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[2]Rotaxanes containing pyridinium–phosphonium axles and 24-crown-8 ether wheels†

Norma Georges, Stephen J. Loeb,* Jorge Tiburcio and James A. Wisner
Department of Chemistry & Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4. E-mail: loeb@uwindsor.ca; Fax: +1 519 973 7098; Tel: +1 519 253 3000

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A triethylphosphonium group attached to a pyridinium ethane moiety can be used as an axle for the self-assembly of [2]pseudorotaxanes and [2]rotaxanes. Although [2]pseudorotaxane formation is limited due to the bulk of the PR_4^+ group, [2]rotaxanes can be formed utilising 24-crown-8 ether, benzo-24-crown-8 ether and naphtho-24-crown-8 ether. The synthesis of these [2]rotaxanes and the X-ray structure of the [2]rotaxane containing a 24-crown-8 ether wheel are described. When the crown ether contains an aromatic group two possible conformational isomers exist; these are identified at low temperature by ^1H and ^{31}P NMR spectroscopy.

Introduction

A variety of interpenetrated and interlocked molecules have been prepared utilising crown ether wheels and pyridinium axles.[1–9] In particular, we have shown that the combination of bis(pyridinium)ethane axles and 24-membered crown ethers is a versatile motif for forming [2]pseudorotaxanes,[5] [2]rotaxanes,[6] [3]rotaxanes,[7] [2]rotaxane shuttles[8] and [3]catenanes;[9] see Fig. 1 for examples. Since trialkylphosphines are easily alkylated to form tetralkylphosphonium salts, we chose to explore the possibility of incorporating a simple PR_4^+ group in place of a pyridinium group in our rotaxane motif. The synthesis of triphenylphosphonium stoppered dibenzylammonium based [2]rotaxanes was previously reported by Stoddart.[10] The incorporation of these groups allowed their exchange for permanent stoppers using the Wittig reaction.[11] Our initial synthetic target was the hybrid, pyridinium–phosphonium axle 1-triethyl phosphonium-2-(4,4′-bipyridinium)ethane, $\mathbf{2}^{2+}$, shown in Scheme 1. We describe herein 1) the preparation of this hybrid P,N axle, 2) a study of the formation of [2]pseudorotaxanes with this new axle and 24-membered crown ethers, 3) the synthesis of three corresponding [2]rotaxanes and 4) the X-ray structure of the [2]rotaxane incorporating a 24-crown-8 ether wheel.

Results and discussion

The phosphonium containing axle $\mathbf{2}[Br]_2$ was prepared in 71% yield by reacting the alkylbromide $\mathbf{1}[Br]$ with excess triethylphosphine in refluxing MeCN. In order to facilitate solution studies and further reaction chemistry, the bromide salt was converted to the tetrafluoroborate salt; $\mathbf{2}[BF_4]_2$, by precipitation from aqueous $NaBF_4$.

Previous investigations with bis(pyridinium) axles demonstrated that [2]pseudorotaxane formation was possible in MeCN solution with a variety of members of the 24-crown-8 ether family.[5] In MeCN-d_3 at 298 K, association constants for bis(pyridinium) axles varied from ~100 to ~4000 depending on the presence of aromatic rings on the 24C8 framework and the electron-withdrawing or electron-donating nature of substitutions on the rings. Interestingly, our first attempt

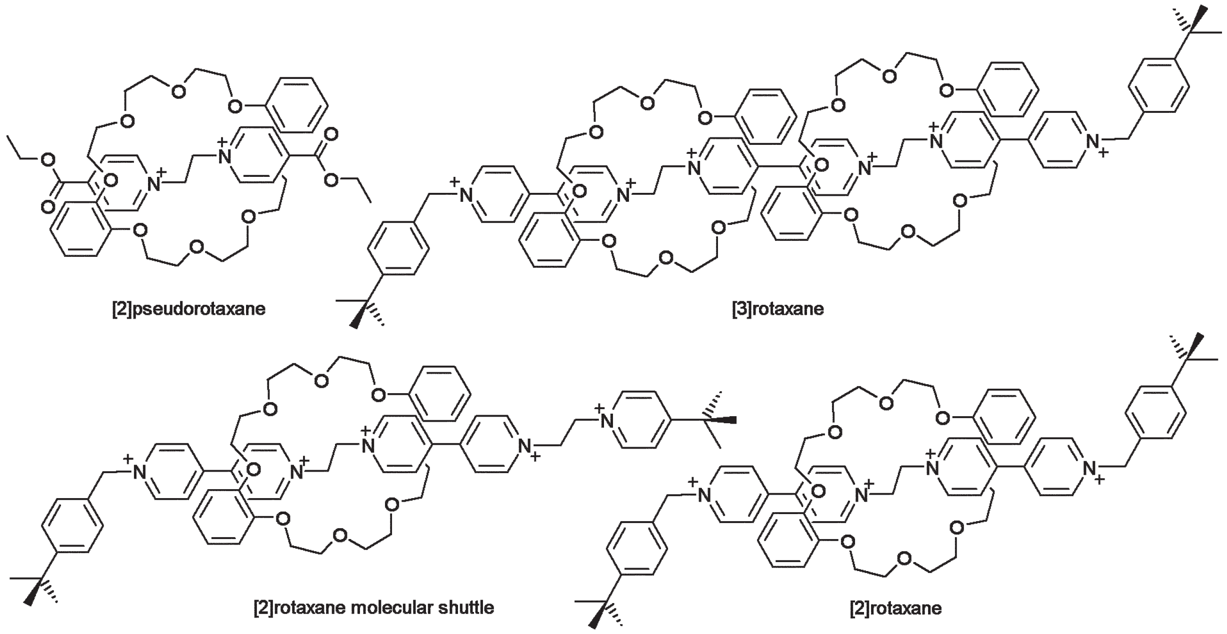

Fig. 1 Interlocked and interpenetrated molecules previously prepared utilising a combination of bis(pyridinium)ethane axles and 24-membered crown ether wheels.

