Chapter I

Pseudorotaxanes and Rotaxanes

1.1. INTRODUCTION

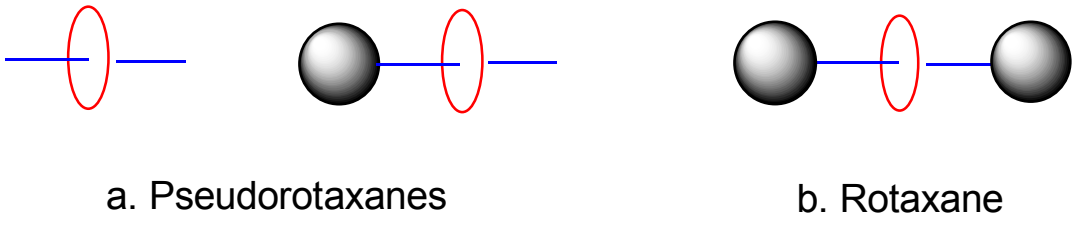
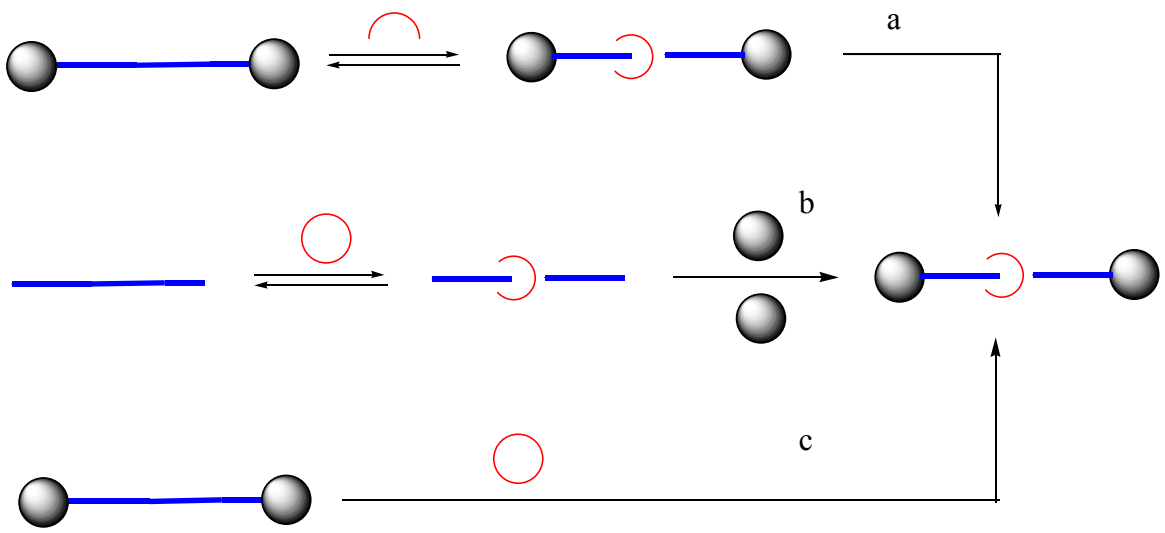


Figure 1. Pseudorotaxanes and rotaxane.

"Rotaxane" is derived from the Latin words for "wheel" and "axle", and describes a compound that consists of a linear species (sometimes called rodlike part or guest) and cyclic species (sometimes called beadlike part or host) bound together in a threaded structure by non-covalent forces. "Pseudo" means false, so "pseudorotaxane" means false rotaxane. A rotaxane and two kinds of pseudorotaxanes[1] are shown schematically in Figure 1. The black balls here represent stoppers. They are bulky groups and can prevent the dethreading of the cyclic component. Furthermore, sometimes a pseudorotaxane with only one stopper is called semirotaxane. At least three different mechanisms (Scheme 1)

