

*Writing and Revising*  
*the Disciplines*

*Edited by*

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# Writing (and Drawing) Chemistry

ROALD HOFFMANN (Chemistry)

IN the chemical profession our stock in trade is not the book, but the scientific (chemical) article, published in a periodical. I have written 450 of them in my years at Cornell University; my colleague Harold Scheraga has published over 1000. We have promoted an assistant professor to tenure at Cornell with 11 published papers, and we have not promoted one with over 80.

## THE NATURE OF THE BEAST

It is instructive to see the article untamed, roaming its range. For this I would like to begin with some pages from the chemical journal that is arguably the world's best (at least in inorganic and organic chemistry, not in physical chemistry or biochemistry); publication venues and their prestige carry much baggage of history and fashion. The journal is not an American one. It is *Angewandte Chemie*, published out of Germany, it appears simultaneously in German and English editions. Despite its name, the journal contains precious little applied chemistry.

*Angewandte Chemie*, under the inspired and proactive leadership of its editor, Peter Götz, has cultivated an effective mix of largely solicited review or feature articles, short highlights, and many "Communications." These are brief accounts of novel chemistry, presumably worthy of urgent publication. And publication, following review by one to three anonymous (to the author) referees, is certainly rapid. Several Communications in the Nov. 2, 1998 issue of the journal carry June submission dates; the latest is dated July 1, 1998. For my friends in the humanities (I'm there

too; I have been waiting over two years for a paper to appear in the *Canadian Review of Comparative Literature*, all I can say is "It can be done."

Let us leaf (see figures 1–5) through some pages in the Nov. 2, 1998 issue of *Angewandte Chemie* which arrived in my mailbox the week of November 9. (The original lecture on which this text is based was presented on Nov. 16, 1998.)

From these five sequential pages, as well as perusal of a greater sample, one notes:

(1) The authorship is international.

(2) There are many authors per paper; one of the differences between the sciences and the humanities and arts (theater and film are exceptions), is that the sciences have mastered the ethics of collaboration.

(3) The usual scholarly apparatus is there: author affiliations, end-notes (often numerous), acknowledgments of granting agencies and individual assistance or discussion.

(4) An unusual feature, particular to *Angewandte Chemie*, is the mandatory inclusion at the end of any experimental paper of an experimental section, detailing procedures for at least part of the experiments carried out.

(5) Most striking is the remarkable density of graphic material, most of it quasi-iconic representations of microscopic molecular structure. It is this feature of chemistry—the high graphical content of the literature and the science—which led me to include the parenthetical clause in my title (see Hoffmann and Laszlo, 1991). I will return to it, for now I hope I have convinced you that it is not my stylistic prejudice when I say that it is impossible to write chemistry without drawing molecules.

I also note that while there are some graphs and plots of observables, these are relatively few. And still fewer equations. This is not physics.

Is what these figures present typical? Yes, it certainly is so, of the literature of organic, inorganic, and biological chemistry. Physical chemistry is quite different, for its literature (viewed phenomenologically) carries more equations, and fewer depictions of molecules.

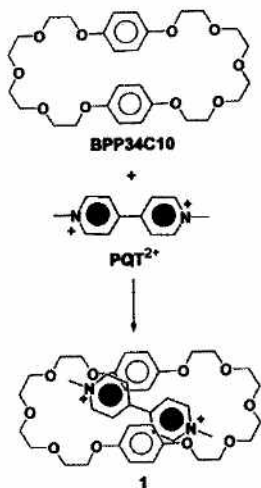
#### CALIXARENES

Let us now zoom in on one article, and read it together. I do this for the ostensible reason of analyzing this contemporary text as a text. But I must also 'fess up; I do it because I will not pass up the chance of teaching any audience, including the audience of the present volume, some chemistry.