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† Electronic supplementary information (ESI) available: aromatic region of the ^1H NMR spectrum for $\mathbf{8}^{3+}$ at 300 K and 213 K; atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $\mathbf{6}[BF_4]_3$. See http://www.rsc.org/suppdata/ob/b4/b407653b/

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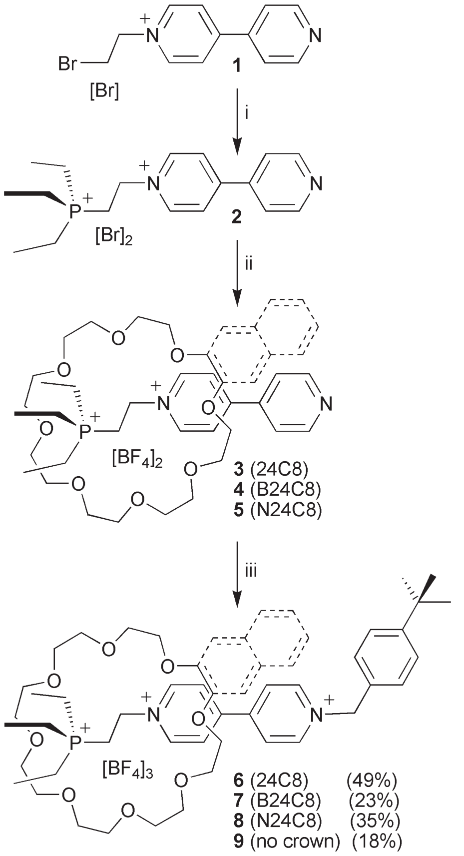
Table 1 Association constants[a] for [2]pseudorotaxanes formed between the phosphonium axle $\mathbf{2}[BF_4]_2$ and various 24-membered crown ethers

	Axle		[2]Pseudorotaxane			
Crown	δ (ppm)	Integral[b]	δ (ppm)	Integral[b]	K_a/M^{-1}	$\Delta G°$/kJmol^{-1}
24C8 (**3**)	4.85	6.38	5.07	1.00	36	−8.9
B24C8 (**4**)	4.85	4.45	5.15	1.00	55	−9.9
N24C8 (**5**)	4.85	4.70	5.12	1.00	52	−9.8

[a] In MeCN-d_3 solution at 298 K with slow exchange on the NMR time scale. [b] Based on NCH_2 resonances.



Scheme 1 i) 14 equivalents of PEt_3 in MeCN at reflux for 5 days, ii) 6 equivalents of crown ether in $MeNO_2$/$NaBF_4$(aq), iii) 5 equiv. of 4-***tert***-butylbenzylbromide at room temperature for 72 h.

at formation of a [2]pseudorotaxane between $\mathbf{2}[BF_4]_2$ and dibenzo-24-crown-8 ether, DB24C8, resulted in no evidence of any interaction between the two components; $K_a < 5$ M^{-1}. We ascribed this lack of interpenetration to steric problems between the tetrahedral phosphonium group and the aromatic rings of DB24C8 which must be oriented towards each other. To alleviate the problem we focussed our attention on simpler crown ethers containing either no aromatic rings, 24C8, or those with only one aromatic ring, B24C8 and N24C8. Subsequent solution studies showed that [2]pseudorotaxanes could be formed between $\mathbf{2}[BF_4]_2$ and 24C8, B24C8 and N24C8 respectively but the association constants were in the range of only ~30–50 M^{-1}, see Table 1.

Our conclusion was that even though the positive charge on the phosphorus atom should provide significant ion–dipole contributions towards stabilizing [2]pseudorotaxane formation, the bulk of the PR_4^+ group must be a significant perturbation working against formation of the interpenetrated geometry observed in our bis(pyridinium) systems. Nonetheless, we were interested in exploring the possibility of creating [2]rotaxanes with a phosphonium stopper. To this end, we reacted the axle $\mathbf{2}[BF_4]_2$ with *tert*-butylbenzylbromide in the presence of a large excess of crown ether to favour, as much as possible, interpenetration and ultimately, by kinetic trapping, the permanently interlocked [2]rotaxane. This crude methodology was successful in producing the [2]rotaxanes **6**–**8** in 49, 23 and 35% yields respectively; Scheme 1.

The [2]rotaxanes **6**–**8** were characterised in solution by ^{1}H and ^{31}P NMR spectroscopy (see Fig. 2 for numbering scheme) and mass spectrometry. Chemical shifts were consistent with the proposed interlocked structures while high resolution electrospray mass spectrometry unambiguously identified the proposed formulation. The most significant interactions between the P,N axle and crown ether were evident from the downfield shifts of the ethylene linkage protons (*c* and *d*) and the α-pyridinium protons (*e*) in the [2]rotaxanes when compared to resonances in the analogous "naked" axle **9**. Shifts ranged from 0.21 to 0.39 ppm due to these CH···O interactions.