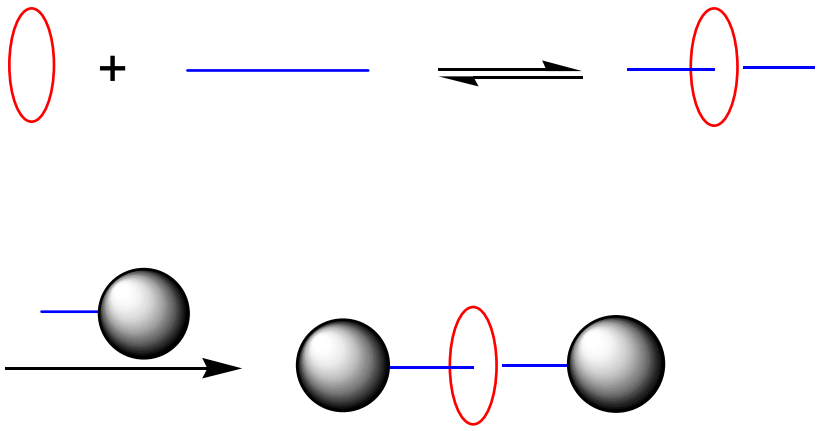
for the constructuion of rotaxanes can be identified.[2] Pseudorotaxanes and rotaxanes can be classified according to different standards. Based on the difference in construction mechanism, pseudorotaxanes and rotaxanes can be divided into clipping, threading, slipping, and other types. According to the difference in the main driving forces for the threading, pseudorotaxanes and rotaxanes can be divided into seven types: statistical threading, chemical conversion, hydrogen bonding, hydrophilic-hydrophobic interaction, metal-ligand complexation, π-π stacking and charge transfer, and others. Here we will use the second standard and discuss the seven kinds of pseudorotaxanes and rotaxanes separately. In this way we will have a clear picture about how these molecular interactions work in the construction of the four supramolecular materials and we will know how we can combine different interactions together in order to increase the association constant, a very important parameter, which we will discuss later.



Scheme 1. Three different approaches to the construction of rotaxanes: (a) "clipping"; (b)"threading"; (c)"slipping".

1.2. STATISTICAL THREADING ROUTES TO PSEUDOROTAXANES AND ROTAXANES

Statistical threading method (Scheme 2) was originally introduced by Harrision and Harrison in 1967.[3] The formation of pseudorotaxanes and rotaxanes by this method is based on a purely statistical progress without any apparent attractive force between the linear species and the cyclic molecules.