# A New Motif for the Self-Assembly of [2]Pseudorotaxanes; 1,2-Bis(pyridinium)ethane Axles and [24]Crown-8 Ether Wheels\*\*

Stephen J. Loeb\* and James A. Wisner

The threading of the paraquat dication  $\text{PQT}^{2+}$  through the cavity of bis(paraphenylene)[34]crown-10 (BPP34C10) to form the [2]pseudorotaxane [(BPP34C10)(PQT)] $^{2+}$  (**1**) was the genesis of a diverse range of molecules that contain mechanical linkages (rotaxanes, catenanes, molecular shuttles, and switches) derived from this basic interaction, and stands as a landmark discovery in the area of supramolecular chemistry (Scheme 1).<sup>[1]</sup> Many examples of rotaxanes have

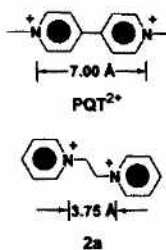


Scheme 1. Formation of the [2]pseudorotaxane **1** by insertion of the linear dicationic axle  $\text{PQT}^{2+}$  through the cavity of the neutral crown ether wheel BPP34C10.

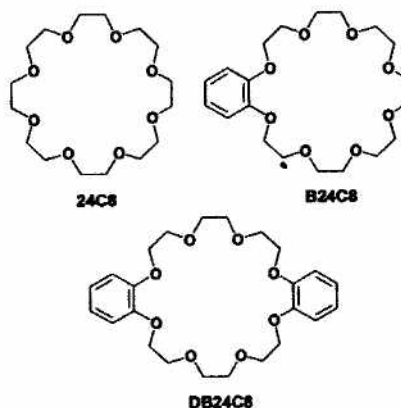
now been reported involving  $\pi$  stacking between electron-rich and electron-poor aromatic rings,<sup>[2]</sup> hydrogen bonding between secondary dialkylammonium ions and crown ethers<sup>[3]</sup> or between amides and large ring lactams,<sup>[4]</sup> hydrophobic interactions within the cavity of a cyclodextrin,<sup>[5,6]</sup> and metal-ligand interactions between transition metal ions and cyclic ligands.<sup>[7-9]</sup> In many of these systems the ion-dipole interaction between positively charged atoms of one component and the Lewis basic atoms of the other component makes a significant contribution to the binding. Although these electrostatic interactions are not directional and predictable in the same manner as hydrogen bonds or metal-ligand

bonds, they are nonetheless extremely important. For example, the  $\text{PQT}^{2+}$  ion in **1** is tilted away from perpendicular by  $62^\circ$  so as to maximize the  $\text{N}^+ \cdots \text{O}$  interactions and also form weak  $\text{CH} \cdots \text{O}$  hydrogen bonds along with the major  $\pi$ -stacking components.<sup>[1]</sup>

Herein, we present a new motif for the design of [2]pseudorotaxanes based on the simple concept of optimizing  $\text{N}^+ \cdots \text{O}$  interactions between pyridinium ions and simple crown ethers.<sup>[10]</sup> The  $\text{N}^+ - \text{N}^+$  distance in  $\text{PQT}^{2+}$  is about 7.00 Å while in the isomeric 1,2-bis(pyridinium)ethane dication **2a** it is only about 3.75 Å (Scheme 2). Although Stoddart et al. have reported that the interaction between dibenzylparaquat and DB24C8 is negligible,<sup>[11,12]</sup> an examination of CPK and computer models suggested a good match between **2a** (the "axle") and the 24-membered crown ethers (wheels) 24C8, B24C8, and DB24C8 (Scheme 3) that should



Scheme 2. Comparison of the intramolecular  $\text{N}^+ - \text{N}^+$  distances in the isomeric pyridinium ions  $\text{PQT}^{2+}$  and [pyCH<sub>2</sub>CH<sub>2</sub>py] $^{2+}$  (**2a**).



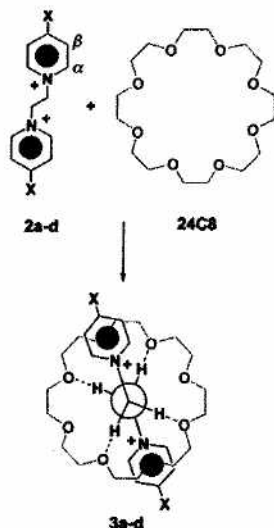
Scheme 3. Formation of [2]pseudorotaxanes from 24C8, B24C8, and DB24C8.

optimize the  $\text{N}^+ \cdots \text{O}$  interactions. Scheme 4 shows how two sets of  $\text{N}^+ \cdots \text{O}$  interactions might be accompanied by a series of four  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds that are formed with alternate oxygen atoms in the crown ether. The question remains as to whether these interactions are sufficient to produce a stable [2]pseudorotaxane in the absence of the  $\pi$ -stacking interactions found in **1** and related molecules.