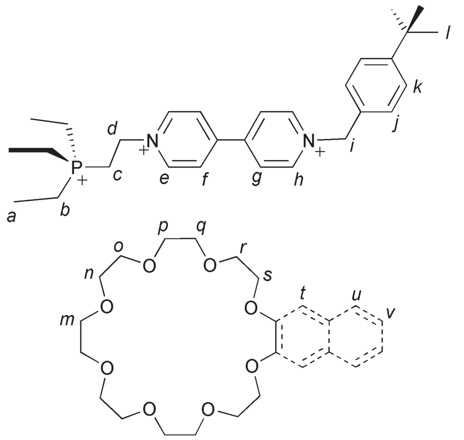


Fig. 2 The basic numbering scheme used for all NMR spectral data is shown for the phosphonium based axle and the three crown ethers used, 24-crown-8 (24C8), benzo-24-crown-8 (B24C8) and naphtho-24-crown-8 ether (N24C8).

For [2]rotaxanes **7** and **8**, which contain aromatic rings on the crown ether, π-stacking was also identifiable in the ^{1}H NMR spectra as the aromatic protons *f*, *g* and *h* of the axle and *t*, *u* and *v* of the crown ethers exhibited upfield shifts. Also, solutions of **7** and **8** were orange in colour, typical of charge transfer between the electron-poor pyridinium groups of the axle and the electron-rich catechol rings of the crown.[5–9]

A unique feature of **6**, which unambiguously demonstrates its interlocked nature, is the multiplet observed for the methylene crown ether protons shown in Fig. 3. Although the ^{1}H NMR spectrum of free 24C8 consists of only a single resonance, when 24C8 is penetrated by the unsymmetrical P,N axle, protons on opposite faces of the crown ether become inequivalent. Since the components are permanently interlocked, there is no mechanism to interconvert them and two sets of closely coupled resonances give rise to an AA′BB′ multiplet.

The other major contributor to the non-covalent interaction between wheel and axle must be the ion dipole interactions between the positively charged N or P atom and the electronegative O-atoms of the crown ether. In our bis(pyridinium) systems, this was not directly observable in solution, but the availability of a ^{31}P NMR spectroscopic handle allows for the potential of direct observation in this new system. Unfortunately, although there were differences observed among the

Table 2 Hydrogen bonding parameters for [2]rotaxane, $\mathbf{6}[BF_4]_3$

H-Atoms	Molecule 1[a]		Molecule 2[b]	
	Distance/Å[e]	Angle/°	Distance/Å	Angle/°
α-Py	3.60 (2.75)	152.1	3.21 (2.28)	174.2
	3.16 (2.27)	160.6	3.32 (2.48)	149.4
NCH_2	3.26 (2.37)	152.0	3.27 (2.33)	163.6
	3.40 (2.60)	139.7	3.30 (2.41)	151.7
	3.55 (2.80)	134.1		
PCH_2	3.27 (2.33)	163.9	3.34 (2.38)	167.6
	3.34 (2.44)	155.1	3.32 (2.38)	164.4

H-Atoms	Molecule 3[c]		Molecule 4[d]	
	Distance/Å	Angle/°	Distance/Å	Angle/°
α-Py	3.20 (2.27)	174.5	3.66 (2.85)	147.1
	3.13 (2.20)	176.1	3.10 (2.22)	156.1
NCH_2	3.78 (2.85)	163.0	3.25 (2.29)	172.4
	3.30 (2.37)	161.4	3.23 (2.44)	138.8
			3.34 (2.70)	123.9
PCH_2	3.48 (2.54)	163.0	3.33 (2.38)	164.2
	3.26 (2.30)	169.7	3.43 (2.47)	169.6

[a] Molecule 1 is numbered starting at P(1). [b] Molecule 2 is numbered starting at P(101). [c] Molecule 3 is numbered starting at P(201). [d] Molecule 4 is numbered starting at P(301). [e] Distance given are O···C and O···H in parentheses.

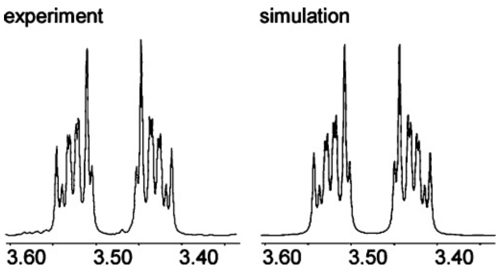


Fig. 3 The observed (left) and calculated (right) ^1H NMR spectra of **6** showing the OCH_2CH_2O protons of the penetrated 24C8. δ 3.52 and 3.43 (m and m′) ppm; $^2J_{m,m'} = -11.5$, $^3J_{m,n} = 6.5$, $^3J_{m,n'} = 1.6$ Hz.

^{31}P chemical shifts for these compounds, there was no obvious correlation to be made.

