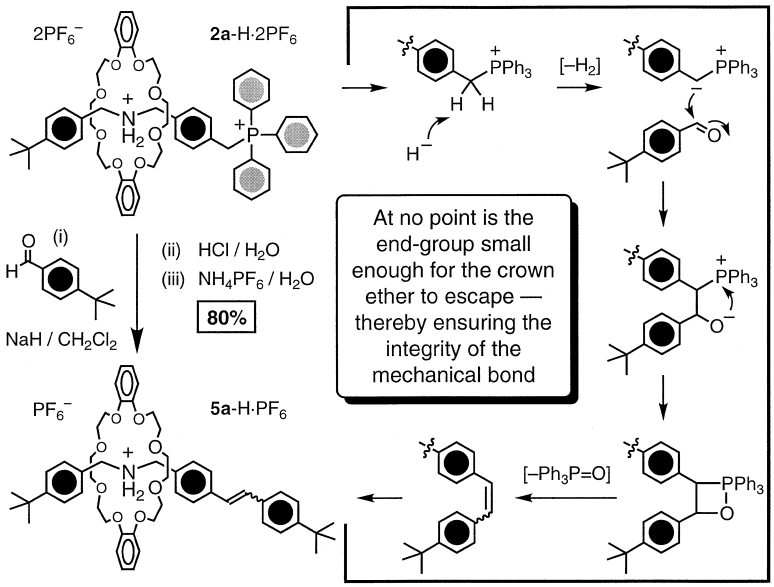


Figure 3. The cationic portion of the solid-state structure of the [2]rotaxane **4a**-H·3PF$_6$. The hydrogen bonding geometries, X···O, H···O [Å], and X–H···O [°]: a) 3.05, 2.26, 147; b) 2.96, 2.15, 151; c) 3.33, 2.44, 153; d) 3.21, 2.41, 156; e) 3.22, 2.33, 156.

In contrast to the near parallel π–π stacking between one of the phenylene rings of the dication and one of the catechol rings observed in **2a**-H·2PF$_6$, here, the analogous ring systems are inclined by approximately 20° (with a centroid···centroid separation of 4.14 Å), thus reducing appreciably any potential π–π stabilization. The only inter[2]rotaxane interaction of note is π–π stacking between the phenylene ring on the convex side of the DB24C8 component in one molecule and one of the phenyl rings of the Ph_3P^+ stoppers positioned on the convex face of the crown ether in another. These rings are inclined by 6° with centroid···centroid and mean interplanar separations of 3.75 and 3.56 Å, respectively.

With this selection of triphenylphosphonium-ion-stoppered [2]rotaxanes (**2a**-H·2PF$_6$, **2b**-H·2PF$_6$, **4a**-H·3PF$_6$, and **4b**-H·3PF$_6$) at our disposal, we were able to start examining their potential as interlocked synthetic intermediates in Wittig reactions by treating them with a range of mono-, di-, and trialdehydes in the presence of base.

To demonstrate that the triphenylphosphonium-ion stoppers of these rotaxanes can be converted into alternative stoppers through Wittig reactions, we first examined reactions with the mono(triphenylphosphonium)-ion-stoppered rotaxane **2a**-H·2PF$_6$. Reaction of **2a**-H·2PF$_6$ with *p*-*tert*-butylbenzaldehyde in the presence of an excess of NaH in CH_2Cl_2 afforded **5a**-H·PF$_6$ (Scheme 3)—as a mixture of *E* and *Z* isomers—in 80% yield, after acidic work up and counterion exchange (NH_4PF_6/H_2O). One might expect dethreading to occur under the basic Wittig reaction conditions, since the noncovalent stabilizing interactions between DB24C8 and the dialkylammonium ion will be "switched off" by the deprotonation of the NH_2^+ center. We have demonstrated, however, that the triphenylphosphonium ion stopper on [2]rotaxane **2a**-H·2PF$_6$ can be exchanged for a 4-*tert*-butyl one to generate a new [2]rotaxane **5a**-H·PF$_6$, while maintaining the interlocked nature of the [2]rotaxanes. This important observation can be explained by examining the mechanism (Scheme 3) of the Wittig reaction. This examination reveals that at each stage of the reaction—ylide, betaine, oxaphosphetane, and alkene—the DB24C8 macrocycle is trapped along the axle of the dumbbell-shaped component because of the presence of triphenylphosphine- and *tert*-butylphenyl-derived stoppers, irrespective of the presence or lack of hydrogen bonding interactions between the two components. To convert both the *Z* and *E* isomers into a common product, hydrogenation of the *cis* and *trans* double bonds in the rotaxane was achieved by using Adams' catalyst[29] (PtO_2)/H_2,



Scheme 3.

and the homogeneous [2]rotaxane **6a**-H·PF$_6$ was obtained in 61% yield (Figure 4). ^{1}H NMR spectra recorded during the transformation become much simpler after hydrogenation of **5a**-H·PF$_6$. Two pairs of *tert*-butyl signals in the region $\delta = 1.21 - 1.32$ of the spectrum of **5a**-H·PF$_6$, which indicate that the ratio of the *E*/*Z* isomers is around 1:2, were converted into only one pair of signals in the spectrum of **6a**-H·PF$_6$ after hydrogenation of the double bonds. The disappearance of the signals for the olefinic protons and the appearance of the corresponding signal at $\delta = 2.83$ for the bismethylene protons confirms that the reduction proceeded to completion. The upfield shifts of the signals for the α-, β-, and γ-OCH_2 protons of the DB24C8 macrocycle ($\delta = 4.08$, 3.75, and 3.47, respectively), compared to those for uncomplexed DB24C8 ($\delta = 4.24$, 3.76, and 3.61), support the interlocked nature of the two components of **6a**-H·PF$_6$ and the existence of strong hydrogen bonding interactions between the DB24C8 ring and the

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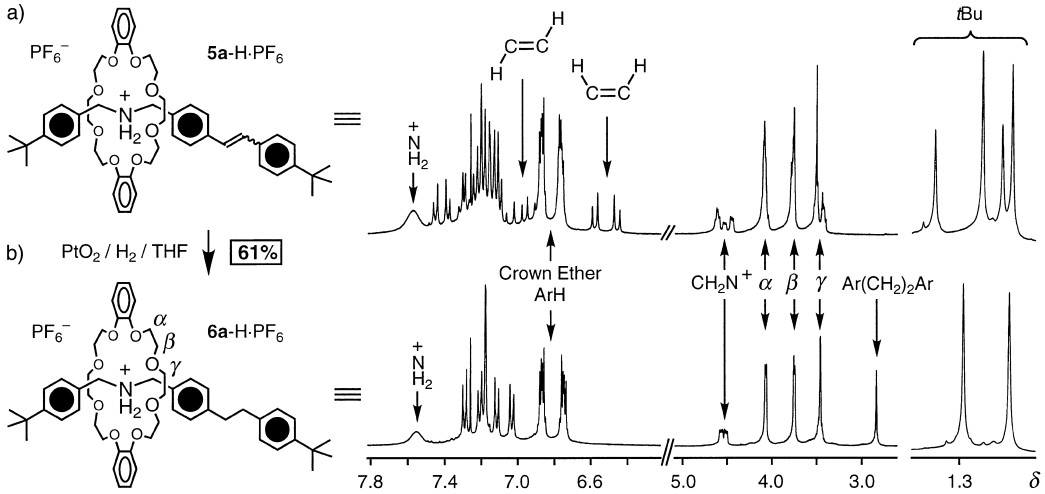


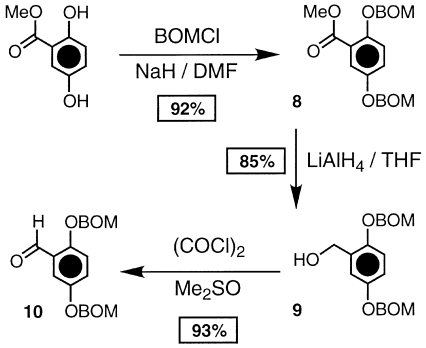
Figure 4. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of a) the *E*/*Z* isomer mixture of [2]rotaxanes **5a**-H · PF_6 and b) the hydrogenated [2]rotaxane **6a**-H · PF_6.

dialkylammonium ion center with dumbbell-shaped component.

After successfully exchanging the one single triphenylphosphonium stopper in the [2]rotaxane **2a**-H · 2 PF_6, we decided to examine the possibility of exchanging two triphenylphosphonium ion stoppers in one step to build a symmetrical [2]rotaxane. And so, the Wittig chemistry was repeated, but this time with the [2]rotaxanes **4a**-H · 3 PF_6 and **4b**-H · 3 PF_6 as substrates. Reaction of **4a**-H · 3 HF_6 with *p-tert*-butylbenzaldehyde in the presence of an excess of NaH in CH_2Cl_2 (Scheme 4) afforded an *E*/*Z* mixture of olefins after protonation (1N HCl) and counterion exchange (NH_4PF_6/H_2O). This isomeric mixture of olefins was hydrogenated with the aid of PtO_2 as a catalyst to produce the [2]rotaxane **7a**-H · PF_6 from **4a**-H · 3 PF_6 in 50% yield.