The addition of one equivalent of 24C8 to a solution of one equivalent of **2a**(BF<sub>4</sub>)<sub>2</sub> in MeCN gave the [2]pseudorotaxane **5a**. An association constant  $K_a$  of  $165 \text{ M}^{-1}$  was measured for this interaction by <sup>1</sup>H NMR titration in MeCN at 298 K. By variation of the substituent X on the pyridinium ring other axes can be incorporated and a more detailed understanding of the overall interaction can be obtained. The strength of the interaction can be controlled by varying X as shown in Table 1. In particular, the introduction of the electron-with-

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Scheme 4. Newman projection along the C–C vector of the N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup> portion of the dication [XpyCH<sub>2</sub>CH<sub>2</sub>pyX]<sup>2+</sup>, 2a–d, (X = H, Me, Ph, CO<sub>2</sub>Et). This combination of N<sup>+</sup>...O ion–dipole interactions and C–H...O hydrogen bonds might stabilize the formation of [2]pseudorotaxanes with 24C8.

drawing group CO<sub>2</sub>Et results in the largest association constant for each of the three crown ethers.

Incorporation of aromatic groups into the crown ether provides the possibility of  $\pi$  stacking between the pyridinium rings and the catechol rings of the crown ether. In the <sup>1</sup>H NMR spectra of the two pseudorotaxanes derived from 2a (X = CO<sub>2</sub>Et) with B24C8 (4d) and DB24C8 (5d)  $\pi$  stacking in solution is clearly evident: the signals for the  $\beta$  protons of the pyridine group shift upfield ( $\delta$  = 8.56, 8.36, and 8.14 for the pseudorotaxanes with 24C8, B24C8, and DB24C8, respectively). This trend is mirrored by a uniform increase in  $K_a$  from 320 to 740 to 1200 M<sup>-1</sup> and an increase in the intensity of a charge transfer absorption band at about 370 nm (Figure 1).

In addition, 3d–5d show significant downfield shifts ( $\delta$  =

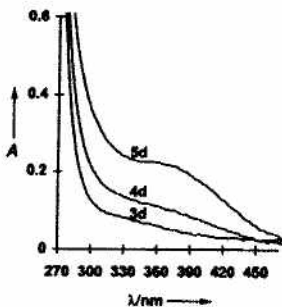


Figure 1. UV absorption spectra of 3d, 4d, and 5d. The intensity of the charge-transfer band in the region 270–470 nm increases with increased capacity for  $\pi$ -stacking interactions.

0.20–0.31) for the  $\alpha$  and NCH<sub>2</sub> protons, which is indicative of the formation of C–H...O hydrogen bonds to the oxygen atoms of the crown ether.

These results and the threading conformation proposed in Scheme 4 are supported by the solid-state structure of [(EtO<sub>2</sub>CpyCH<sub>2</sub>CH<sub>2</sub>pyCO<sub>2</sub>Et)(DB24C8)]<sup>2+</sup> (5d; py = C<sub>2</sub>H<sub>4</sub>N<sup>+</sup>).<sup>[1]</sup> Figures 2 and 3 show different views of the threading of the dicationic axle through the cavity of the DB24C8 macrocycle. The [2]pseudorotaxane is stabilized by 1) eight N<sup>+</sup>...O interactions (N–O 3.76–4.88 Å), 2) eight C–H...O hydrogen bonds (the four predicted ones between the bridging ethane unit and alternate ether oxygen atoms as well as four others between  $\alpha$ -pyridinium hydrogen atoms and symmetry related O5 atoms

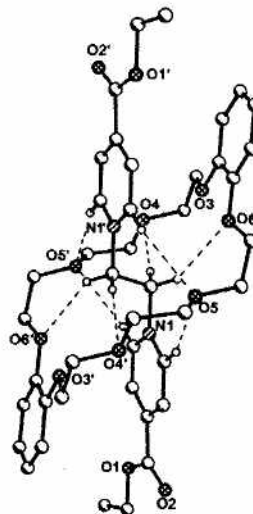


Figure 2. A ball-and-stick representation of the crystal structure of 5d, formed from [EtO<sub>2</sub>CpyCH<sub>2</sub>CH<sub>2</sub>pyCO<sub>2</sub>Et]<sup>2+</sup> (2d) and DB24C8.