X-Ray quality crystals of $\mathbf{6}[BF_4]_3$ were grown by slow evaporation of an acetonitrile solution of the compound. Initially, a room temperature data set was collected but a satisfactory solution was not possible due to extremely poor atomic resolution. A satisfactory solution from data collected at low temperature (173 K) demonstrated why the room temperature structure was problematic. There are *four* distinct molecules of **6** in the asymmetric unit with slightly different conformations of axle and wheel. At room temperature these were manifest as a single overlapping solution with large disorder. Each individual molecule has the same interlocked nature and demonstrates essentially the same set of non-covalent interactions. As an example, one of these molecules is shown in Fig. 4. All four of the NCH_2 and PCH_2 hydrogen atoms of the central ethylene link and the pyridinium α-hydrogens form C–H···O hydrogen bonds to the crown ether oxygen atoms; see Table 2. This array of hydrogen bonds and the ion dipole interactions between the N^+ or P^+ ion and the ether oxygen atoms are the non-covalent interactions which initially direct formation of the [2]pseudorotaxane *via* threading and dictate the observed conformations of the [2]rotaxane. Fig. 5 shows the four different molecules in the asymmetric unit. Since the 24C8 wheel is approximately circular it is clearly differences in conformations of the axles and how they interact with the wheel that give rise to four slightly different species in the solid state. It is also should be noted that in spite of all the research into the complexation of cationic guests by crown ether hosts[12] this is, to the best of our knowledge,[13] the first report of a crystal structure containing the parent 24-membered crown ether, 24C8.

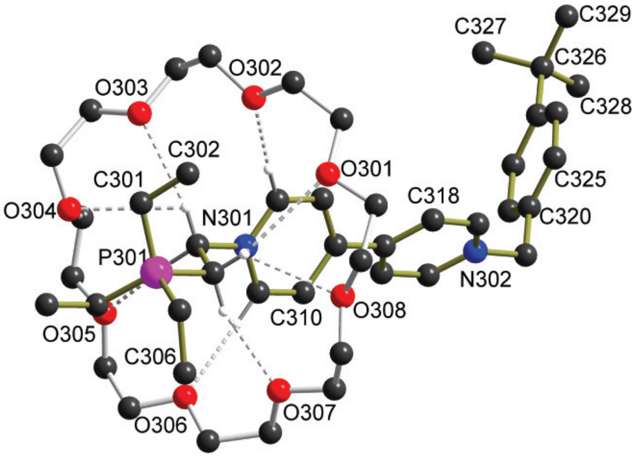


Fig. 4 A ball-and-stick representation of the X-ray crystal structure of [2]rotaxane $\mathbf{6}^{3+}$ containing a phosphonium–pyridinium axle and a 24C8 wheel. There are four independent molecules in the asymmetric unit. This molecule is shown as an example. The minor differences are outlined in the text and Table 2.

An interesting feature of the [2]rotaxanes $\mathbf{7}^{3+}$ and $\mathbf{8}^{3+}$ is that they are constructed of an unsymmetrical P,N axle and an unsymmetrical wheel (B24C8 or N24C8). This means that each is capable of existing in either of two conformational isomers as shown in Fig. 6. At room temperature, the ^1H and ^{31}P NMR spectra of these [2]rotaxanes show only a single set of resonances but at lower temperature it is possible to identify resonances for both isomers. Fig. 7 shows the aromatic region of the ^1H NMR spectrum for $\mathbf{7}^{3+}$ in which both a major and a minor isomer are clearly visible (for $\mathbf{8}^{3+}$ see ESI). Peak assignments were verified by low temperature, ^1H EXSY NMR spectroscopy. The major isomer is consistent with π-stacking of the benzo group of the crown over the dipyridinium group of the axle and hydrogen bonding of the α-pyridinium protons, *e*. The minor isomer has the obvious steric problem of positioning the benzo unit close to the phosphonium group and shows hydrogen bonding to α-pyridinium protons, *h*. These observations are consistent with the assignment of major and minor isomers as shown. For $\mathbf{7}^{3+}$ (benzo) and $\mathbf{8}^{3+}$ (naphthyl), the ratios of major to minor isomers are 2.1 : 1 and 15.5 : 1 respectively. Activation barriers for this process were estimated from variable temperature NMR data to be 46.1 and 48.3 kJ mol^{-1} respectively.

The existence of two conformational isomers for these types of [2]rotaxanes is reminiscent of similar scenarios for molecular shuttles and other molecular machines. As it may be possible to control or manipulate this motion, we are currently investigating the scope of this phenomenon.

Experimental

1,2-Dibromoethane, 4,4′-bipyridine, triethylphosphine, DB24C8, and sodium tetrafluoroborate were purchased from Aldrich Chemicals and used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. All solvents were purchased from EM Science. Crown ethers 24C8, B24C8, and N24C8 were synthesized according to literature methods.[12] The high resolution ESI mass spectra were recorded on a Micromass LCT time-of-flight spectrometer from acetonitrile solutions in lockmass mode. ^1H NMR spectra were recorded on a Brüker Avance 500 spectrometer locked to the deuterated solvent at 500.1 MHz. All peak positions are listed in ppm relative to TMS. ^{31}P NMR spectra were recorded on a Brüker Avance 300 spectrometer at 121.49 MHz and peak positions listed in ppm relative to H_3PO_4 (85%). All peak assignments for hydrogen atoms were made using standard 2D NMR NOESY and COSY experiments. Chemical shifts and coupling constants for certain second order multiplets were determined