The challenge of synthesizing a sterically bulky aldehyde for the Wittig reaction can easily be resolved by using a protecting-group approach, that is, by adding sterically bulky groups to a small aldehyde in order to increase its steric size and transform it into a true stopper for the synthesis of a rotaxane. To demonstrate this approach, 2,5-bis(benzyloxymethoxy)benzaldehyde (**10**) was prepared from methyl 2,5-dihydroxybenzoate by 1) benzyloxymethoxy (BOM) protection to give the ester **8**, 2) $LiAlH_4$ reduction of the ester to yield the alcohol **9**, and 3) Swern oxidation of the alcohol to afford the aldehyde **10** in 72% overall yield (Scheme 5). The

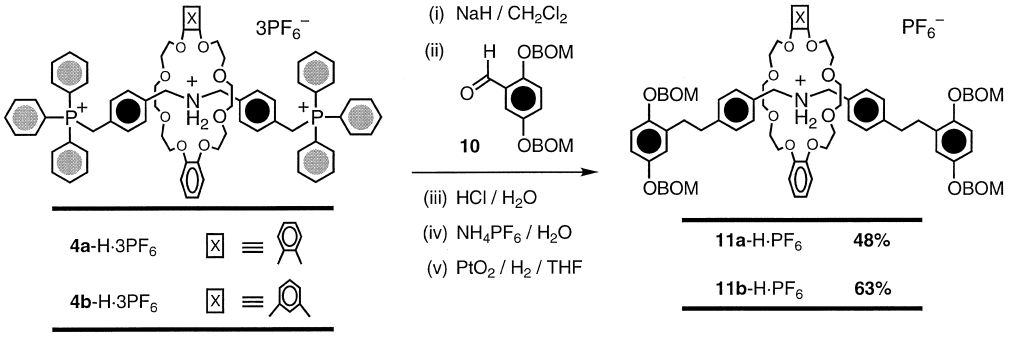
Scheme 4.



Scheme 5.

[2]rotaxane **4a**-H · 3 PF_6 was treated with the aldehyde **10** to yield a [2]rotaxane **11a**-H · PF_6 after catalytic hydrogenation (Scheme 6); this rotaxane bears potentially removable BOM groups at its termini. The BMP25C8-derived [2]rotaxane **4b**-H · 3 PF_6 also undergoes the Wittig reaction with 2,5-bis(benzyloxymethoxy)benzaldehyde, followed by hydrogenation, to yield the corresponding [2]rotaxane **11b**-H · PF_6 in 63% yield. These results suggest that the 2,5-bis(benzyloxymethoxy)-phenyl groups are sterically impassable by both the DB24C8 and BMP25C8 macrocycles. When the BOM protecting groups of the rotaxane **11a**-H · PF_6 were removed under acidic conditions (5% HCl/THF), substituted hydroquinone rings were revealed at the termini of the thread. A large amount of free DB24C8 was observed, however, in the crude reaction mixture; this suggests that the hydroquinone rings

0947-6539/02/0822-5174 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 22



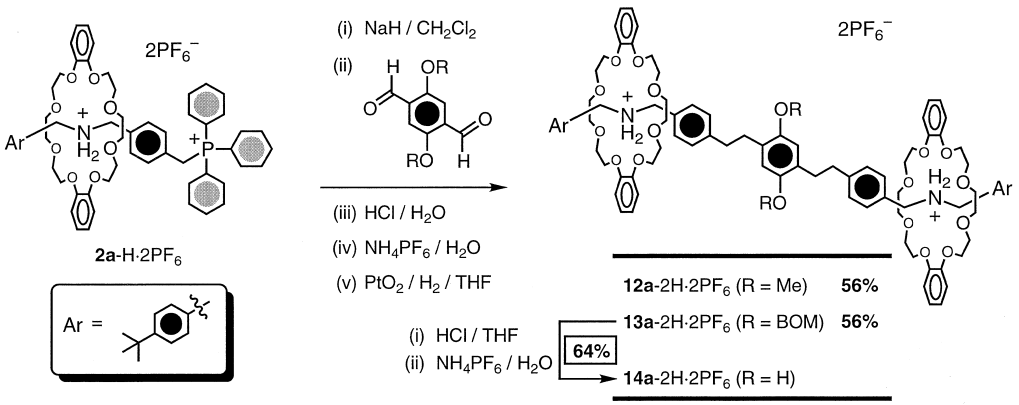
Scheme 6.

are not large enough to serve as mechanical stoppers for DB24C8 and so decomplexation of the macrocycle from the thread occurs. Since the BOM-protected hydroquinone units are true stoppers, while the simple hydroquinone units are not, the procedures described above represent a simple method for constructing a [2]rotaxane by a protecting-group approach and its conversion into a [2]pseudorotaxane by the removal of the protecting groups under acidic conditions.

Having demonstrated that new [2]rotaxanes can be generated by reacting mono- and bis(triphenylphosphonium) ion-stoppered [2]rotaxanes with mono-aldehydes, we turned our attention to the reaction of these same rotaxanes with dialdehydes (Scheme 7). When 2,5-dimethoxyterephthaldehyde and 2,5-bis(benzyloxymethoxy)terephthaldehyde[30] were used as the partners to **2a**-H·2PF$_6$ in Wittig reactions, the [3]rotaxanes **12a**-2H·2PF$_6$ and **13a**-2H·2PF$_6$, respectively, were isolated after hydrogenation. These results suggest that the 2,5-dimethoxyphenylene unit is also sterically bulky enough to prevent the dethreading of the DB24C8 macrocycles during the Wittig reaction.

The bulky BOM groups that separate the two DB24C8 macrocycles in **13a**-2H·2PF$_6$ were removed under acidic conditions to give a [3]rotaxane with a hydroquinone-core: **14a**-2H·2PF$_6$. Since the bridging unit no longer contains the BOM groups, the DB24C8 macrocycles may be able, in theory, to traverse the linker between the two ammonium centers. However, the [3]rotaxane **14a**-2H·2PF$_6$ was not stable. It decomposed in less than seven days at ambient temperature. Evidence for free DB24C8 was observed in the resulting ^{1}H NMR spectrum, suggesting that the backbone of the dumbbell-shaped component undergoes cleavage. The hydroquinone ring is most likely to be the site of this cleavage, possibly as a result of an oxidative free-radical process.

Having treated **2a**-H·2PF$_6$ and **2b**-H·2PF$_6$ with dialdehydes to produce [3]rotaxanes, we were intrigued at the prospect of treating a triphenylphosphonium-ion-stoppered rotaxane with a trialdehyde, namely triformylbenzene, and so possibly providing a route to dendrimer-like rotaxanes. When 1,3,5-triformylbenzene[31] was added to a CH_2Cl_2 solution of **2a**-H·2PF$_6$ in the presence of an excess of NaH, the branched [4]rotaxane **15a**-3H·3PF$_6$ was isolated as a complex mixture of stereoisomers (Scheme 8). No rotaxanes were isolated in which the three Wittig reactions had occurred with the loss of one or more DB24C8 rings. If it is assumed that the first step is the addition of a single ylide derived from [2]rotaxane **2a**-H·2PF$_6$ to $C_6H_3(CHO)_3$, then the formyl groups on the 3′ and 5′ positions of the benzene ring in the putative intermediate must presumably be large enough to prevent dethreading of the DB24C8 macrocycle, otherwise the analogue of **15a**-3H·3PF$_6$, having lost one DB24C8, would also have been isolated. The complicated ^{1}H NMR spectrum (Figure 5) of the olefinic [4]rotaxane mixture **15a**-3H·3PF$_6$ was dramatically simplified after hydrogenation, an outcome that suggests the formation of the highly symmetrical dendritic [4]rotaxane **16a**-3H·3PF$_6$. The interlocked nature of the macrocycles was confirmed by the upfield shifts of the α-, β-, and γ-OCH_2 proton signals. The ^{1}H NMR signal of the methylene groups adjacent to the NH_2^+ center was found to be a triplet and shifted downfield to $\delta = 4.59$, an observation which suggests the existence of hydrogen bonding between the crown ethers



Scheme 7.

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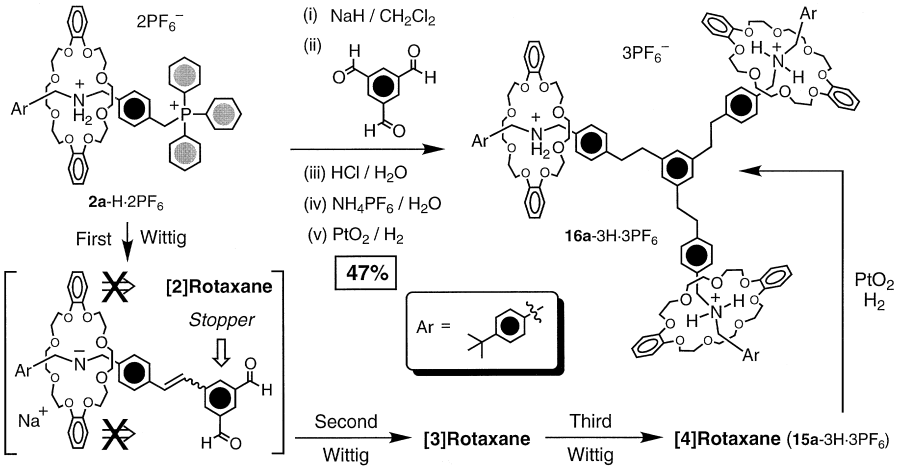


Scheme 8.