Figure 3. A ball-and-stick representation of the crystal structure of 5d, shown along the C9–C9' bond. This view corresponds to the Newman projection shown schematically in Scheme 4. N<sup>+</sup>...O distances: N1<sup>+</sup>–O3 4.88, N1<sup>+</sup>–O4 4.43, N1<sup>+</sup>–O5 3.76, N1<sup>+</sup>–O6 4.66 Å. C–H...O hydrogen bonds (lengths [Å] and angles [°]): H9A–O4' 2.54, H9B–O6' 2.66, H6A–O5 2.36, H7A–O5' 2.54; C9–H9A–O4' 165.0, C7–H7A–O5' 141.0, C6–H6A–O5 154.2, C9–H9B–O6' 150.0.

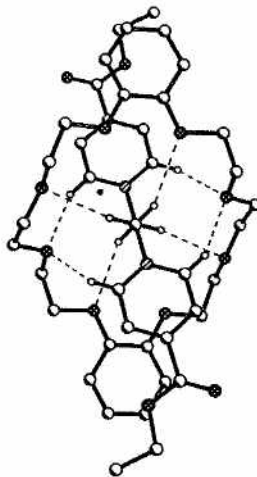


Table 1. Association constants ( $K_a$ ) and free energies of complexation ( $\Delta G$ ) for 3a–d, 4a–d, and 5a–d formed from [X-pyCH<sub>2</sub>CH<sub>2</sub>py-X]<sup>2+</sup>, 2a–d, and 24C8, B24C8, or DB24C8 in MeCN at 298 K.<sup>[a]</sup>

X	24C8		B24C8		DB24C8	
	$K_a$ [M <sup>-1</sup> ]	$-\Delta G$ [kJ mol <sup>-1</sup> ]	$K_a$ [M <sup>-1</sup> ]	$-\Delta G$ [kJ mol <sup>-1</sup> ]	$K_a$ [M <sup>-1</sup> ]	$-\Delta G$ [kJ mol <sup>-1</sup> ]
H (a)	165	12.7	195	13.1	180	12.9
Me (b)	105	11.6	205	13.2	230	13.5
Ph <sup>[b]</sup> (c)	160	12.6	300	14.2	320	14.3
CO <sub>2</sub> E <sup>[a]</sup> (d)	320	14.3	740	16.4	1200	17.6

[a] Sample concentrations  $2.0 \times 10^{-3}$ – $5.0 \times 10^{-3}$  M. [b] Chemical exchange was slow on the NMR time scale and peaks were observed for both complexed and uncomplexed species.  $K_a$  was determined by integration from a 1:1 mixture. All other  $K_a$  values were determined by NMR titration experiments by using the program EQNMR.<sup>[10]</sup> Estimated errors: < 10% for  $K_a > 100$ .

FIGURE 2

(C–O 2.36–2.66 Å), and 3)  $\pi$ -stacking interactions between the electron-rich catechol rings of the crown ether and the electron-poor aromatic rings and ester group of the pyridinium salt.

The new binding motif for the formation of [2]pseudorotaxanes presented herein demonstrates for the first time that simple crown ethers can be used to form [2]pseudorotaxanes. The ability to easily tune the interaction strength and the availability of these simple components bodes well for the extension of this motif to more complex supramolecular systems with interlocked [n]rotaxanes and [n]catenanes.

