Some Adventures in
Secondary Ammonium Ion
Binding

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requirements for the degree Doctor of Philosophy
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by

Stuart James Cantrill

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The dissertation of Stuart James Cantrill is approved.

Jon M Fukuto

Miguel A Garcia-Garibay

J Fraser Stoddart, Committee Chair

University of California, Los Angeles

2001
For my parents

Pamela and Barrie

and

for my wife

Maggie
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Chapter 2: The Influence of Macroyclic Polyether Constitution upon Ammonium Ion Binding

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Chapter 4: Kinetic and Thermodynamic Approaches for the Synthesis of Ammonium Ion/Crown Ether-Based Interlocked Molecules

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Figure 4.7. Schematic representations of dynamic interlocked structures (catenanes I-II and rotaxanes III-V) which differ in the location of the reversible covalent bonds. For example, whereas the dumbbell of III can be formed and broken reversibly, it is the ring component of IV that contains the reversible covalent bonds. Consequently, dynamic rotaxane III would be formed by a ‘stoppering’ approach, whereas IV would required a clipping strategy. Rotaxane V, in which both components contain reversibly-formed linkages, could be assembled via either pathway.

Figure 4.8. Schematic representations of ‘magic’ interlocked molecules!

Figure 4.9. Conceptually, the assembly of an amino-functionalized [2]semirotaxane and subsequent reaction with a bulky isocyanate leads to the formation of a ureido-[2]rotaxane.

Figure 4.10. The structure of the [2]rotaxane 1-H-O₂CCF₃, showing the labeling scheme for both (i) the dumbbell and (ii) the crown ether components, used in describing its NMR spectroscopic properties. The schematic representation (ii) highlights the unsymmetrical nature of the dumbbell. The protons (α¹, β¹, γ¹) on one face of the DB24C8 macrocycle are oriented toward the 3,5-di-tert-butylphenyl stopper, whereas those protons (α², β², γ²) on the opposite face of the macrocycle are directed toward the 2,6-diisopropylphenyl stopper, i.e., the protons located on opposite faces of the crown ether are diastereotopic.

Figure 4.11. The partial ¹H NMR spectrum (400 MHz, CD₂Cl₂) of 1-H-O₂CCF₃.

Figure 4.12. The partial T-ROESY spectrum (400 MHz, CD₂Cl₂) of 1-H-O₂CCF₃. The most significant probe protons are H-2 and H-3, which each show a correlation to only one set of protons on only one face of the crown ether.
The molecular structures of the two crystallographically-independent [2]rotaxanes present in the crystals of 1-HO2CCF3. Hydrogen bonding distances and angles \([X \cdot \cdot \cdot O], [H \cdot \cdot \cdot O]\) distances (Å), \([X-H \cdot \cdot \cdot O]\) angles (°): for molecule (i); (a) 2.85, 2.01, 156; (b) 2.89, 2.16, 137; (c) 3.31, 2.36, 171; (e) 2.89, 2.03, 159; (f) 2.86, 2.16, 137; (b) 3.01, 2.23, 145; (c) 3.41, 2.51, 171; (d) 3.25, 2.41, 147; (e) 2.76, 1.92, 163; (f) 2.91, 2.02, 168. The centroid-centroid distances \((g)\) for molecules (i) and (ii) are 4.48 and 4.54 Å, respectively.

The partial \(^1\)H NMR spectrum (400 MHz, CD2Cl2) of 7-HO2CCF3. Note (*) that the broad peak at δ = 9.4 ppm is a background signal arising from the NMR probe.

The structure of the [2]rotaxane 7-HO2CCF3, showing the labeling scheme for the protons on both (i) the dumbell and (ii) the crown ether components, used in describing its NMR spectroscopic parameters. The through-space correlations determined by T-ROESY measurements are also highlighted in (i) by double-headed arrows. The schematic representation (ii) highlights the unsymmetrical nature of the dumbell. The protons \((\alpha_1, \beta_1, \gamma_1, \delta_1, \epsilon_1, \phi_1)\) on one face of the BMP25C8 macrocycle are oriented toward the 3,5-di-tert-butylphenyl stopper, whereas those protons \((\alpha_2, \beta_2, \gamma_2, \delta_2, \epsilon_2, \phi_2)\) on the opposite face of the macrocycle are directed toward the 2,6-diisopropylphenyl stopper.

Partial \(^{13}\)C NMR spectra (125 MHz, CD3CN:CD3SOCD3 3:1), recorded at various temperatures, showing the coalescence of the signal arising from the carbon atom of the methyl groups that constitute the isopropyl groups.

A Ramachandran-like plot depicting the energy profile of bond rotations associated with the 2,6-diisopropylphenyl stopper moiety.