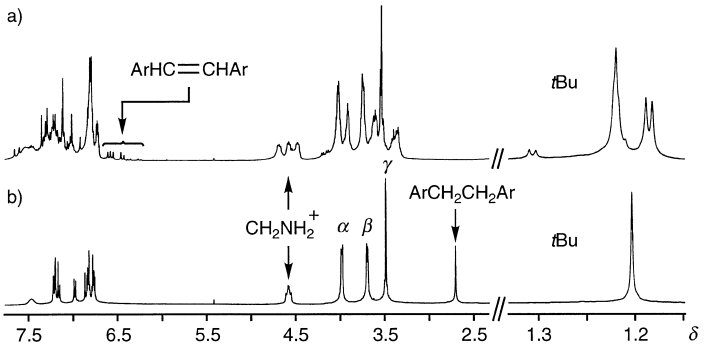


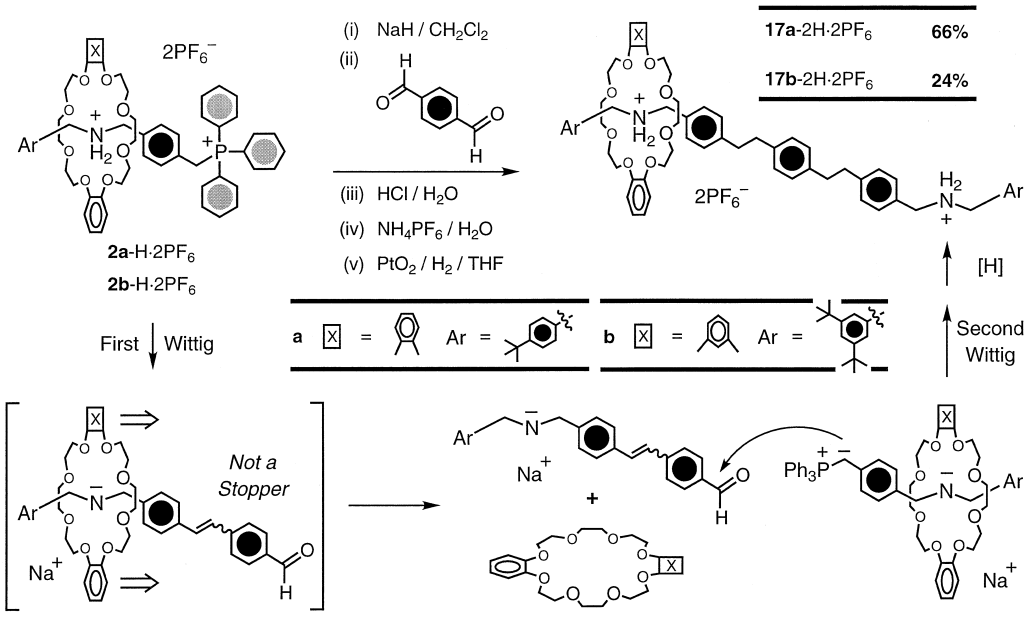
Figure 5. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of a) the *E*/*Z* isomer mixture of [4]rotaxanes **15a**-3H·3HF$_6$ and b) the hydrogenated [4]rotaxane **16a**-3H·3HF$_6$.

and the encircled ammonium ion centers in **16a**-3H·3PF$_6$. The dendritic [4]rotaxane **16a**-3H·3PF$_6$ was obtained in an impressive 47% yield after the sequence of six reactions, namely three Wittigs followed by three hydrogenations.

Thus far, we have demonstrated that, when the hydrogen bonding between the crown ether and the NH_2^+ center is "switched off" under basic Wittig reaction conditions, the triphenylphosphonium ion-stoppered [2]rotaxanes **2a**-H·2PF$_6$, **2b**-H·2PF$_6$, **4a**-H·3PF$_6$, and **4b**-H·3PF$_6$ can react with sterically bulky aldehydes to form a variety of new [2]-, [3]-, and [4]rotaxanes without losing their macrocyclic components.

We now describe how we extended our studies of these systems to utilize aldehydes with little steric bulk in order to take advantage of the expected dethreading of the rotaxanes' components during the Wittig reaction (Scheme 9). Interestingly, we discovered that reaction of **2a**-H·2PF$_6$ under basic conditions with terephthaldehyde—an aldehyde that is not large enough to prevent the dethreading of DB24C8 after the first Wittig reaction—affords *only* a mixture of the unsaturated [2]rotaxanes (Scheme 9). Hydrogenation of this olefin mixture was achieved by using H_2/PtO_2 to yield (66% overall yield from **2a**-H·2PF$_6$) a molecular shuttle **17a**-2H·2PF$_6$, which contains only one DB24C8 ring that is shared between its two degenerate NH_2^+ recognition sites. The [3]rotaxane, which would have contained two DB24C8 rings, that is, one ring located at each recognition site, was *not* observed as a product of the reaction sequence outlined in Scheme 9.

The outcome of this reaction sequence is significant for at least two reasons. Firstly, it demonstrates that the aldehyde which was used in the Wittig reaction is not large enough to prevent the dethreading of the crown ether once its NH_2^+ binding site has been deprotonated. In the synthesis of



Scheme 9.

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[2]rotaxane **17a**-2H·2PF$_6$, after the first Wittig reaction of **2a**-H·2PF$_6$ with OHCC$_6$H$_4$CHO, the DB24C8 ring slips off the semirotaxane[32] because the formyl-terminated end of the rivet-shaped component is not large enough to prevent dethreading of the macrocycle. However, during the second Wittig reaction, this time using the formyl-terminated intermediate, with another equivalent of **2a**-H·2PF$_6$, dethreading is impossible because both ends of the newly created dumbbell-shaped component are sufficiently large (*tert*-butylphenyl) to retain the DB24C8 macrocycle. Secondly, it gives immediate access to [2]rotaxanes that can behave as molecular shuttles[4] and so provides a simple means of building this kind of prototypical molecular machinery. A previous study[4c] on bis(dialkylammonium)-ion-containing molecular shuttles (which was prepared by a more laborious route) has demonstrated that the passage of a DB24C8 macrocycle across a *p*-phenylene ring is slow on the ^{1}H NMR timescale at 400 MHz, even at elevated temperatures and in highly polar solvents. The slightly larger ring macrocycle BMP25C8 is expected, however, to shuttle along such a thread with somewhat greater ease. Therefore, we prepared the analogous BMP25C8-containing [2]rotaxane **17b**-2H·2PF$_6$ (Scheme 9) by utilizing the mono(triphenylphosphonium)-ion-stoppered rotaxane **2b**-H·2PF$_6$ with the Wittig reaction/hydrogenation protocol. The resulting [2]rotaxane **17b**-2H·2PF$_6$ does behave as a molecular shuttle on the ^{1}H NMR timescale. Consequently, we examined the shuttling of the BMP25C8 macrocycle along the linker, which contains three *p*-phenylene rings-positioned between the two NH_2^+ centers. The partial ^{1}H NMR spectrum (Figure 6a) of **17b**-2H·2PF$_6$ in CD$_3$CN at ambient temperature shows that the dumbbell has two distinct halves, as highlighted by the observation of two peaks at $\delta = 2.73$ and 2.86 for the two pairs of CH_2CH_2 groups that link the three *p*-phenylene rings of the spacer unit together, suggesting that the BMP25C8 macrocycle shuttles slowly between the NH_2^+ centers on the ^{1}H NMR timescale at 400 MHz. In one of these halves, the NH_2^+ center is encircled, in characteristic fashion, by the BMP25C8 macrocyclic ring, while in the other it is free, that is, not encircled. Since kinetic studies in most nonpolar solvents are limited by the slow rate of exchange of the macrocycle between the NH_2^+ centers, we investigated the kinetic behavior of molecular shuttle **17b**-2H·2PF$_6$ in CD$_3$OD, which is polar enough to weaken the BMP25C8/dialkylammonium-ion interaction and so make coalescence easier to achieve. The ^{1}H NMR spectrum of **17b**-2H·2PF$_6$ in CD$_3$OD at ambient temperature also shows two distinct signals for two pairs of Ar-CH_2CH_2-Ar groups. However, these two signals coalesce (Figure 6b) at 336 K with a limiting frequency difference ($\Delta\nu$) of 46.8 Hz, which corresponds to a value of k_c of 104 s^{-1} for the process of the macrocycle shuttling between the NH_2^+ centers. By using the Eyring equation, a free energy of activation of 16.6 kcal mol^{-1} was obtained[4c] for the shuttling process at the coalescence temperature T_c of 336 K.

Conclusion

Unless we can devise the means to modify covalently the constitutions of rotaxanes by transforming them into yet more organized and sophisticated arrays, they are destined to occupy a place in the hall of fame for chemical compounds that earns them the accolade of being exotic and only very occasionally, potentially useful. Hence, there is a need to bring about the ways and means to be able to process rotaxanes after their initial supramolecularly assisted template-directed syntheses. In this full paper, we have described how Wittig chemistry can be called into action to achieve a whole range of different structural objectives of a post-assembly nature. Some of the transformations that can be carried out on benzylic triphenylphosphonium-stoppered, NH_2^+-centered/crown-ether-based [2]rotaxanes, although routine in nature, establish a principle of considerable significance to the chemistry of interlocked molecular compounds beyond simple catenanes and rotaxanes: they open up, for example, completely new pathways to intriguing interlocked macromolecules, including polyrotaxanes of the conventional,[33] dendritic,[34] and daisy chain[35] types. Yet other carefully designed transformations make it possible to construct, with incredible control, molecular machines—for example, the molecular shuttle reported herein—of a precisely defined nature that are preordained by the reagents and conditions employed in carrying out the Wittig reactions. The story that begins to unfold in this full paper about how Wittig chemistry can be used in a post-assembly fashion to take rotaxanes, as starting materials in synthesis, onto a higher level of structure and function, is surely no more than a beginning. Post-assembly processing of rotaxanes (and catenanes)

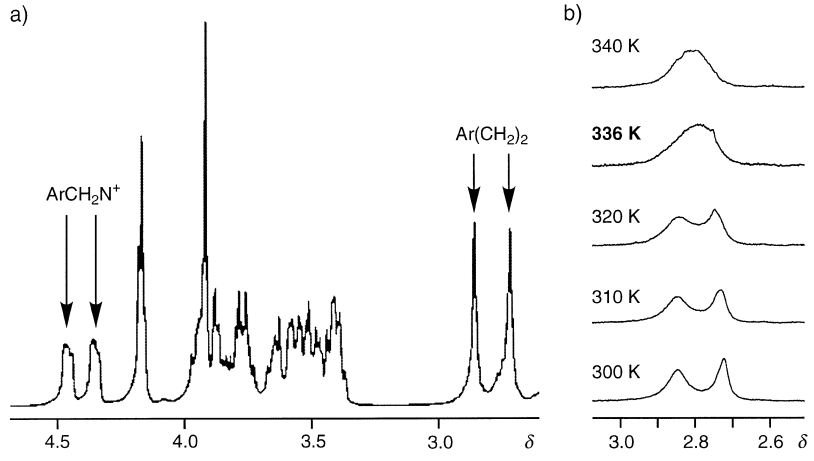

Figure 6. a) Partial ^{1}H NMR spectrum (400 MHz, CD$_3$CN, 298 K) of the two-station molecular shuttle **17b**-2H·2PF$_6$ depicting the asymmetrical nature of the shuttle at ambient temperature. b) Partial variable temperature ^{1}H NMR spectra (400 MHz, CD$_3$OD) of molecular shuttle **17b**-2H·2PF$_6$ highlighting the signals of the Ar-CH_2CH_2-Ar groups, which coalesce at 336 K.