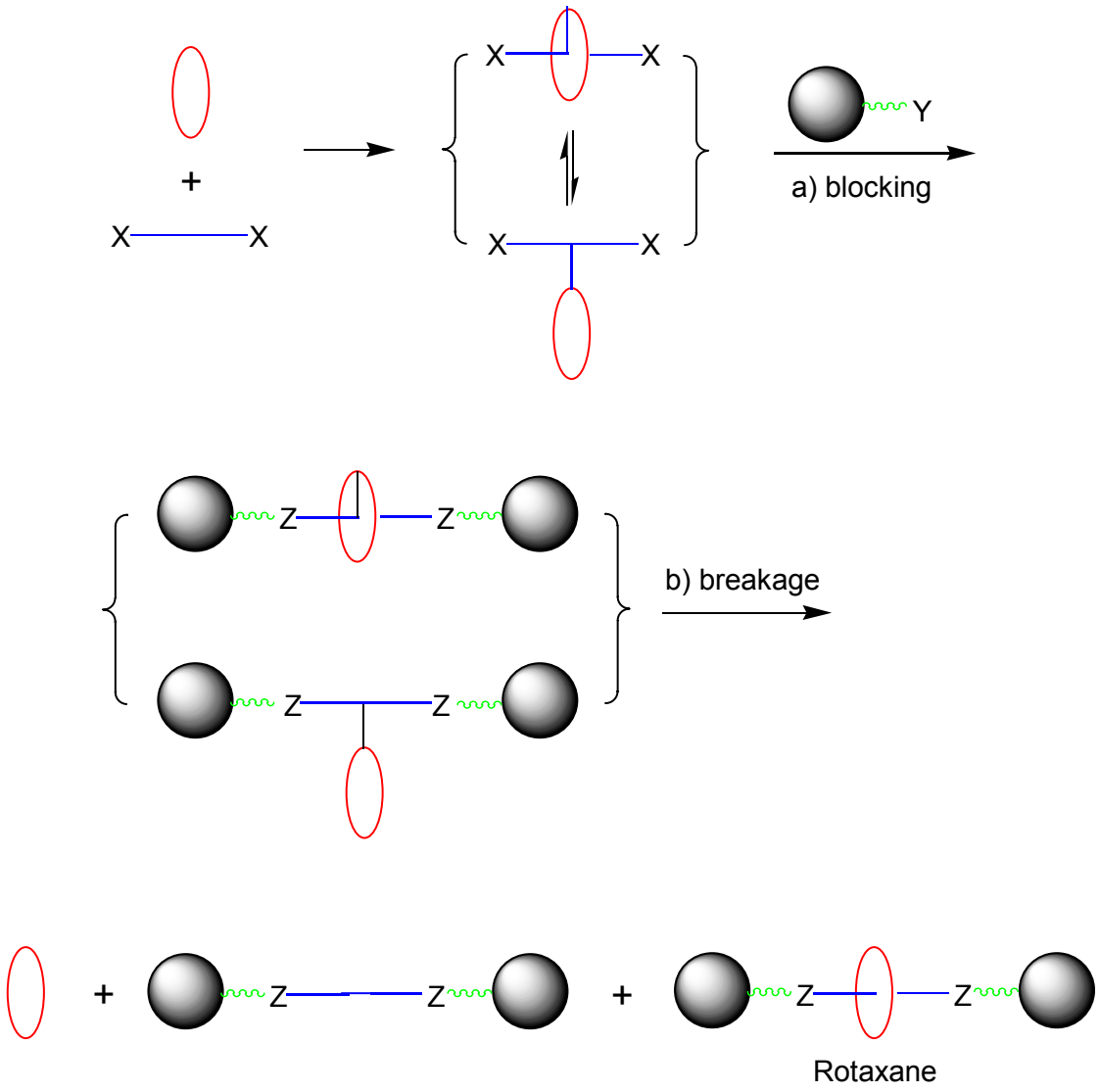


Scheme 2. Formation of a pseudorotaxane and rotaxane by statistical threading.

Compared with other methods, the statistical threading method is not very effective in the preparation of rotaxanes because ΔH is nearly zero or so and ΔS is almost always negative toward threading. Statistical threading methods have rarely been employed in the synthesis of pseudorotaxanes and rotaxanes in recent years, but it still can be used in conjugation with other synthetic methods.[4]

1.3. CHEMICAL CONVERSION ROUTES TO PSEUDOROTAXANES AND ROTAXANES

This method was introduced by Schill et al. in 1960's.[5] It is shown in Scheme 3. This method involves a lot of steps and therefore is time-consuming and not effective in terms of overall yield, so it has not been widely used in the recent years.



Scheme 3. Syntheses of rotaxanes by chemical conversion routes.

1.4. HYDROGEN BONDING ROUTES TO PSEUDOROTAXANES AND ROTAXANES

Some atoms with high electronegativity, such as N and O, on cyclic/linear molecules can hydrogen bond with hydrogen atoms of some groups, such as –NH, -OH, and NH_2^+, on linear/cyclic molecules. During the last decade, this interaction has been used widely in the preparation of pseudorotaxanes and rotaxanes.

Stoddart's group got a thermally stable rotaxane **1** with two triphenylphosphonium stoppers at the ends of the linear species by hydrogen bonding of dibenzo-24-crown-8 (DB24C8) and the ammonium ion (Figure 2).[6] This is a novel approach to synthesize rotaxanes that relies upon the supramolecular assistance inherent in the recognition between a secondary dialkylammonium center and the cavity of a crown ether.

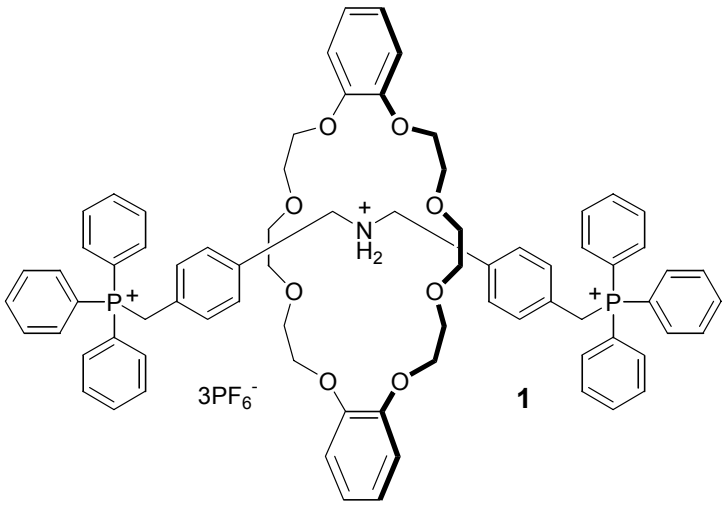


Figure 2. [2]rotaxane based on dibenzo-24-crown-8 and an ammonium salt.