The molecular structures of the two crystallographically-independent [2]rotaxanes present in the crystals of 7-HO2CCF3. Hydrogen bonding distances and angles \([X \cdot \cdot \cdot O], [H \cdot \cdot \cdot O]\) distances (Å), \([X-H \cdot \cdot \cdot O]\) angles (°): for molecule (i); (a) 2.90, 2.07, 152; (b) 2.92, 2.17, 140; (c) 3.06, 2.26, 149; (d) 3.34, 2.48, 149; (e) 2.83, 1.95, 163; (f) 2.88, 2.00, 166; for molecule (ii); (a) 2.83, 1.94, 170; (b) 2.95, 2.34, 125; (c) 3.13, 2.26, 163; (d) 3.30, 2.43, 150; (e) 2.93, 2.04, 170; (f) 2.89, 2.00, 172; (g) 3.22, 2.42, 141. The centroid-centroid distances \((h)\) for molecules (i) and (ii) are 4.22 and 4.29 Å, respectively.

Signals for the resonances corresponding to (i) free crown ether 5 (ii) uncomplexed thread 9-HPF6 and (iii) the 1:1 pseudorotaxane complex \([5\cdot 9-H]PF6\) formed between the two individual components can be observed in the \(^1\)H NMR spectrum. This phenomenon indicates that the free and complexed species are equilibrating slowly on the NMR timescale and therefore allows for the simple calculation of \(K_a\) by utilizing the so-called single-point method.

Left: Partial \(^1\)H NMR spectra (400 MHz, CD3CN, 300 K), recorded over time, of an initial mixture of dialdehyde 9-HPF6 (20 mM) and 3,5-di-tert-butylaniline 12 (40 mM). Right: The dynamic equilibrium established in solution, and the corresponding percentages of
each of the three species at equilibrium. The probe protons of, and the associated resonances for, the dialdehyde are labeled ‘9’ (i.e., corresponding to compound 9-H·PF₆), those of the monoaldehyde (monoimine) ‘13’, and those of the diimine dumbell ‘14’.

**Figure 4.21.** Top: A schematic representation of the dynamic process under spectroscopic investigation. Bottom: The partial ¹H NMR spectrum (400 MHz, CD₃CN, 300 K), recorded over time, of an initial mixture of 9-H·PF₆ (20 mM), 3,5-di-tert-butyl-aniline 12 (40 mM), which was allowed to reach equilibrium (spectrum at t = 0 min) prior to the addition of DB24C8 (5) (20 mM). Peaks corresponding to species containing an NH₂⁺ center not bound/occupied by a DB24C8 ring are colored black, while those which correspond to species that are bound/occupied are shaded grey and, furthermore, the numerical labels attached to these peaks are suffixed with an asterisk. The signals associated with the dialdehyde {9}, monoaldehyde {13} and diimine {14} probe protons are highlighted as described in Figure 4.20.

**Figure 4.22.** Top: A schematic representation of the dynamic process under spectroscopic investigation. Bottom: The partial ¹H NMR spectrum (400 MHz, CD₃CN, 300 K) recorded over time, of an initial mixture of 9-H·PF₆ (20 mM), 3,5-di-tert-butylaniline 12 (40 mM) and DB24C8 (5) (20 mM). Peaks are annotated in the same fashion as in Figure 4.21.

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Table 4.1. The torsion angles (w, x, y and z) observed for the DB24C8- and BMP25C8-containing rotaxanes, 1-H-O2CCF3 and 7-H-O2CCF3, respectively. In each structure, there are two crystallographically-independent molecules (i and ii) in the asymmetric unit.