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will extend far beyond the influence of Wittig chemistry in the fullness of time. A principle has been established and it is bound to find expression elsewhere in this branch of chemistry: it is one in which the mechanical bond can be preserved totally or modified very precisely, according to the diktat of the synthetic chemist.

Experimental Section

Materials and methods: All glassware, stirrer-bars, syringes, and needles were either oven- or flame-dried prior to use. All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous CH_2Cl_2 and MeCN were obtained by distillation from CaH_2 under Ar. Anhydrous THF was obtained by distillation from Na/Ph_2CO under N_2. Reactions were carried out under a N_2 or Ar atmosphere. Thin-layer chromatography (TLC) was performed on Analtech 0.25 mm silica gel GHLF. Column chromatography was carried out over silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on either Bruker AC360 (360 and 90 MHz, respectively) or ARX400 (400 and 100 MHz, respectively) spectrometers. The deuterated solvent was used as the lock, while either the solvent's residual protons or TMS was employed as the internal standard. Chemical shifts are reported in parts per million (ppm). Mutiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (mutiplet), and br (broad). Coupling constants are in hertz. Fast-atom bombardment (FAB) mass spectra were obtained using a ZAB-SE mass spectrometer, equipped with a krypton primary atom beam, utilizing a *m*-nitrobenzyl alcohol matrix. Microanalyses were performed by Quantitative Technologies, Inc (USA).

{[2]-{(*N*-4-*tert*-Butylbenzyl)-*N*-{4-[(triphenylphosphonio)methyl]benzyl}-ammonium}(dibenzo[24]crown-8)rotaxane} bis(hexafluorophosphate) (2a-H·2PF$_6$): A solution of **1a**-H·PF_6 (1.0 g, 2.0 mmol) and DB24C8 (1.0 g, 2.2 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 10 min. PPh_3 (0.6 g, 2.3 mmol) was added, and the reaction mixture was stirred for 12 h at ambient temperature. The solvent was evaporated under reduced pressure, and the solid residue was dissolved in MeCN (30 mL), aqueous NH_4PF_6 (2 g in 30 mL H_2O) was added, and the organic solvent was evaporated under reduced pressure. The residue was partitioned between CH_2Cl_2 (100 mL) and H_2O (50 mL), and the organic phase was washed with H_2O (2 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated. The product was purified by column chromatography (SiO_2; MeCN/CH_2Cl_2 (1:9)). The rotaxane **2a**-H·$2PF_6$ was isolated as a white solid (2.0 g, 80%). M.p. 229–231 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 1.22 (s, 9H), 3.45–3.55 (m, 8H), 3.59–3.75 (m, 8H), 3.94–4.00 (m, 8H), 4.39 (d, J = 14.8 Hz, 2H), 4.45–4.52 (m, 2H), 4.70–4.75 (m, 2H), 6.64 (dd, J = 2.4, 8 Hz, 2H), 6.70–6.79 (m, 4H), 6.79–6.88 (m, 4H), 7.15 (d, J = 8 Hz, 2H), 7.23 (s, 4H), 7.43–7.49 (m, 6H), 7.61–7.66 (m, 6H), 7.83–7.87 (m, 3H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 29.4 (J(P,C) = 48.2 Hz), 30.5, 34.2, 51.7, 52.2, 67.8, 70.1, 70.6, 112.3, 117.1 (J(P,C) = 85.7 Hz), 121.3, 125.6, 127.6 (d, J(P,C) = 8.3 Hz), 128.7, 129.2, 129.8, 130.2 (d, J(P,C) = 12.5 Hz), 131.0 (d, J(P,C) = 5.3 Hz), 133.0 (d, J(P,C) = 3.3 Hz), 134.1 (d, J(P,C) = 9.7 Hz), 135.3 (d, J(P,C) = 3 Hz), 147.3, 152.3; ^{31}P NMR (162 MHz, CD_3CN, 298 K): δ = −143.6 (septet, J = 708 Hz, PF_6^-), 22.6 (PhP^+); MS (FAB): m/z: 1122 $[M-PF_6]^+$, 976 $[M-H-2PF_6]^+$; elemental analysis calcd (%) for $C_{61}H_{72}NO_8P_3F_{12}$ (1268): C 57.77, H 5.72, N 1.10; found: C 57.54, H 5.54, N 1.05; Single crystals, suitable for X-ray crystallography, were grown by liquid diffusion of MeOH into a solution of the [2]rotaxane **2a**-H·$2PF_6$ in CH_2Cl_2. Crystal data for **2a**-H·$2PF_6$: $[C_{61}H_{72}NO_8P][PF_6]_2\cdot CH_2Cl_2$, M_r = 1353.0, triclinic, space group $P\bar{1}$ (no. 2), a = 13.722(1), b = 15.241(1), c = 17.972(1) Å, α = 109.50(1), β = 102.75(1), γ = 96.36(1)°, V = 3385.3(3) Å^3, Z = 2, ρ_{calcd} = 1.327 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 22.6 cm^{-1}, $F(000)$ = 1408, T = 293 K; clear prismatic blocks, 0.47 × 0.40 × 0.13 mm, Siemens P4/RA diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, ω-scans, 9779 independent reflections. The structure was solved by direct methods and the full occupancy non-hydrogen atoms were refined anisotropically (the phenyl rings of the triphenylphosphonium moiety were refined as idealized rigid bodies). Disorder was found in the *tert*-butyl group of the thread and in both of the hexafluorophosphate anions; in each case this was resolved into two partial occupancy orientations and the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically). The included dichloromethane solvent molecule was also found to be disordered, but over three partial occupancy sites; again only the major occupancy non-hydrogen atoms were refined anisotropically, the others isotropically. The C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2\,U_{eq}(C)$ [$U(H) = 1.5\,U_{eq}$(C-Me)], and allowed to ride on their parent atoms. The N–H hydrogen atoms were located from a ΔF map and refined isotropically subject to an N–H distance constraint (0.90 Å). Refinements were by full matrix least-squares based on F^2 to give R_1 = 0.076, wR_2 = 0.208 for 7278 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$] and 850 parameters. All computations were carried out using the SHELXTL PC program system.[36] CCDC-187101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk).

{[2]-{*N*-(3,5-Di-*tert*-butylbenzyl)-*N*-{4-[(triphenylphosphonio)methyl]benzyl}ammonium}(benzometaphenylene[25]crown-8)rotaxane} bis(hexafluorophosphate) (2b-H·2PF$_6$): A solution of **1b**-H·PF_6 (1.0 g, 1.8 mmol) and BMP25C8 (1.0 g, 2.2 mmol) in $MeNO_2$ (10 mL) was stirred at room temperature for 10 min. PPh_3 (0.6 g, 2.3 mmol) was added and the reaction mixture was stirred for 12 h at ambient temperature. The solvent was removed under reduced pressure, and the solid residue was dissolved in MeCN (30 mL). Aqueous NH_4PF_6 (2 g) in H_2O (30 mL) was added, and the organic solvent was evaporated under reduced pressure. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (30 mL). The organic layer was washed with H_2O (30 mL), dried ($MgSO_4$), and evaporated to dryness. The crude product was purified by column chromatography (SiO_2; MeCN/CH_2Cl_2 (1:9)). The rotaxane **2b**-H·PF_6 was isolated as a white solid (0.75 g, 32%). M.p. 123–125 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 1.22 (s, 18H), 3.30–3.97 (m, 20H), 4.01–4.20 (m, 4H), 4.35–4.50 (m, 6H), 6.49–6.53 (m, 3H), 6.59–6.64 (m, 2H), 6.64–6.70 (m, 2H), 6.85–6.90 (m, 2H), 7.09–7.18 (m, 3H), 7.33 (d, J = 1.7 Hz, 2H), 7.46–7.55 (m, 7H), 7.60–7.68 (m, 6H), 7.72–7.88 (m, 5H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 30.3 (J(P,C) = 48.3 Hz), 31.5, 35.6, 52.7, 53.8, 68.6, 68.9, 70.1, 71.0, 71.1, 72.0, 104.4, 108.4, 113.1, 118.2 (d, J(P,C) = 85.7 Hz), 122.5, 124.9 (d, J(P,C) = 13.6 Hz), 129.2 (d, J(P,C) = 8.4 Hz), 131.1, 131.2, 131.3, 131.4, 131.6, 132.0 (d, J(P,C) = 5.4 Hz), 132.5 (d, J(P,C) = 3.8 Hz), 135.0 (d, J(P,C) = 9.8 Hz), 136.4 (d, J(P,C) = 2.9 Hz), 147.1, 152.7, 160.8; ^{31}P NMR (162 MHz, CD_3CN, 298 K): δ = −143.6 (septet, J = 708 Hz, PF_6^-), 22.6 (PhP^+); MS (FAB): m/z: 1178 $[M-PF_6]^+$, 1033 $[M-H-2PF_6]^+$; elemental analysis calcd (%) for $C_{65}H_{80}NO_8P_3F_{12}$ (1324): C 58.93, H 6.09, N 1.06; found: C 58.53, H 6.09, N 0.99.