Later they prepared another rotaxane **2** (Figure 3) and found that dipyrido-24-crown-8 (DP24C8) was a more efficient receptor for dialkylammonium cations than DB24C8.[7] The reason is the nitrogen atoms on macrocycle also can form hydrogen bonds with the hydrogen atoms on dialkylammonium cations.

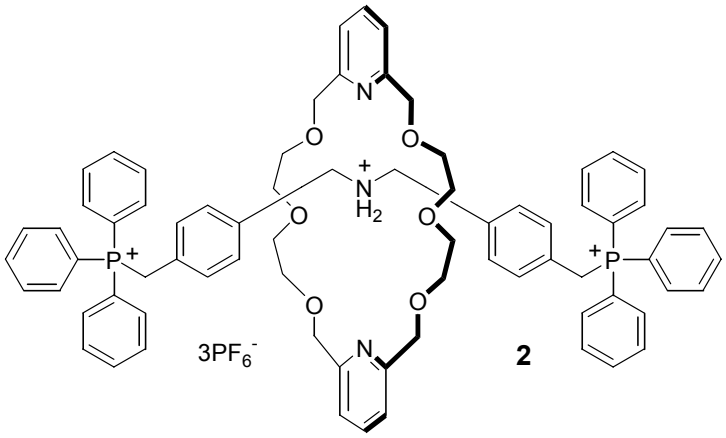


Figure 3. [2]rotaxane based on dipyrido-24-crown-8 and a ammonium salt.

They introduced the concept of fullerenes into the field of pseudorotaxanes and made a fullerene-containing [2]pseudorotaxane[8] (Figure 4). Studies demonstrated that the threading of the fullerene ammonium salt into DB24C8 changes the luminescence properties of the catechol moieties in the crown ether. These properties can be used to monitor the pH-dependent, reversible formation (on/off-switching) of pseudorotaxane-like complex.

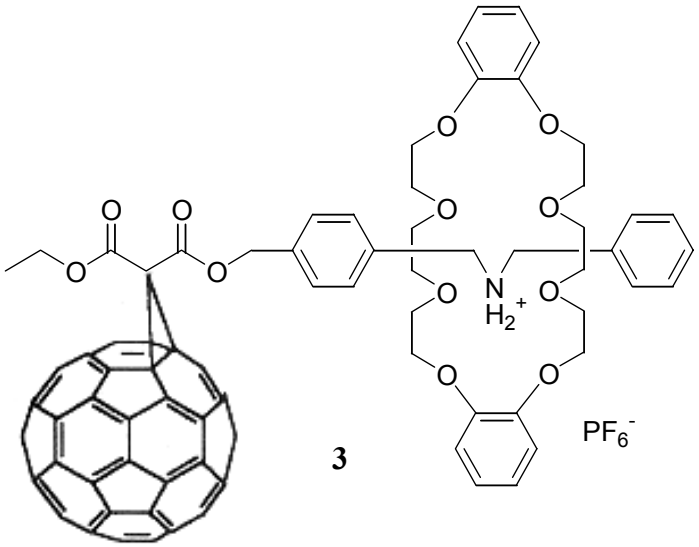


Figure 4. A fullerence-containing [2]pseudorotaxane.

Furthermore Vogtle and coworkers[9] synthesized a rotaxane based on hydrogen bonding between amide groups of cyclic species and an NH group of a linear species.

Leigh et al.[10] successfully prepared a rotaxane by hydrogen bonding between the amide NH on the beadlike part and carbonyl oxygen groups on the rodlike part through a very interesting approach.

Photoinduced shuttling processes in rotaxanes have interested people a lot of because of their potential applications in the construction of future devices.[11] Recently Leigh and coworkers[12] made a rotaxane **4** (Figure 5) for which a photoinduced co-conformational change occurred in nonpolar solvents at room temperature without external assistance. What is more important is that this change took place on a subnanosecond time scale. The

proposed mechanism of the excited-state dynamics of this rotaxane is also shown in Figure 5. Upon the stimulus of light, a considerable amount of charge transfers to the carbonyl oxygen atom near to the anthracene stopper. Therefore it can form much stronger hydrogen bonding with NH group on the linear part. This makes the cyclic component move toward the stopper until the second conformation is formed.