LIST OF SYMBOLS AND ABBREVIATIONS

Å Ångstroms
B24C8 Benzo[24]crown-8
BMP25C8 Benzometaphenylene[25]crown-8
BPP34C10 Bisparaphenylene[34]crown-10
COSY Correlation Spectroscopy
DBA Dibenzylationmonium
DMAP 4-Dimethylaminopyridine
DMF N,N-Dimethylformamide
DMSO Dimethylsulfoxide
DP Degree of Polymerization
EIMS Electron Impact Mass Spectrometry
Et2O Diethyl Ether
Et3N Triethylamine
EtOAc Ethyl Acetate
EPR Electron Paramagnetic Resonance
FABMS Fast Atom Bombardment Mass Spectrometry
GC Gas Chromatography
HMQC Heteronuclear Multiple Quantum Correlation
HRMS High Resolution Mass Spectrometry
Ka Association Constant
kcal Kilocalories
kJ Kilojoules
LSIMS Liquid Secondary Ion Mass Spectrometry
Me2CO Acetone
MeCN Acetonitrile
MeNO2 Nitromethane
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>MeOH</td>
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<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>mM</td>
<td>Millimolar</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>PCC</td>
<td>Pyridinium Chlorochromate</td>
</tr>
<tr>
<td>PhMe</td>
<td>Toluene</td>
</tr>
<tr>
<td>PhSeH</td>
<td>Benzeneselenol</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>TB24C8</td>
<td>Tetrabenzo[24]crown-8</td>
</tr>
<tr>
<td>TB27C9</td>
<td>Tribenzo[27]crown-9</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>TPP51C15</td>
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<td>TPP68C20</td>
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<tr>
<td>T-ROESY</td>
<td>Transverse Rotating-Frame Overhauser Enhancement Spectroscopy</td>
</tr>
<tr>
<td>TsCl</td>
<td>4-Toluenesulfonyl Chloride</td>
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Note: When a standard chemical formula (i.e., one containing symbols only representing chemical elements and not functional group abbreviations) is used to describe a compound in this Thesis, the formula is not reproduced in the table above.
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The research reported in this Thesis not only spans just over four and a half years, but also two continents. This journey began at the University of Birmingham in the UK, and now draws to a close some 5000 or so miles distant, at the University of California, Los Angeles. Therefore, not only has working in Fraser’s group been a thoroughly enjoyable experience, but it has given me the opportunity to see much more of the world than I ever thought I would! I feel very privileged to have been a part of the Stoddart group, and to have known some of the people who have shared the experience with me. Therefore, whereas the words and pictures on the pages of this Thesis tell the story of the science that has interested, intrigued, frustrated, and occasionally amused me over the past few years, this small—but significant—section features the people who have made it all possible.

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VITA

April 12, 1974
Born, Lichfield, England

1995
Frankland Prize for Excellence in Practical Chemistry
University of Birmingham
Edgbaston, Birmingham, England

1996
BSc (Hons) First Class, Chemistry & Bioorganic Chemistry
University of Birmingham
Edgbaston, Birmingham, England

1997
MPhil (Sci), Chemistry
University of Birmingham
Edgbaston, Birmingham, England

1999
Cram Research Award
University of California, Los Angeles
Los Angeles, California, USA

2000
Winstein Dissertation Award
University of California, Los Angeles
Los Angeles, California, USA

PUBLICATIONS AND PRESENTATIONS


**Cantrill, S. J.**, “Ammonia”, In *World of Chemistry*; Young, R. V.; Sessine, S., Eds.; Gale Group, 1999; pp. 44.


ABSTRACT OF THE DISSERTATION

Some Adventures in
Secondary Ammonium Ion
Binding

by

Stuart James Cantrill
Doctor of Philosophy in Chemistry
University of California, Los Angeles, 2001
Professor J Fraser Stoddart, Chair

A range of secondary ammonium (R₂NH₂⁺) ions have been shown to thread through the cavities of appropriately-sized crown ethers to afford interwoven complexes. X-Ray crystallographic investigations to probe the solid-state properties of these supermolecules have revealed (Chapter 1) that many subtle factors—e.g., solvents of crystallization, crown ether conformations and anion interactions—can influence the nature of the overall three-dimensional superstructures. Furthermore, a comparison of differently-substituted crown ethers—possessing either [24]crown-8 or [25]crown-8 constitutions—has revealed (Chapter 2) that relatively small mutations in the structure of the macrocyclic polyether
can have profound consequences upon its ability to bind R₂NH₂⁺ ions. Substitution of
the [24]crown-8 framework with increasing numbers of benzo rings is observed to lower
the stability constants (Kₐ’s) from >10³ to ~0 M⁻¹ in acetonitrile, and a pronounced
decrease in Kₐ values also occurs when the [24]crown-8 constitution is expanded to give a
macroring containing 25 atoms. Building upon the results obtained for these simple
binary systems, self-complementary daisy chain monomers—in which a secondary
ammonium ion-containing arm is grafted onto a macrocycle with either a [24]- or
[25]crown-8 constitution—were synthesized, and shown (Chapter 3) to form small
aggregates in the ‘gas’, solution, and solid phases. Finally, both kinetic and
thermodynamic approaches have been employed (Chapter 4) in the synthesis of
rotaxanes based upon the secondary ammonium ion/crown ether recognition site. The
reaction between amino and isocyanate groups has been exploited for the
synthesis—under kinetic control—of both DB24C8- and BMP25C8-containing ureido-
[2]rotaxanes, the latter of which represents the first example of an interlocked structure
incorporating this particular crown ether. Conversely, a thermodynamically-control
synthesis is achieved when DB24C8 is added to a solution containing a diimine dumbbell-
like component, wherein the dynamic nature of the system (i.e., imine
hydrolysis/reformation) offers the ring component access to the NH₂⁺ center, allowing
the self-assembly of the corresponding ‘dynamic’ [2]rotaxane to occur. Furthermore, the
'fixing' of this [2]rotaxane can be achieved upon reduction of the imine bonds, affording a