{[2]-{Bis{4-[(triphenylphosphonio)methyl]benzyl}ammonium}(dibenzo-[24]crown-8)rotaxane} tris(hexafluorophosphate) (4a-H·3PF$_6$): PPh_3 (287 mg, 1.1 mmol) was added to a solution of **3**-H·PF_6 (200 mg, 0.38 mmol) and DB24C8 (508 mg, 0.66 mmol) in CH_2Cl_2/MeCN (1:1, 3.8 mL), and the reaction was then left to stir at room temperature overnight. MeCN (50 mL) and NH_4PF_6 (0.5 g) in H_2O (10 mL) were added, the organic solvent was removed under reduced pressure and then the milky aqueous solution was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2; CH_3CN/CH_2Cl_2 (1:9)), to yield the [2]rotaxane **4a**-H·$3PF_6$ (340 mg, 55%). M.p. 147–149 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 3.48–3.55 (m, 8H), 3.65–3.66 (m, 8H), 3.91–3.93 (m, 8H), 4.42 (d, J = 14.8 Hz, 4H), 4.55–4.62 (m, 4H), 6.66–6.70 (m, 8H), 6.79–6.85 (m, 4H), 7.13 (d, J = 8 Hz, 4H), 7.45–7.50 (m, 14H), 7.61–7.66 (m, 12H), 7.83–7.87 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 29.4 (J(P,C) = 48.5 Hz), 51.9, 67.6, 70.1, 70.6, 112.2, 117.4 (d, J(P,C) = 85.7 Hz), 121.3, 128.0 (d, J(P,C) = 8.3 Hz), 129.8, 130.2 (d, J(P,C) = 12.5 Hz), 131.2 (d, J(P,C) = 5.4 Hz), 132.6 (d, J(P,C) = 3.8 Hz), 134.1 (d, J(P,C) = 9.7 Hz), 135.4 (d, J(P,C) = 3 Hz), 147.1; ^{31}P NMR (162 MHz, CD_3CN, 298 K): δ = −143.6 (septet, J = 708 Hz, PF_6^-), 22.8 (PhP^+); MS (FAB) m/z: 1486 $[M-PF_6]^+$, 1341 $[M-H-2PF_6]^+$; elemental analysis calcd (%) for $C_{76}H_{80}NO_8P_5F_{18}$ (1631): C 55.92, H 4.94, N 0.86; found: C 55.73, H 4.78, N 0.75. Single crystals, suitable for X-ray crystallography, were grown by slow evaporation of a CH_2Cl_2/MeOH solution of the [2]rotaxane **4a**-H·$3PF_6$. Crystal data for **4a**-H·$3PF_6$:

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$[C_{76}H_{80}NO_8P_2][PF_6]_3 \cdot 5\,CH_3OH$, $M_r = 1792.5$, monoclinic, space group $I2/a$ (no. 15), $a = 29.055(7)$, $b = 16.315(5)$, $c = 38.179(12)$ Å, $\beta = 102.67(2)^\circ$, $V = 17659(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.348$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.00$ cm^{-1}, $F(000) = 7472$, $T = 293$ K; clear blocks, $1.00 \times 0.93 \times 0.83$ mm, Siemens P4/PC diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, ω-scans, 11433 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms of the [2]rotaxane and the hexafluorophosphate anions were refined anisotropically (the phenyl rings of the triphenylphosphonium moieties were refined as idealized rigid bodies). The included methanol solvent molecules were found to be both highly disordered and distributed over numerous full and partial occupancy sites; only the major occupancy non-hydrogen atoms were refined anisotropically, the others isotropically; their associated C–H and O–H hydrogen atoms were not located. The C–H hydrogen atoms of the [2]rotaxane were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2\,U_{eq}(C)$, and allowed to ride on their parent atoms. The N–H hydrogen atoms were located from a ΔF map and refined isotropically subject to an N–H distance constraint (0.90 Å). Refinements were by full matrix least-squares based on F^2 to give $R_1 = 0.092$, $wR_2 = 0.223$ for 4889 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 45^\circ$] and 1037 parameters. All computations were carried out using the SHELXTL PC program system.[36] CCDC-187102 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk). The corresponding dumbbell compound (179 mg, 35%) was also isolated. M.p. 222–224 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): $\delta = 4.12$ (br, 4H), 4.65 (d, $J = 14.9$ Hz, 4H), 6.99 (dd, $J = 2.4$, 8 Hz, 4H), 7.29 (d, $J = 8$ Hz, 4H), 7.50–7.56 (m, 12H), 7.65–7.69 (m, 12H), 7.84–7.89 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): $\delta = 29.4$ (J(P,C) = 48.5 Hz), 50.7, 117.3 (J(P,C) = 85.8 Hz), 129.0 (J(P,C) = 8.4 Hz), 130.2 (J(P,C) = 12.5 Hz), 130.9 (J(P,C) = 3 Hz), 131.1 (J(P,C) = 3.9 Hz), 131.5 (J(P,C) = 5.4 Hz), 134.1 (J(P,C) = 9.8 Hz), 135.4 (J(P,C) = 3 Hz); ^{31}P NMR (162 MHz, CD_3CN, 298 K): $\delta = -143.6$ (septet, $J = 708$ Hz, PF_6^-), 23.7 (PhP^+); HRMS (FAB): m/z calcd for $C_{52}H_{47}NP_3F_6$ $[M - H - 2PF_6]^+$: 892.2826; found: 892.2826.

{[2]-{Bis{4-[(triphenylphosphonio)methyl]benzyl}ammonium}(benzometaphenylene-[25]crown-8)rotaxane} tris(hexafluorophosphate) (4b-H · 3PF$_6$): PPh_3 (600 mg, 2.3 mmol) was added to a solution of **3**-H · PF_6 (400 mg, 0.75 mmol) and BMP25C8 (1.0 g, 2.2 mmol) in $MeNO_2$ (4 mL), and the reaction was then left to stir at room temperature overnight. MeCN (50 mL) and NH_4PF_6 (1.0 g) in H_2O (10 mL) were added, the organic solvent was removed under reduced pressure, and then the milky aqueous solution was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (SiO_2; MeCN/CH_2Cl_2 (1:9)). [2]Rotaxane **4b**-H · 3PF_6 (380 mg, 43%) was recovered as a white solid. M.p. 124–126 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 3.42$–3.51 (m, 8H), 3.53–3.62 (m, 4H), 3.70–3.91 (m, 8H), 4.05–4.15 (m, 4H), 4.30–4.49 (m, 8H), 6.45 (s, 1H), 6.50–6.55 (m, 2H), 6.60–6.70 (m, 2H) 6.75–6.95 (m, 6H), 7.10–7.20 (m, 5H), 7.40–7.50 (m, 12H), 7.60–7.95 (m, 20H); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 30.3$ (d, J(P,C) = 49.4 Hz), 52.2, 68.0, 68.1, 69.7, 70.7, 70.8, 71.7, 103.5, 107.5, 112.2, 116.2, 117.1, 121.7, 128.2 (d, J(P,C) = 8.3 Hz), 130.0, 130.4 (d, J(P,C) = 12.6 Hz), 131.5, 131.6 (d, J(P,C) = 5.3 Hz), 133.9 (d, J(P,C) = 9.6 Hz), 135.6 (d, J(P,C) = 2.8 Hz), 146.0, 159.8; MS (FAB): m/z: 1486 $[M - PF_6]^+$, 1341 $[M - H - 2PF_6]^+$; elemental analysis calcd (%) for $C_{76}H_{80}NO_8P_5F_{18}$ (1631): C 55.92, H 4.94, N 0.86; found: C 55.83, H 4.80, N 0.84. The corresponding dumbbell compound (450 mg, 51%) was also isolated and characterized. See the previous subsection.

{[2]-{*N*-(4-*tert*-Butylbenyl)-*N*-{4-[2-(*tert*-butylphenyl)ethyl]benzyl}ammonium}(dibenzo[24]crown-8]rotaxane} hexafluorophosphate (6a-H · PF$_6$): 4-*tert*-Butylbenzaldehyde (0.2 mmol) was added to a mixture of **2a**-H · 2PF_6 (100 mg, 80 μmol) and NaH (8 mg, 0.3 mmol) in CH_2Cl_2 (2.6 mL), and the mixture was left to stir at ambient temperature for 12 h. The reaction was quenched with 1N HCl (10 mL) and the aqueous phase was extracted with CH_2Cl_2. The solvent was evaporated, the residue was dissolved in MeCN (10 mL), and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered off, washed with water and then dried under vacuum. Flash column chromatography (SiO_2; CH_2Cl_2/MeOH 100:0 → 95:5), yielded the rotaxane **5a**-H · PF_6 as a white solid, which was then dissolved in THF (2 mL). PtO_2 (3 mg) was added and the mixture was stirred under an H_2 atmosphere for 30 min. The mixture was then filtered, the solvent evaporated, and the residue purified by flash column chromatography (SiO_2; CH_2Cl_2/MeOH 100:0 → 95:5) to yield the hydrogenated [2]rotaxane **6a**-H · PF_6 as a clear oil (33 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 1.24$ (s, 9H), 1.30 (s, 9H), 2.83 (br, 4H), 3.44–3.48 (m, 8H), 3.74–3.76 (m, 8H), 4.05–4.10 (m, 8H), 4.50–4.62 (m, 4H), 6.73–6.78 (m, 4H), 6.85–6.90 (m, 4H), 7.03 (d, $J = 8$ Hz, 2H), 7.11 (d, $J = 8$ Hz, 2H), 7.16–7.19 (m, 4H), 7.21 (d, $J = 8$ Hz, 2H), 7.35 (d, $J = 8$ Hz, 2H), 7.55 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 31.2$, 31.4, 34.4, 34.6, 36.8, 37.0, 52.2, 52.3, 68.2, 70.1, 70.6, 112.6, 121.6, 125.2, 125.5, 128.1, 128.6, 128.7, 128.9, 129.3, 138.3, 143.1, 147.5, 147.8, 148.8, 152.4; HRMS (FAB): m/z calcd for $C_{54}H_{72}NO_8$ $[M - PF_6]^+$: 862.5258; found: 862.5257.