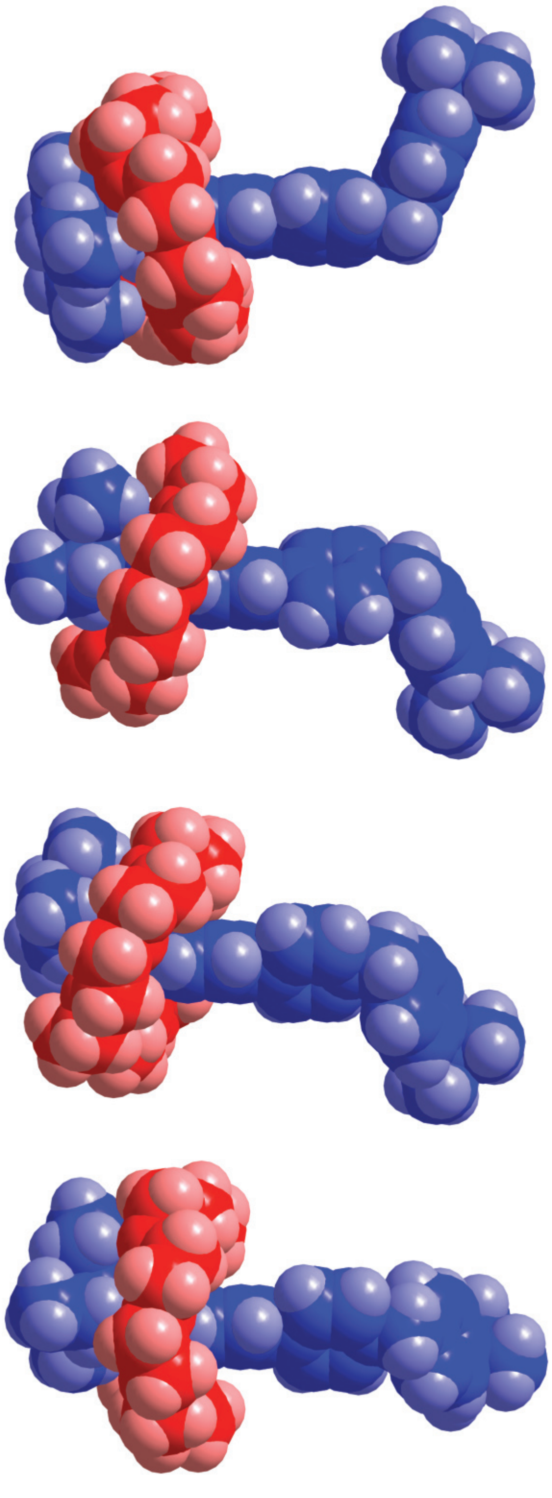


Fig. 5 Space-filling CPK-type diagrams of the four independent [2]rotaxanes in the asymmetric unit of **6**$^{3+}$. The phosphonium axles are shown in blue and the 24-crown-8 wheels in red.

by a full line iteration using the program gNMR.[14] Diagrams for the X-ray crystal structure were generated with the program DIAMOND.[15]

Preparation of 1-triethylphosphonium-2-(4,4′-bipyridinium)-ethane tetrafluoroborate 2[BF$_4$]$_2$

Pyridinium salt, **1**[Br], (1.00 g, 2.91 mmol), prepared by the literature method,[5] was dissolved in acetonitrile (45 mL) and triethylphosphine (6 mL, 14 mmol) added with stirring; the solution immediately turned green in colour. The solution was heated at reflux for 5 days. The mixture was cooled to room temperature and the resulting white precipitate collected by vacuum filtration, washed with diethyl ether (10 mL) and dried. Yield 874 mg (65%) of **2** as the bromide salt. ^{1}H NMR (D$_2$O): δ 9.02 (d, 2H, $^3J_{HH}$ = 6.6 Hz, *e*), 8.72 (d, 2H $^3J_{HH}$ = 6.0 Hz, *h*), 8.43 (d, 2H, $^3J_{HH}$ = 6.6 Hz, *f*), 7.87 (d, 2H, $^3J_{HH}$ = 6.0 Hz, *g*), 5.01 (m, 2H, *d*), 3.13 (m, 2H, *c*), 2.39 (m, 6H, *b*), 1.27 (m, 9H, *a*). The bromide salt of **2** (874 mg) was then combined with a saturated aqueous solution of NaBF$_4$ (10 mL) and solid NaBF$_4$ (395 mg) and this mixture gently heated at reflux until all the solid had dissolved. The solution was allowed to cool slowly to room temperature, stored at 10 °C for 12 h and the beige solid produced isolated by filtration. Yield 349 mg (39%) of **2**[BF$_4$]$_2$. ^{1}H NMR (CD$_3$CN): δ 8.92 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *e*), 8.86 (d, 2H, $^3J_{HH}$ = 6.2 Hz, *h*), 8.41 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *f*), 7.83 (d, 2H, $^3J_{HH}$ = 6.2 Hz, *g*), 4.85 (m (8), 2H, $^2J_{HdHd'}$ = −16.0 Hz, $^3J_{HdHc}$ = 13.2 Hz, $^3J_{HdHc'}$ = 4.5 Hz, $^3J_{HdP}$ = 4.6 Hz, *d*), 2.95 (m (14), 2H, $^2J_{HcHc'}$ = −14.6 Hz, $^2J_{HcP}$ = 14.8 Hz, *c*), 2.35 (m (8), 6H, $^3J_{HaHb}$ = 7.7 Hz, $^2J_{HbP}$ = 12.9 Hz, *b*), 1.29 (m (6), 9H,