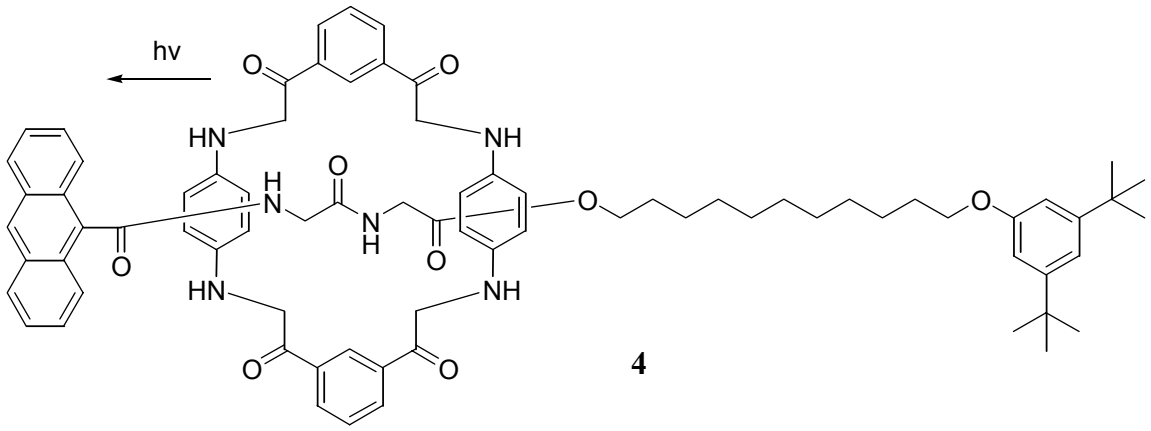


Figure 5. Proposed mechanism for the excited-state dynamics of photoinduced co-conformation changing rotaxane.

Other recently published papers about pseudorotaxanes and rotaxanes driven by hydrogen bonding are summarized in reference 13.

1.5. HYDROPHILIC-HYDROPHOBIC INTERACTION ROUTES TO PSEUDOROTAXANES AND ROTAXANES

Up to now all of hydrophilic-hydrophobic interaction routes to pseudorotaxanes and rotaxanes were based on cyclodextrins (CDs). They can form pseudorotaxanes and rotaxanes with a number of linear species. These pseudorotaxanes and rotaxanes are also called inclusion complexes. The formation of these inclusion complexes is a result of CDs' geometry and functionality. The CDs have cylindrical cavities that posses hydroxyl functionalities on the two rims and hydrocarbon and ether moieties in the interior of the cavity.[1f,14] Therefore CDs have a hydrophobic interior and hydrophilic external faces. The three most commonly used CDs, α-, β-, and γ-CD, are shown in Figure 6. The typical structure of linear species is also shown in Figure 8. Its two ends are hydrophilic but the middle part is hydrophobic. When a guest like this and a CD dissolve in water or a polar solvent, the hydrophobic part of the guest species will insert the inside of CD while the hydrophilic parts will stay outside to produce an inclusion complex.

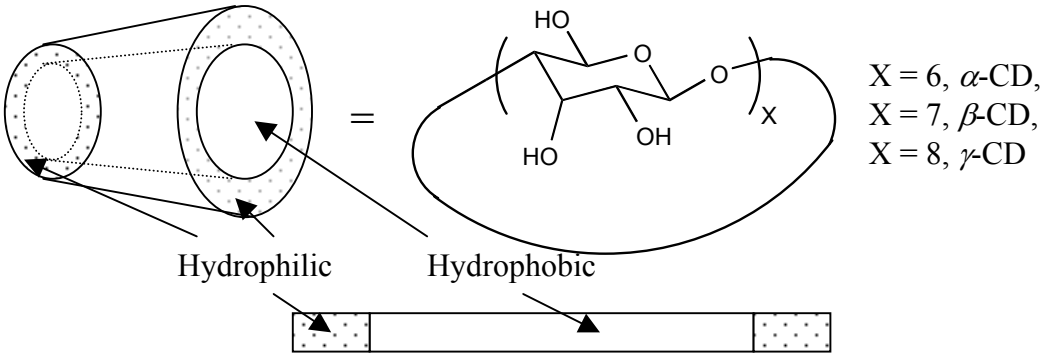


Figure 6. Cyclodextrins and their guest.

The first rotaxane incorporating CD was prepared in 1981 by Ogino.[15] Several years later, the same method was employed by Yamanari et al. to make very similar rotaxanes.[16] Recently, Wenz[17] prepared rotaxanes involving α-CD and α, ω-amino acids that contain long hydrophobic segments.