{[2]-{Bis{4-[2-(4-*tert*-butylphenyl)ethyl]benzyl}ammonium}(dibenzo[24]crown-8)rotaxane} hexafluorophosphate (7a-H · PF$_6$): A mixture of **4a**-H · 3PF_6 (100 mg, 60 μmol) and NaH (10 mg, 0.4 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 30 min, and then a solution of *p*-*tert*-butylbenzaldehyde solution (28 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) was added slowly. The mixture was stirred at room temperature for 18 h before MeOH (0.2 mL) was added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was washed with 5% HCl (2 × 30 mL), dried ($MgSO_4$), and concentrated. The crude product was dissolved in MeCN (1 mL), and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The solid was filtered, washed with H_2O, and dried under vacuum. The dry solid was dissolved in THF (4 mL), PtO_2 (6 mg) was added, and the mixture stirred under an H_2 atmosphere for 30 min. The solvent was removed under reduced pressure, and the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was washed with 5% HCl (2 × 30 mL), dried ($MgSO_4$), and evaporated to dryness. The crude product was dissolved in MeCN (1 mL) and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. After filtration, the solid was purified by column chromatography (SiO_2; MeOH/CH_2Cl_2 1:24) yielding the [2]rotaxane **7a**-H · PF_6 (30 mg, 50%). ^{1}H NMR (400 MHz, CD_3CN, 298 K): $\delta = 1.26$ (s, 18H), 2.79 (s, 8H), 3.69 (s, 8H), 3.60–3.70 (m, 8H), 3.95–4.03 (m, 8H), 4.51–4.60 (m, 4H), 6.70–6.86 (m, 8H), 6.98 (d, $J = 8.1$ Hz, 4H), 7.10 (d, $J = 7.5$ Hz, 4H), 7.28 (d, $J = 7.5$ Hz, 4H), 7.46 (d, $J = 8.1$ Hz, 4H), 7.45 (br, 2H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): $\delta = 30.6$, 34.0, 36.3, 36.6, 52.1, 67.9, 70.1, 70.5, 112.5, 121.3, 125.1, 128.1, 128.5, 129.3, 129.5, 138.6, 142.9, 147.5, 148.7; HRMS (FAB): m/z calcd for $C_{62}H_{80}NO_8$ $[M - PF_6]^+$: 966.5884; found: 966.5910.

Methyl 2,5-bis(benzyloxymethoxy)benzoate (8): A mixture of methyl 2,5-dihydroxybenzoate (1.5 g, 8.9 mmol) and NaH (0.63 g, 26 mmol) was cooled to 0 °C. DMF (25 mL) was added slowly, and the reaction mixture was stirred at 0 °C for 1 h. Benzyloxymethyl chloride (3.3 mL) was added to the reaction mixture dropwise by syringe for 30 min. The solution was warmed up slowly to room temperature and stirred for 18 h. MeOH (3 mL) was added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (200 mL) and H_2O (200 mL). The organic layer was separated, washed with 5% HCl(aq) (3 × 100 mL), dried ($MgSO_4$), and concentrated. Purification by column chromatography using an EtOAc/hexanes (1:2) mixture as the eluent gave the ester **8** (3.36 g, 92%). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 3.83$ (s, 3H), 4.69 (s, 2H), 4.73 (s, 2H), 5.26 (s, 2H), 5.27 (s, 2H), 7.13–7.21 (m, 2H), 7.22–7.40 (m, 10H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 52.7$, 70.9, 71.0, 94.0, 95.0, 118.3, 119.4, 119.8, 122.3, 124.1, 128.7, 128.9, 128.9, 129.3, 138.6, 138.6, 151.9, 152.7, 167.0 (one signal is "missing", presumably because of two overlapping signals); HRMS (EI): m/z calcd for $C_{24}H_{24}O_6$: 408.1573; found: 408.1573.

2,5-Bis(benzyloxymethoxy)benzylalcohol (9): $LiAlH_4$ (1.43 g, 37.6 mmol) was added in small portions to a solution of ester **8** (3.1 g, 7.5 mmol) in THF (30 mL) over a period of 1 h. The reaction mixture was stirred at room temperature for 18 h. MeOH (10 mL) was slowly added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (200 mL) and H_2O (200 mL). The organic layer was separated, washed with 5% HCl(aq) (3 × 100 mL), dried ($MgSO_4$), and concentrated. Purification by column chromatography by using an EtOAc/hexanes (1:3) mixture as the eluent gave the alcohol **9** (2.45 g, 85%). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 3.22$ (t, $J = 6$ Hz, 1H), 4.63 (d, $J = 6$ Hz, 2H), 4.70 (s, 4H), 5.25 (s, 2H), 5.26 (s, 2H), 6.94 (dd, $J = 3$ Hz, 8.9 Hz, 1H), 7.06 (d, $J = 8.9$ Hz, 1H), 7.17 (d, $J = 3$ Hz, 1H), 7.21–7.41 (br, 10H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 60.1$, 70.7, 70.9, 94.1, 94.2, 116.4, 116.5, 117.3, 118.3, 128.7, 128.7, 128.8, 128.9, 129.3,

133.5, 138.8, 138.8, 150.2, 153.1; HRMS (FAB): m/z calcd for $C_{23}H_{24}O_5$: 380.1624; found: 380.1623.

2,5-Bis(benzyloxymethoxy)benzaldehyde (10): A mixture of oxalyl chloride (0.31 mL, 3.55 mmol) and CH_2Cl_2 (10 mL) was cooled to $-78\,^{\circ}C$. DMSO (0.42 mL, 5.9 mmol) was added slowly to the mixture, and the solution was stirred at $-78\,^{\circ}C$ for 30 min. Compound **9** (0.89g, 2.17 mmol) in CH_2Cl_2 (10 mL) was slowly added into the solution mixture by means of a syringe. The reaction mixture was stirred at $-78\,^{\circ}C$ for 40 min. Et_3N (1.4 mL, 10 mmol) was added, and the reaction mixture was slowly warmed up to room temperature. The mixture was partitioned between CH_2Cl_2 (200 mL) and H_2O (200 mL). The organic layer was separated, washed with H_2O (3×100 mL), dried ($MgSO_4$), and concentrated. Purification by column chromatography with an EtOAc/hexanes (1:2) mixture as the eluent gave the aldehyde **10** (0.825 g, 93 %). ^1H NMR (400 MHz, CD_3CN): $\delta=4.68$ (s, 2H), 4.74 (s, 2H), 5.27 (s, 2H), 5.38 (s, 2H), 7.20–7.38 (m, 12H), 7.44 (d, $J=3$ Hz, 1H), 10.37 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN): $\delta=$ 70.9, 71.5, 94.0, 94.4, 114.8, 118.3, 118.3, 125.6, 127.2, 128.7, 128.8, 128.9, 129.0, 129.3, 138.5, 138.6, 152.9, 155.7, 190.0; HRMS (EI): m/z calcd for $C_{23}H_{22}O_5$: 378.1467; found: 378.1475.

{[2]-{Bis{4-[2-(2,5-bis(benzyloxymethyleneoxy)phenyl]ethyl}benzyl}ammonium}(dibenzo[24]crown-8)rotaxane} hexafluorophosphate (11a-H·PF_6): A mixture of **4a**-H·$3PF_6$ (100 mg, 60 μmol) and NaH (10 mg, 0.4 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 30 min, and then a solution of **10** (70 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) was added slowly. The mixture was stirred at room temperature for 18 h before MeOH (0.2 mL) was added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was washed with 5 % HCl (2×30 mL), dried ($MgSO_4$), and concentrated. The crude product was dissolved in MeCN (1 mL), and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The solid was filtered, washed with H_2O, and dried under vacuum. The dry solid was dissolved in THF (4 mL), PtO_2 (6 mg) was added, and the mixture stirred under an H_2 atmosphere for 30 min. The solvent was removed under reduced pressure, and the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was washed with 5 % HCl (2×30 mL), dried ($MgSO_4$), and evaporated to dryness. The crude product was dissolved in MeCN (1 mL), and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. After filtration, the solid was purified by column chromatography (SiO_2; MeOH/CH_2Cl_2 1:24) yielding the [2]rotaxane **11a**-H·PF_6 as a clear, thick oil (45 mg, 48 %). ^1H NMR (400 MHz, CD_3CN, 298 K): $\delta=2.70-2.90$ (m, 8H), 3.40–3.52 (m, 8H), 3.68–3.80 (m, 8H), 3.97–4.10 (m, 8H), 4.56–4.64 (m, 4H), 4.65 (s, 4H), 4.70 (s, 4H), 5.18 (s, 4H), 5.24 (s, 4H), 6.70–6.91 (m, 12H), 6.91–7.10 (m, 6H), 7.16 (d, $J=7.8$ Hz, 4H), 7.21–7.40 (m, 20H), 7.45 (br, 2H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): $\delta=32.5$, 36.2, 53.1, 68.8, 70.7, 71.0, 71.0, 71.5, 94.2, 94.3, 113.4, 115.8, 116.5, 119.7, 122.2, 128.7, 128.7, 128.8, 128.8, 129.3, 129.4, 129.5, 130.3, 130.5, 133.0, 138.8, 138.9, 143.9, 148.4, 151.2, 152.8; MS (FAB): m/z: 1399.5 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{86}H_{96}NO_{16}PF_6$ (1545): C 66.87, H 6.26, N 0.91; found: C 66.56, H 6.47, N 0.82.