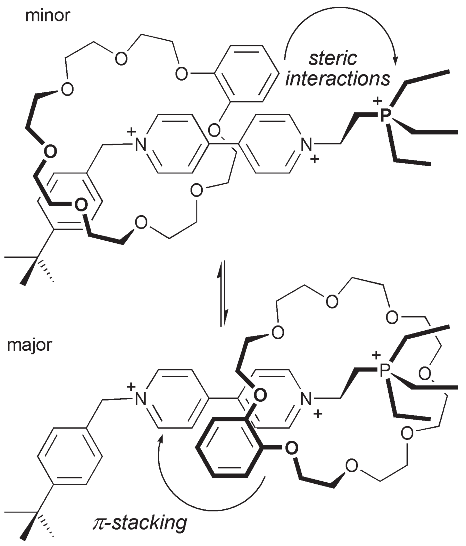


Fig. 6 The two conformational isomers of **7**$^{3+}$ are shown in which the position of the aromatic ring of the crown ether aligns with either the dipyridinium unit (major) or the phosphonium group (minor).

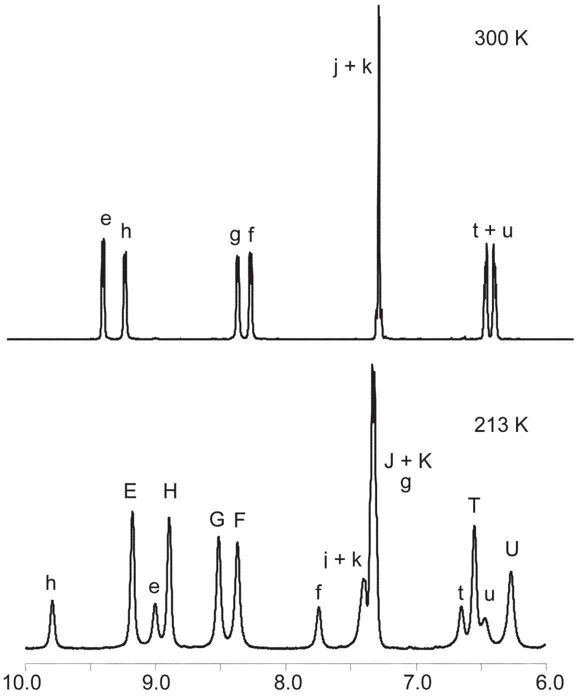


Fig. 7 The aromatic region of the ^{1}H NMR spectra for **7**$^{3+}$ in CD$_2$Cl$_2$. Top: at 300 K only averaged resonances are observed for the two conformational isomers. Bottom: at 213 K resonances for both the major (upper case) and minor (lower case) isomers are clearly visible.

$^3J_{HaP}$ = 19.1 Hz, *a*). ^{31}P NMR: δ 39.79 ppm. HR-ESI-MS: Calcd. for $C_{18}H_{27}BF_4N_2P$ [M − BF$_4$]$^+$ *m*/*z* 389.1941, found 389.1946 (1.3 ppm).

Determination of association constants for [2]pseudorotaxanes 3, 4 and 5

^{1}H NMR spectra were recorded in CD_3CN at 500 MHz for 1 : 1 mixtures of equimolar solutions (5×10^{-3} M) containing the phosphonium stoppered axle **2**[BF$_4$]$_2$ and a crown ether (24C8, B24C8 and N24C8). In each case, the equilibrium was observed to be slow on the NMR time-scale allowing for a single-point determination of the K_a by integration of the corresponding N*CH$_2$* resonances of the ethylene link in the axle and [2]pseudorotaxane. Values are summarized in Table 1.

Preparation of the [2]rotaxane 6[BF$_4$]$_3$

Axle **2**[BF$_4$]$_2$ (100 mg, 0.210 mmol) and 24C8 (1.00 g, 2.84 mmol) were dissolved in acetonitrile (10 mL). An excess of 4-*tert*-butylbenzylbromide (230 mg, 1.01 mmol) was then added and the yellow solution stirred for 4 days. The solvent was removed under vacuum to give an oily orange residue. Ethyl ether (10 mL) was added and the mixture stirred for 12 h to remove excess 24C8. The diethyl ether was removed by decantation and the orange residue dried under vacuum. A saturated aqueous solution of NaBF$_4$ (~5 mL) and solid NaBF$_4$ (130 mg) were added and the mixture warmed until a clear soution was produced. After cooling to 10 °C for 12 h, the aqueous phase was removed and the oily orange residue dissolved in CH_2Cl_2 (~12 mL) and the solution dried using anhydrous MgSO$_4$. The mixture was filtered through a pad of cotton wool, Celite and MgSO$_4$ to give a clear orange solution. The solvent was removed under vacuum and the orange residue recrystallized by slow evaporation of an acetonitrile solution of the product. Yield 110 mg (49%). ^{1}H NMR (CD_3CN): δ 9.39 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *e*), 9.06 (d, 2H, $^3J_{HH}$ = 6.9 Hz, *h*), 8.52 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *f*), 8.49 (d, 2H, $^3J_{HH}$ = 6.9 Hz, *g*), 7.55 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *k*), 7.48 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *j*), 5.82 (s, 2H, *i*), 5.14 (m (8), 2H, $^2J_{HdHd'}$ = −16.0 Hz, $^3J_{HdHc}$ = 13.8 Hz, $^3J_{HdHc'}$ = 4.3 Hz, $^3J_{HdP}$ = 4.0 Hz, *d*), 3.52, 3.43 (m (AA′BB′), 32H, $^2J_{HmHm'}$ = −11.5 Hz, $^3J_{HmHn}$ = 6.5 Hz, $^3J_{HmHn'}$ = 1.6 Hz, *m*, *m*′, *n* and *n*′), 3.24 (m (14), 2H, $^2J_{HcHc'}$ = −14.5 Hz, $^2J_{HcP}$ = 14.6 Hz, *c*) 2.34 (m (8), 6H, $^3J_{HaHb}$ = 7.7 Hz, $^2J_{HbP}$ = 12.7 Hz, *b*), 1.34 (m (6), 9H, $^3J_{HaP}$ = 19.1 Hz, *a*), 1.32 (s, 9H, *l*). ^{31}P NMR (CD_3CN): δ = 39.10. HR-ESI-MS: Calcd. for $C_{45}H_{74}B_2F_8N_2O_8P$ [M − BF$_4$]$^+$ *m*/*z* 975.5241, found 975.5232 (0.9 ppm).