Except α, ω-amino acids, other compounds that have been used in the construction of rotaxanes incorporating CDs are α,ω-diamine,[15,16] α,ω-diammonium,[18] and N,N'-dialkyl-4,4'-bipridinium derivatives.[19] N,N'-dialkyl-4,4'-bipridinium derivatives were also used to prepare pseudorotaxanes.[20]

It is obvious that this kind of pseudorotaxane and rotaxane only forms in polar solvents.

Other recently published papers about pseudorotaxanes and rotaxanes driven by hydrophilic-hydrophobic interactions are summarized in reference 21.

1.6. METAL-LIGAND COMPLEXATION ROUTES TO PSEUDOROTAXANES AND ROTAXANES

The study of electron transfer between porphyrins or analogues is very important because of its high biological relevance.[22] Sauvage's group[23] synthesized a series of metal-complexed [2]rotaxanes (Figure 7) containing one or two Zn(II) porphyrin-incorporating units (the electron donor) and one Au (III) porphyrin-incorporating unit (the electron acceptor) in order to study the process of electron transfer from the electron donor to the electron acceptor. For rotaxanes[23a,b] of type a in Figure 7, electron transfer may proceed through covalent bonds or through space because the donor and acceptor porphyrins are linked by covalent bonds. However, for rotaxanes[23c-h] of type b and c, electron transfer proceeds through space (mechanical bonds) because the donor and acceptor porphyrins are not linked by covalent bonds.