{[2]-{Bis{4-{2-[2,5-bis(benzyloxymethyleneoxy)phenyl]ethyl}benzyl}ammonium}(benzometaphenylene[25]crown-8)rotaxane} hexafluorophosphate (11b-H·PF_6): A mixture of **4b**-H·$3PF_6$ (100 mg, 60 μmol) and NaH (10 mg, 0.4 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 30 min, and then **10** (70 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) was added slowly. The mixture was stirred at room temperature for 18 h, and then MeOH (0.2 mL) was added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was washed with 5 % HCl (2×30 mL), dried ($MgSO_4$), and concentrated. The crude product was dissolved in MeCN (1 mL), and then saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered, washed with H_2O, and dried under vacuum. The dry solid was dissolved in THF (4 mL), PtO_2 (6 mg) was added, and the mixture was stirred under an H_2 atmosphere for 30 min. The solvent was removed under reduced pressure, and the residue was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was washed with 5 % HCl (2×30 mL), dried ($MgSO_4$) and concentrated. The crude product was dissolved in MeCN (1 mL) and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. After filtration, the solid was purified by column chromatography (SiO_2; MeOH/CH_2Cl_2 1:24) yielding the [2]rotaxane **11b**-H·PF_6 as clear thick oil (60 mg, 63 %). ^1H NMR (400 MHz, CD_3CN, 298 K): $\delta=2.73-2.88$ (m, 8H), 3.44–3.51 (m, 8H), 3.52–3.61 (m, 4H), 3.72–3.85 (m, 8H), 4.10–4.17 (m, 4H), 4.28–4.38 (m, 4H), 4.65 (s, 4H), 4.70 (s, 4H), 5.18 (s, 4H), 5.24 (s, 4H), 6.49–6.59 (m, 3H), 6.60–6.65 (m, 2H), 6.78–6.90 (m, 6H), 7.10–7.35 (m, 31H), 7.64 (br, 2H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): $\delta=32.5$, 36.2, 53.0, 68.6, 68.9, 70.3, 70.7, 71.0, 71.1, 71.3, 72.0, 94.2, 94.3, 104.4, 108.4, 113.0, 115.8, 116.5, 119.7, 122.3, 128.7, 128.7, 128.8, 128.8, 129.3, 129.4, 129.5, 129.7, 130.5, 131.4, 132.9, 138.8, 138.9, 144.4, 147.4, 151.2, 152.8, 160.8; MS (FAB): m/z: 1398.8 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{86}H_{96}NO_{16}PF_6$ (1545): C 66.87, H 6.26, N 0.91; found: C 66.87, H 6.48, N 0.55.

{[3]-(Dibenzo[24]crown-8){2,5-bis{2-[4-(4-*tert*-butylbenzylammoniomethyl)phenyl]ethyl}-1,4-dimethoxybenzene}(dibenzo[24]crown-8)rotaxane} bis(hexafluorophosphate) (12a-2H·2PF_6): A mixture of **2a**-H·PF_6 (50 mg, 40 μmol) and NaH (6 mg, 0.25 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred at room temperature for 30 min before 2,5-dimethoxyterephthaldehyde (4 mg, 20 μmol) in CH_2Cl_2 (0.5 mL) was added slowly by means of a syringe. The reaction mixture was stirred for 12 h at ambient temperature, H_2O (0.1 mL) was added to quench the reaction, and the mixture was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was washed with H_2O (2×30 mL), dried ($MgSO_4$), and evaporated to dryness. The residue was purified by column chromatography (SiO_2; MeCN/CH_2Cl_2 1:9). The [3]rotaxane **12a**-2H·$2PF_6$ was isolated as a white solid (21 mg, 56 %). M.p. 155–157 °C; ^1H NMR (360 MHz, CD_3CN, 298 K): $\delta=1.20$ (s, 18H), 2.73 (s, 8H), 3.50 (s, 16H), 3.69 (s, 6H), 3.73–3.80 (m, 16H), 3.99–4.08 (m, 16H), 4.53–4.66 (m, 8H), 6.70 (s, 2H), 6.70–6.88 (m, 16H), 7.00 (d, $J=9.1$ Hz, 4H), 7.14–7.25 (m, 12H), 7.48 (br, 4H); ^{13}C NMR (90 MHz, CD_3CN, 298 K): $\delta=31.4$, 32.4, 35.2, 36.3, 53.1, 53.2, 56.8, 69.0, 71.1, 71.5, 113.5, 114.3, 122.3, 126.4, 129.1, 129.5, 130.1, 130.2, 130.3, 130.5, 144.2, 148.6, 152.3, 153.1; MS (FAB): m/z: 1741 $[M-PF_6]^+$, 1595 $[M-H-2PF_6]^+$.

{[3]-(Dibenzo[24]crown-8){2,5-bis{2-[4-(4-*tert*-butylbenzylammonio)methylphenyl]ethyl}-1,4-bis(benzyloxymethyleneoxy)benzene}(dibenzo[24]crown-8)rotaxane} bis(hexafluorophosphate) (13a-2H·2PF_6): A mixture of **2a**-H·$2PF_6$ (150 mg, 0.12 mmol) and NaH (16 mg, 0.67 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 30 min before 2,5-bis(benzyloxymethyleneoxy)terephthaldehyde (24 mg, 60 μmol) in CH_2Cl_2 (0.75 mL) was added slowly by means of a syringe. The mixture was stirred overnight at room temperature before H_2O (0.3 mL) was added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL), and the organic layer was washed with H_2O (2×50 mL), dried ($MgSO_4$), and evaporated to dryness. The residue was purified by column chromatography (SiO_2; MeOH/CH_2Cl_2 1:19), and the [3]rotaxane **13a**-2H·$2PF_6$ was isolated as a white solid (70 mg, 56 %). M.p. 104–106 °C; ^1H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta=1.26$ (s, 18H), 2.83 (s, 8H), 3.42–3.52 (m, 16H), 3.68–3.78 (m, 16H), 4.00–4.10 (m, 16H), 4.52–4.63 (m, 8H), 4.75 (s, 4H), 5.28 (s, 4H), 6.72–6.94 (m, 16H), 7.00 (s, 2H), 7.03–7.12 (m, 4H), 7.20–7.40 (m, 22H), 7.55 (br, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): $\delta=31.3$, 32.5, 34.8, 36.3, 52.6, 52.6, 68.4, 70.4, 70.6, 71.0, 93.8, 112.8, 116.8, 121.9, 125.8, 128.1, 128.2, 128.7, 129.0, 129.1, 129.3, 129.6, 129.7, 129.8, 138.0, 143.8, 147.9, 150.3, 152.7; MS (FAB): m/z: 1952 $[M-PF_6]^+$, 1806 $[M-H-2PF_6]^+$; elemental analysis calcd (%) for $C_{110}H_{138}N_2O_{20}P_2F_{12}$ (2098): C 62.96, H 6.63, N 1.33; found: C 62.56, H 6.71, N 1.17.

{[3]-(Dibenzo[24]crown-8){2,5-bis{2-[4-(4-*tert*-butylbenzylammoniomethyl)phenyl]ethyl}-2,5-dihydroxybenzene}(dibenzo[24]crown-8)rotaxane} bis(hexafluorophosphate) (14a-2H·2PF_6): The [2]rotaxane **13a**-2H·$2PF_6$ (20 mg, 10 μmol) in 5 % HCl/THF (1:19; 5 mL) was heated under reflux overnight before being cooled to room temperature. A solution of NH_4PF_6 (20 mg) in H_2O (2 mL) was added, the THF was evaporated, and the residue was partitioned between H_2O (20 mL) and CH_2Cl_2 (20 mL). The organic layer was washed with H_2O (2×20 mL), dried ($MgSO_4$), and then the solvent was evaporated. The residue was purified by column chromatography (SiO_2; MeCN/CH_2Cl_2 1:9), and the [3]rotaxane **14a**-2H·$2PF_6$ was isolated (11 mg, 64 %). ^1H NMR (400 MHz, CD_3CN, 298 K): $\delta=1.21$ (s, 18H), 2.60–2.80 (m, 8H), 3.44–3.52 (m, 16H), 3.63–3.72 (m, 16H), 3.93–4.04 (m, 16H), 4.52–4.67 (m, 8H), 6.22 (s, 2H), 6.49 (s, 2H), 6.71–6.87 (m, 16H), 6.99 (d, $J=8.1$ Hz, 4H), 7.16–7.23 (m, 12H), 7.55 (br, 4H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): $\delta=31.4$, 32.1, 35.1, 36.0, 53.0, 53.1, 68.9, 71.1, 71.5, 113.4, 117.5, 122.2, 126.3, 127.1, 129.5,130.0, 130.2, 130.3, 130.5, 144.2, 148.5, 148.5, 153.0; MS (FAB): m/z: 1711 $[M-PF_6]^+$, 1565 $[M-H-2PF_6]^+$.