Preparation of the [2]rotaxane 7[BF$_4$]$_3$

Axle **2**[BF$_4$]$_2$ (113 mg, 0.238 mmol) and B24C8 (537 mg, 1.34 mmol) were dissolved in acetonitrile (10 mL). An excess of 4-*tert*-butylbenzylbromide (139 mg, 0.612 mmol) was added and the orange mixture stirred for 3 days. The volume of the resulting solution was concentrated (~3 mL) by roto-evaporation and diethyl ether (2 × 30 mL) added to precipitate the pyridinium salts and allow removal of the excess B24C8. After decanting the solvent, the solid residue was dried under vacuum. The crude [2]rotaxane was purified by column chromatography on silica gel, using a mixture of $CH_3OH : CH_3NO : NH_4Cl$ (aq, 2M) in the ratio of 3 : 1 : 1 as the mobile phase. Solvents were removed from the yellow fractions containing the product (as monitored by TLC) and the resulting yellow solid dissolved in water (20 mL) and this solution transferred to a freshly prepared solution of NaBF$_4$ (sat'd, aq) (~10 mL). The mixture was heated slightly and allowed to cool slowly at 10 °C to precipitate an orange solid. Yield 60 mg (23%). ^{1}H NMR (CD_3CN): δ 9.38 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *e*), 9.17 (d, 2H, $^3J_{HH}$ = 6.4 Hz, *h*), 8.49 (d, 2H, $^3J_{HH}$ = 6.4 Hz, *g*), 8.37 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *f*), 7.55 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *k*), 7.49 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *j*), 6.81, 6.74 (m, 4H, *t* and *u*), 5.86 (s, 2H, *i*), 5.18 (m, 2H, *d*), 4.12–3.45 (m, 28H, *m–s*), 3.26 (m, 2H, *c*), 2.24 (m (8), 6H, $^3J_{HaHb}$ = 7.7 Hz, $^2J_{HbP}$ = 12.7 Hz, *b*), 1.32 (s, 9H, *l*), 1.25 (m (6), 9H, $^3J_{HaP}$ = 18.9 Hz, *a*). ^{31}P NMR (CD_3CN): δ = 37.85 ppm. HR-ESI-MS: Calcd. for $C_{49}H_{74}B_2F_8N_2O_8P$ [M − BF$_4$]$^+$ *m*/*z* 1023.5241, found 1023.5262 (2.0 ppm).

Preparation of the [2]rotaxane 8[BF$_4$]$_3$

Axle **2**[BF$_4$]$_2$ (100 mg, 0.210 mmol) and N24C8 (1.00 g, 2.22 mmol) were dissolved in acetonitrile (10 mL). An excess of 4-*tert*-butylbenzylbromide (221 mg, 0.972 mmol) was added and the orange solution stirred for four days. The solvent was removed by roto-evaporation and diethyl ether (50 mL) added to the residue to dissolve excess N24C8 and precipitate the pyridinium salts. The mixture was stirred for 5 min, the solids allowed to settle and ether removed by decantation. This process was repeated once again, and the residue dried in vacuum. The crude [2]rotaxane was purified by column chromatography on silica gel, using a mixture of CH_3OH, CH_3NO_2 and NH_4Cl (aq, 2M) in the ratio of 3 : 1 : 1 as the mobile phase. Solvents were removed from the fractions containing the [2]rotaxane (orange bands monitored by TLC) and the residue dissolved in water (~20 mL). This was transferred slowly by pipette to a freshly prepared solution of NaBF$_4$ (sat'd, aq) (~10 mL). An orange solid precipitated and was collected by vacuum filtration. Further purification was achieved by re-precipitation with diethyl ether from a concentrated acetone solution. Yield 85 mg (35%). ^{1}H NMR (CD_3CN): δ 9.34 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *e*), 8.66 (d, 2H, $^3J_{HH}$ = 6.7 Hz, *h*), 8.13 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *f*), 7.81 (d, 2H, $^3J_{HH}$ = 6.7 Hz, *g*), 7.65 (d, 2H, $^3J_{HH}$ = 8.3 Hz, *k*), 7.51 (d, 2H, $^3J_{HH}$ = 8.3 Hz, *j*), 7.39 (m, 2H, *u*), 7.05(s, 2H, *t*), 6.94 (m, 2H, *v*), 5.68 (s, 2H, *i*), 5.22 (m (6), 2H, $^2J_{HdHd'}$ = −12.4 Hz, $^3J_{HdHc}$ = 6.8 Hz, $^3J_{HdHc'}$ = 2.4 Hz, $^3J_{HdP}$ = 13.1 Hz, *d*), 4.36–3.13 (m, 28H, *m–s*), 3.38 (m, 2H, *c*), 2.37 (m (8), 6H, $^3J_{HaHb}$ = 7.7 Hz, $^2J_{HbP}$ = 12.7 Hz, *b*), 1.38 (s, 9H, *l*), 1.35 (m (6), 9H, $^3J_{HaP}$ = 18.9 Hz, *a*). ^{31}P NMR (CD_3CN): δ = 39.93 ppm. HR-ESI-MS: Calcd. for $C_{53}H_{76}B_2F_8N_2O_8P$ [M − BF$_4$]$^+$ *m*/*z* 1073.5398, found 1073.5399 (0.1 ppm).