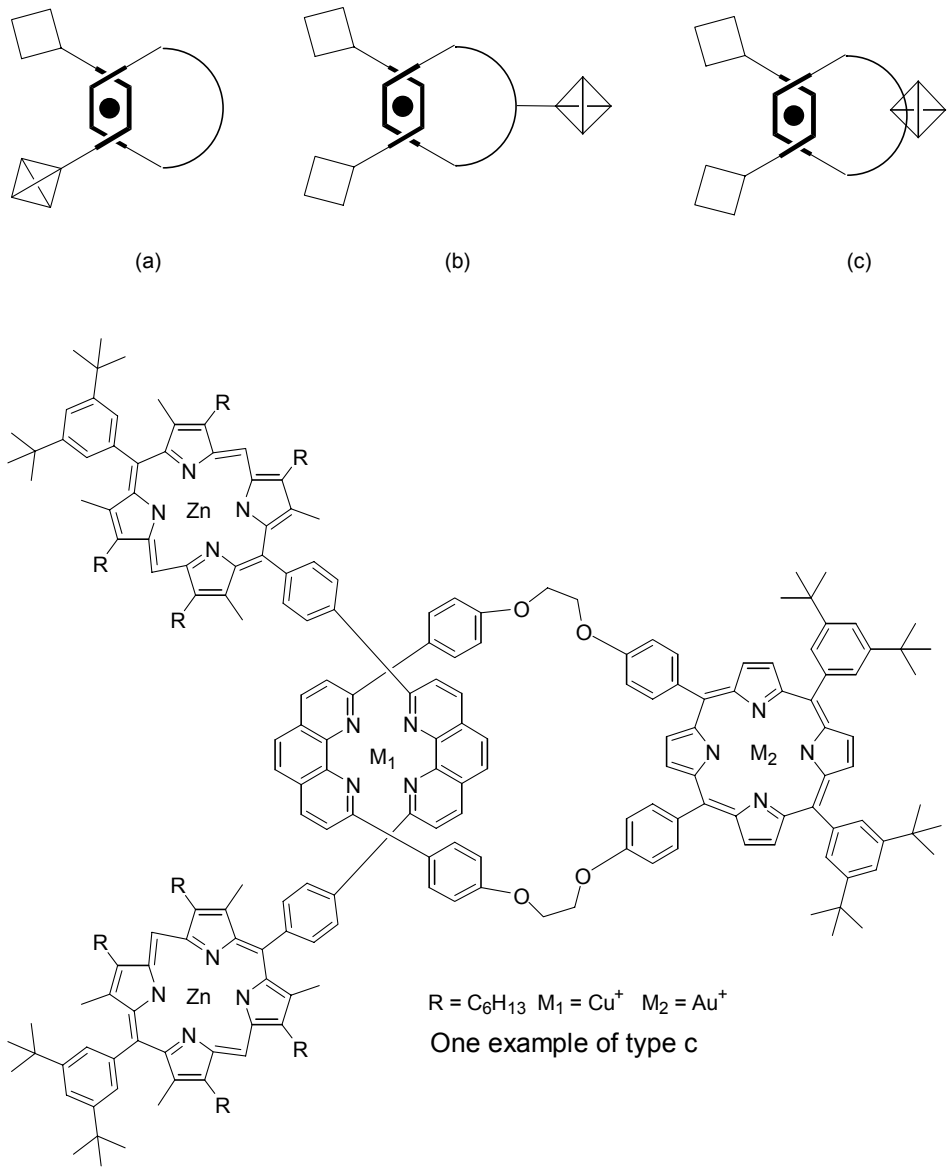


Figure 7.[23h] Some metal-complexed rotaxanes made by Sauvage's group. The thick lines represent chelating fragments, the black disk is a metal cation, the empty diamonds are Zn(II) porphyrins, and the hatched diamonds are Au(III) porphyrins.

A detailed comparison of the properties of the free and the Cu(I)-complexed rotaxanes showed that the role of the Cu complexation is important in different perspectives: (i) it

gives a geometric constraint which keeps the reacting partners at a fixed distance; (ii) it connects from an electronic viewpoint the primary electron donor, one of the two zinc porphyrins, and the electron acceptor, the gold porphyrin; and (iii) it offers an energy transfer pathway by means of its MLCT excited state.[23h]

1.7. π-π STACKING AND CHARGE TRANSFER ROUTES TO PSEUDOROTAXANES AND ROTAXANES

Recently Stoddart's group reported the template-directed synthesis of an amphiphilic [2] rotaxane incorporating a tetrathiofulvalene unit.[24a] This synthesis is shown in Figure 8. Here the dumbbell was used as the template for the formation of interlocked cyclobis(paraquat-*p*-phenylene) tetracation from the dicationic precursor and 1,4-bis(bromomethyl)benzene. Furthermore, they designed a series of similar pseudorotaxanes[24b-f] and rotaxanes[24g] used for molecular machines. These pseudorotaxanes and rotaxanes are made up of a π-electron-rich linear component and a π-electron-deficient macrocycle, cyclobis(paraquat-p-phenylene).

Recently the rotaxane in Figure 8 was used to construct molecular-based electronically switchable tunnel junction devices.[24k]