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{[4]-{1,3,5-Tris{2-[4-(4-*tert*-butylbenzylammoniomethyl)phenyl]ethyl}benzene}tris(dibenzo[24]crown-8)rotaxane} tris(hexafluorophosphate) (16a-3H·3PF$_6$): Benzene-1,3,5-tricarboxaldehyde (8.5 mg, 50 μmol) was added to a solution of **2a**-H·2PF$_6$ (200 mg, 0.16 mmol) and NaH (15 mg, 0.6 mmol) in CH_2Cl_2 (2.6 mL), and the mixture was then left to stir at room temperature for 16 h. The reaction was quenched with 1N HCl (10 mL), and the aqueous phase was then extracted with CH_2Cl_2. The solvent was removed from the combined organic phases, the residue was dissolved in MeCN (10 mL) and then saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered off, washed with water, and then dried under vacuum. The resulting solid was further purified by dissolving it in a small amount of CH_2Cl_2 and then reprecipitated with Et_2O. The crude rotaxane **15a**-3H·3PF$_6$ was dissolved in THF (1.5 mL), PtO_2 (6 mg) was added and the mixture stirred under an H_2 atmosphere for 2 h. The reaction mixture was then filtered and purified by flash column chromatography (SiO_2; CH_2Cl_2/MeOH 100:0 → 95:5), yielding the fully hydrogenated [4]rotaxane **16a**-3H·3PF$_6$ as a clear oil (67 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 1.21$ (s, 27H), 2.72 (br, 12H), 3.44–3.48 (m, 24H), 3.74–3.76 (m, 24H), 3.99–4.01 (m, 24H), 4.56–4.63 (m, 12H), 6.75–6.80 (m, 12H), 6.81–6.88 (m, 12H), 6.88 (s, 3H), 6.99 (d, $J = 8$ Hz, 6H), 7.15–7.23 (m, 18H), 7.48 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 30.4$, 34.2, 36.8, 37.0, 52.1, 67.9, 70.1, 70.5, 112.4, 121.2, 125.3, 126.1, 128.5, 129.0, 129.2, 129.4, 129.6, 141.7, 142.9, 147.5, 152.0 (one signal is "missing", presumably because of two overlapping signals); MS (FAB): *m*/*z*: 2554 $[M - PF_6]^+$, 2408 $[M - H - 2PF_6]^+$.

{[2]-{1,4-Bis{2-[4-(4-*tert*-butylbenzylammoniomethyl)phenyl]ethyl}benzene}(dibenzo[24]crown-8)rotaxane} bis(hexafluorophosphate) (17a-2H·2PF$_6$): A solution of terephthaldehyde (10.5 mg, 80 μmol) in CH_2Cl_2 (2.5 mL) was added, over a period of 2 h, to a solution of **2a**-H·2PF$_6$ (200 mg, 0.2 mmol) and NaH (15 mg, 0.6 mmol) in CH_2Cl_2 (2.5 mL). The reaction was then left to stir at room temperature for 15 h, before being quenched with 1N HCl (10 mL), and the aqueous phase was then extracted with CH_2Cl_2. The solvent was evaporated from the combined organic phases, the residue was dissolved in MeCN, and then saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered off, washed with H_2O, and then dried under vacuum. The resulting solid was further purified by dissolving it in a small amount of CH_2Cl_2 and then reprecipitating it by the addition of Et_2O. The crude product was dissolved in THF (3 mL), PtO_2 (6 mg) was added, and the mixture was stirred under an H_2 atmosphere for 1 h. The mixture was then filtered, the solvent evaporated, and the residue purified by flash column chromatography (SiO_2; CH_2Cl_2/MeOH 100:0 → 95:5) to yield the [2]rotaxane **17a**-2H·2PF$_6$ as a clear oil (72 mg, 66%). ^{1}H NMR (400 MHz, CD_3CN, 298 K): $\delta = 1.19$ (s, 9H), 1.29 (s, 9H), 2.78 (s, 4H), 2.83 (s, 4H), 3.41–3.54 (m, 8H), 3.70–3.73 (m, 12H), 3.99–4.02 (m, 8H), 4.54–4.62 (m, 4H), 6.75–6.81 (m, 4H), 6.81–6.88 (m, 4H), 6.93–6.98 (m, 2H), 7.01–7.08 (m, 4H), 7.11–7.30 (m, 12H), 7.34–7.39 (m, 2H), 7.48 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 30.4$, 30.5, 34.1, 34.2, 36.4, 36.7, 36.8, 37.0, 51.9, 52.0, 52.1, 52.2, 67.9, 70.1, 70.5, 112.5, 121.3, 125.2, 125.3, 128.1, 128.3, 128.4, 128.6, 129.0, 129.2, 129.3, 129.6, 139.0, 139.4, 140.8, 142.8, 147.5, 147.8, 150.1, 152.0 (three signals are "missing", presumably because of signal overlap); MS (FAB): *m*/*z*: 1086 $[M - H - 2PF_6]^+$.

{[2]-{1,4-Bis{2-[4-(3,5-di-*tert*-butylbenzylammoniomethyl)phenyl]ethyl}-benzene}(benzometaphenylene[25]crown-8)rotaxane} bis(hexafluorophosphate) (17b-2H·2PF$_6$): A solution of **2b**-H·2PF$_6$ (57 mg, 45 μmol) and NaH (5 mg, 22 μmol) in CH_2Cl_2 (0.6 mL) was stirred at room temperature for 30 min, and then terephthaldehyde (3 mg, 22 μmol) in CH_2Cl_2 (0.6 mL) was added slowly. The mixture was stirred at room temperature for 18 h before MeOH (0.1 mL) was added to quench the reaction. The mixture was partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was separated, washed with 5% HCl (2 × 20 mL), dried ($MgSO_4$), and evaporated to dryness. The residue was dissolved in MeCN (1 mL) and then saturated aqueous NH_4PF_6 was added until no further precipitation was observed. The solid was filtered, washed with H_2O, and dried under vacuum. The solid was dissolved in THF (2 mL), PtO_2 (3 mg) was added, and the mixture was stirred under an H_2 atmosphere for 40 min. The solvent was evaporated under reduced pressure, and the residue was then partitioned between CH_2Cl_2 (30 mL) and H_2O (30 mL). The organic layer was washed with 5% HCl (2 × 20 mL), dried ($MgSO_4$), and concentrated. The crude product was dissolved in MeCN (1 mL), and saturated aqueous NH_4PF_6 was added until no further precipitation was observed. After filtration, the solid was purified by column chromatography (SiO_2; MeOH/CH_2Cl_2 1:19) to yield the [2]rotaxane **17b**-2H·2PF$_6$ as a white solid (16 mg, 24%). ^{1}H NMR (400 MHz, CD_3CN, 298 K): $\delta = 1.21$ (s, 18H), 1.31 (s, 18H), 2.73 (s, 4H), 2.86 (s, 4H), 3.35–4.00 (m, 24H), 4.10–4.21 (m, 4H), 4.30–4.40 (m, 2H), 4.42–4.53 (m, 2H), 6.50–6.65 (m, 3H), 6.65–6.80 (m, 2H), 6.81–7.00 (m, 4H), 7.00–7.50 (m, 17H), 7.80 (br, 4H); ^{13}C NMR (90 MHz, CD_3CN, 298 K): $\delta = 31.6$, 31.7, 35.5, 35.6, 37.4, 37.7, 37.8, 38.1, 53.1, 53.3, 53.6, 53.8, 68.6, 69.0, 70.2, 71.0, 71.2, 71.9, 104.4, 108.4, 113.1, 118.3, 122.4, 122.4, 123.8, 124.8, 124.9, 129.4, 129.5, 129.6, 130.6, 131.5, 131.7, 140.1, 140.4, 147.4, 151.9, 152.5 (seven signals are "missing", presumably because of signal overlap); MS (FAB): *m*/*z*: 1344 $[M - PF_6]^+$, 1198 $[M - H - 2PF_6]^+$.

Acknowledgement

This research was supported by the National Science Foundation (CHE-9910199) and the Petroleum Research Fund, administered by the American Chemical Society. The paper is also based upon work supported by the National Science Foundation under equipment grant number CHE-9974928.

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[28] In order to obtain some information concerning the kinetic acidity of the NH_2^+ groups in the rotaxanes **4a**-H·3PF$_6$ and **4b**-H·3PF$_6$, we treated these rotaxanes (60 mM) with D_2O (7 M) in CD_3CN and monitored the H-D exchange reaction. In both cases, we were unable to observe the NH_2^+ signals after adding D_2O. Instead, the kinetic behavior was estimated by observing the change in the shape of the signal associated with the proton of the methylene groups adjacent to NH_2^+ center from a multiplet to a broad singlet during the exchange process. In contrast to the reported slow kinetic exchange process ($t_{1/2} = 17$ min) of a similar rotaxane containing a DB24C8 unit (N. Kihara, Y. Tachibana, H. Kawasaki, T. Takata, *Chem. Lett*. **2000**, 506 – 507), the exchange rate was much faster for the [2]rotaxane **4a**-H·3PF$_6$ ($t_{1/2} < 3$ min) and **4b**-H·3PF$_6$ ($t_{1/2} < 1$ min). The stronger kinetic acidity of the [2]rotaxane **4b**-H·3PF$_6$ compared to **4a**-H·3PF$_6$ may also reflect the fact that interaction between BMP25C8 and the dialkylammonium ion is weaker than that between DB24C8 and the dialkylammonium ion. The reason for the difference in kinetic behavior of the [2]rotaxane **4a**-H·3PF$_6$ and Takata's rotaxane is not clear. We suspect, however, that the crown ether unit in **4a**-H·3PF$_6$ has more "room" to move around than in Takata's rotaxane—because of the larger distance between the ammonium

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center and the stopper groups—resulting in less steric hindrance for the approach of D_2O toward the ammonium center.

[29] When Pd/C was used as the catalyst for the same hydrogenation, hydrogenlysis (presumably of the benzylic $C-N^+$ bond) took place, a reaction which destroys the backbone of the rotaxane and results in the quantitative isolation of free DB24C8. A similar hydrogenolysis (H_2/PtO_2) occurred when the reaction mixture was hydrogenated for a long period of time.

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Received: June 6, 2002 [F4161]