Preparation of axle 9[BF$_4$]$_3$

An excess of 4-*tert*-butylbenzylbromide (113 mg, 0.499 mmol) and **2**[BF$_4$]$_2$ (137 mg, 0.288 mmol) were dissolved in acetonitrile (30 mL) and the solution heated to reflux for 12 h. After cooling to room temperature, the resulting yellow precipitate was collected by vacuum filtration. Yield 36 mg (18%). ^{1}H NMR (CD_3CN): δ (ppm) 9.01 (d, 2H, $^3J_{HH}$ = 6.5 Hz, *e*), 8.99 (d, 2H, $^3J_{HH}$ = 7.0 Hz, *h*), 8.48 (d, 2H, $^3J_{HH}$ = 6.5 Hz, *f*), 8.43 (d, 2H, $^3J_{HH}$ = 7.0 Hz, *g*), 7.54, 7.44 (d, 2H, $^3J_{HH}$ = 8.0 Hz, *k* and *j*), 5.79 (s, 2H, *i*), 4.93 (m (8), 2H, $^2J_{HdHd'}$ = −15.3 Hz, $^3J_{HdHc}$ = 13.5 Hz, $^3J_{HdHc'}$ = 4.9 Hz, $^3J_{HdP}$ = 3.9 Hz, *d*), 3.14 (m (14), 2H, $^2J_{HcHc'}$ = −14.5 Hz, $^2J_{HcP}$ = 14.8 Hz, *c*) 2.36 (m (8), 6H, $^3J_{HaHb}$ = 7.7 Hz, $^2J_{HbP}$ = 13.0 Hz, *b*), 1.30 (s, 9H, *l*), 1.28 (m (6), 9H, $^3J_{HaP}$ = 19.0 Hz, *a*). ^{31}P NMR (CD_3CN): δ = 39.97 ppm. HR-ESI-MS: Calcd. for $C_{29}H_{42}B_2F_8N_2P$ [M − BF$_4$]$^+$ *m*/*z* 623.3144, found 623.3144 (0.0 ppm).

X-Ray structure determination of [2]rotaxane 6[BF$_4$]$_3$

Pale yellow crystals of **6**[BF$_4$]$_3$ were grown by slow evaporation of an acetonitrile solution of the compound. Crystals were mounted on a short glass fibre attached to a tapered copper pin and the crystal cooled to 173.0(1) K. A full hemisphere of data were collected with 30 s frames on a Brüker APEX diffractometer fitted with a CCD based detector. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with the assigned space group. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data set. The structure was solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against $|F^2|$ data. All

Table 3 Crystal data, solution and structure refinement for **6**[BF_4]$_3$

Empirical Formula	$C_{45}H_{74.5}B_3F_{12}N_2O_{8.25}P$
Formula Weight	1066.97
Temperature/K	173.0(1)
Wavelength/Å	0.71073
Crystal System	Triclinic
Space Group	*P*-1 (No. 2)
a/Å	16.912(6)
b/Å	21.522(8)
c/Å	31.460(12)
α/°	90.638(7)
β/°	102.614(7)
γ/°	105.370(8)
Volume/Å^3	10746(7)
Z	8
Calculated Density/mg m^{-3}	1.319
Absorption Coefficient/mm^{-1}	0.143
F(000)	4500
Crystal Size/mm	0.34 × 0.28 × 0.16
Theta Range/°	1.15 to 23.31
Limiting Indices	$-18 \leq h \leq 11$, $-23 \leq k \leq 23$, $-35 \leq l \leq 34$
Reflections Collected/Unique	47619/30431 [$R_{int} = 0.0796$]
Theta Range	23.31 (98.0%)
Absorption Correction	None
Refinement Method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	30431/29/2566
Goodness-of-Fit on F^2	0.975
Final R Indices [$I > 2\sigma(I)$]	$R_1 = 0.1061$, $wR_2 = 0.2777$
R Indices (All Data)	$R_1 = 0.2402$, $wR_2 = 0.3365$
Largest Diff. Peak/Hole/e Å^{-3}	1.059/−0.468

non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions except those on the solvent water molecule which were not included. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.[16] Crystal, data collection, solution and structure refinement parameters are listed in Table 3.

CCDC reference number 239570. See http://www.rsc.org/suppdata/ob/b4/b407653b/ for crystallographic data in .cif or other electronic format.

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