### Experimental Section

All pyridinium bromide salts were prepared by the literature method.<sup>[14]</sup> The BF<sub>4</sub><sup>-</sup> salts were precipitated from water by the addition of NaBF<sub>4</sub> or NH<sub>4</sub>BF<sub>4</sub> and recrystallized before use. DB24C8 was purchased from Aldrich and used as received. B24C8 and 24C8 were prepared by literature methods.<sup>[15]</sup> In a typical experiment, [2]pseudorotaxanes were formed in solution by mixing equimolar solutions of 2a(BF<sub>4</sub>)<sub>2</sub>–d(BF<sub>4</sub>)<sub>2</sub> and crown ether in MeCN. Typical data for [2]pseudorotaxanes in which X = CO<sub>2</sub>Et: 3d: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 9.27 (d, 4H, J = 5.3 Hz;  $\alpha$ -pyH), 8.56 (d, 4H, J = 5.3 Hz;  $\beta$ -pyH), 5.40 (s, 4H; NCH<sub>2</sub>), 4.50 (q, 4H, J = 7.1 Hz; C(O)OCH<sub>2</sub>), 3.50 (s, 32H; OCH<sub>2</sub>), 1.44 (t, 6H, J = 7.1 Hz; CH<sub>3</sub>); ES-MS *m/z* (%): 770 (5) [M – BF<sub>4</sub>]<sup>+</sup>, 341 (100) [M – 2BF<sub>4</sub>]<sup>2+</sup>. 4d: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 9.24 (d, 4H, J = 6.4 Hz;  $\alpha$ -pyH), 8.36 (d, 4H, J = 6.4 Hz;  $\beta$ -pyH), 6.80 (m, 4H; Ar), 5.46 (s, 4H; NCH<sub>2</sub>), 4.47 (q, 4H, J = 7.1 Hz; C(O)OCH<sub>2</sub>), 4.02 (m, 4H; ArOCH<sub>2</sub>), 3.94 (m, 4H; OCH<sub>2</sub>), 4.83 (m, 8H; OCH<sub>2</sub>), 3.63 (m, 4H; OCH<sub>2</sub>), 3.43 (m, 4H; OCH<sub>2</sub>), 3.18 (m, 4H; OCH<sub>2</sub>), 1.44 (t, 6H, J = 7.1 Hz; CH<sub>3</sub>); ES-MS *m/z* (%): 818 (7) [M – BF<sub>4</sub>]<sup>+</sup>, 365 (100) [M – 2BF<sub>4</sub>]<sup>2+</sup>. 5d: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  = 9.24 (d, 4H, J = 6.7 Hz;  $\alpha$ -pyH), 8.14 (d, 4H, J = 6.7 Hz;  $\beta$ -pyH), 6.74 (m, 8H; Ar), 5.58 (s, 4H; NCH<sub>2</sub>), 4.40 (q, 4H, J = 7.1 Hz; C(O)OCH<sub>2</sub>), 4.00 (m, 24H; OCH<sub>2</sub>), 1.44 (t, 6H, J = 7.1 Hz; CH<sub>3</sub>); ES-MS *m/z* (%): 865 (12) [M – BF<sub>4</sub>]<sup>+</sup>, 389 (100) [M – 2BF<sub>4</sub>]<sup>2+</sup>.

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## [Te<sub>3</sub>N<sub>6</sub>(TeCl<sub>4</sub>)<sub>4</sub>]-Tellurium Nitride Stabilized by Tellurium Tetrachloride

Werner Massa, Carsten Lau, Michael Möhlen, Bernhard Neumüller, and Kurt Dehnicke\*

Exactly 100 years ago tellurium nitride was first obtained by the reaction of tellurium tetrabromide with liquid ammonia.<sup>[1]</sup> The composition TeN was ascribed to this yellow, extremely poorly soluble, and highly explosive substance. Considering the analogy to the crystallographically well characterized homologues S<sub>4</sub>N<sub>4</sub><sup>[2]</sup> and Se<sub>4</sub>N<sub>4</sub>,<sup>[3]</sup> this assignment has not been entirely ruled out to this day.<sup>[4]</sup> However, later analytical work made the composition Te<sub>3</sub>N<sub>4</sub> with tetravalent tellurium probable.<sup>[5–7]</sup> The tellurium compounds with nitride functionalities which were characterized in recent years also derive from tellurium(+IV). Among these are the complexes of type 1 with X = Cl<sup>[8]</sup> and F,<sup>[9]</sup> which correspond to the structure motif A with pyramidal nitride functionality, and the nitride

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