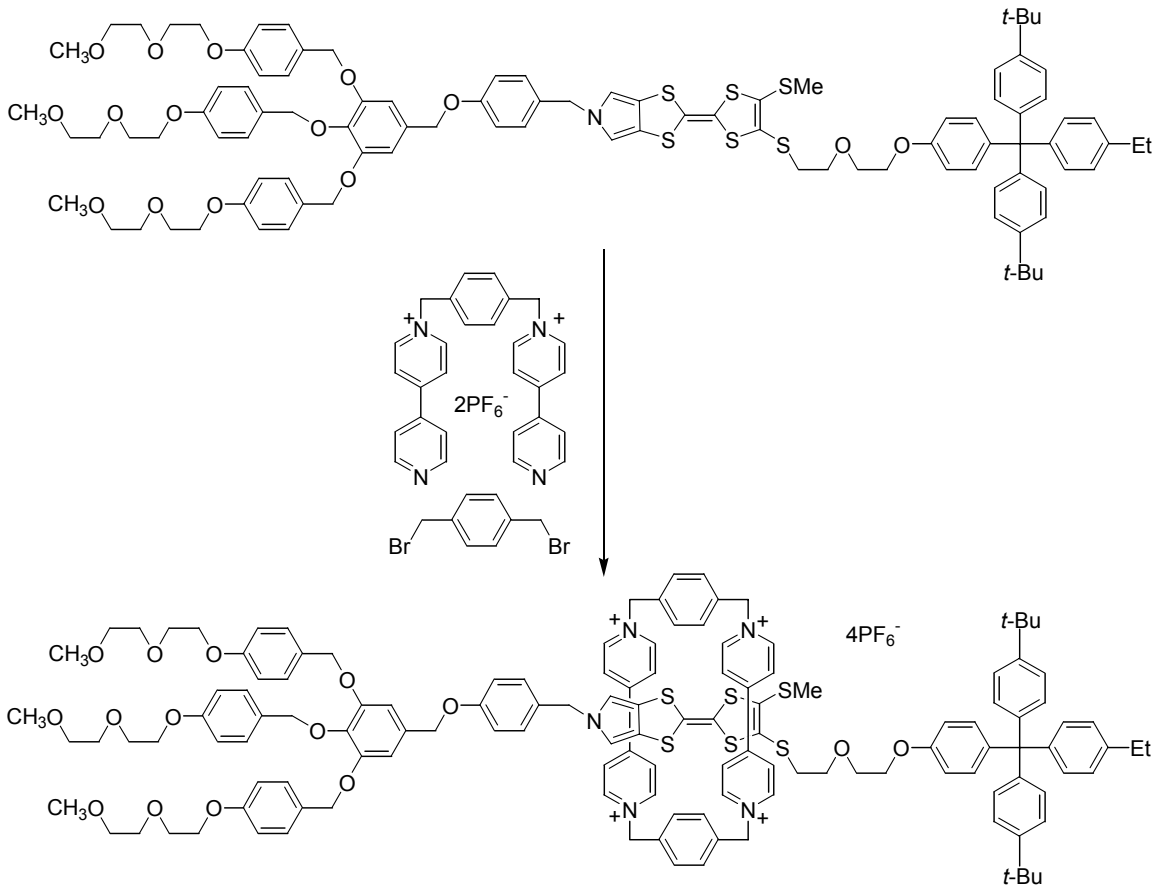


Figure 8. A rotaxane which can be used to construct molecular-based electronically switchable tunnel junction devices.

Another family of pseudorotaxanes[24h] (one of which is shown in Figure 11) and rotaxanes[24i,j] containing a π-electron-deficient linear component and a π-electron-rich macrocycle were also made in this group. All these pseudorotaxanes and rotaxanes are stabilized by a combination of electrostatic and dispersive forces, in particular, (1) charge-transfer, face-to-face, and edge-to-face [C-H···π] interactions and (2) [C-H···O] hydrogen bonds.

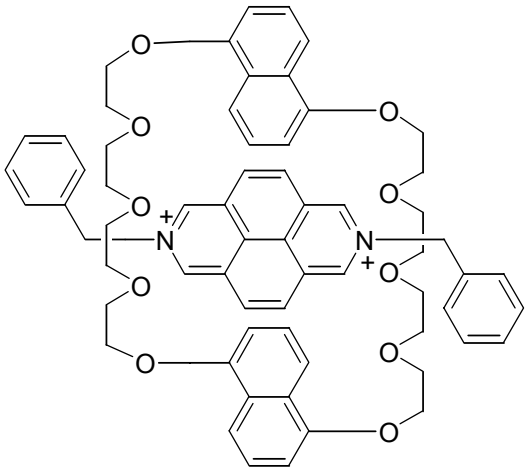


Figure 9. A pseudorotaxane containing a π-electron-deficient linear component and a π-electron-rich macrocycle.

Some other recently published papers about pseudorotaxanes and rotaxanes driven by π-π stacking and charge transfer are summarized in reference 25.

1.8. OTHER PSEUDOROTAXANES AND ROTAXANES

In fact the development of the study of pseudorotoaxanes and rotaxanes has been beyond the limit of their definition, one linear component and one cyclic component. Many recently synthesized pseudorotaxanes and rotaxanes have more than two components. They are named as [n]pseudorotaxanes or [n]rotaxanes (n>2). Here n is the number of linear and cyclic components that make up the pseudorotaxane or rotaxane. Therefore, correspondingly, the pseudorotaxane or rotaxane made up of only one linear species and one cyclic species is called [2] pseudorotaxane or [2]rotaxane.

Stoddart'goup[26a] prepared a [3]pseudorotaxane (Figure 10) containing two DB24C8 macrocycles and one linear scaffold. Its X-ray crystal structure (Figure 10) reveals that intercomponent bonding is via a combination of N^+-H···O and C-H···O hydrogen bonds as well as π-π stacking between one of the catechol rings of each of the DB24C8 units and the central portion of the anthracene unit of the dication linear scaffold. No interactions involving the terminal phenyl rings can be found. Another [3]pseudorotaxane[26b] with similar structure was also prepared by this group. The main driving force for the formation of this rotaxane is also hydrogen bonding. However, when Sauvage's group[26c] synthesize a dicopper[I]-complexed [3]rotaxane with similar structure by a transition-metal-templated strategy involving a bis-chelating molecular thread, the main driving force was metal-ligand complexation.

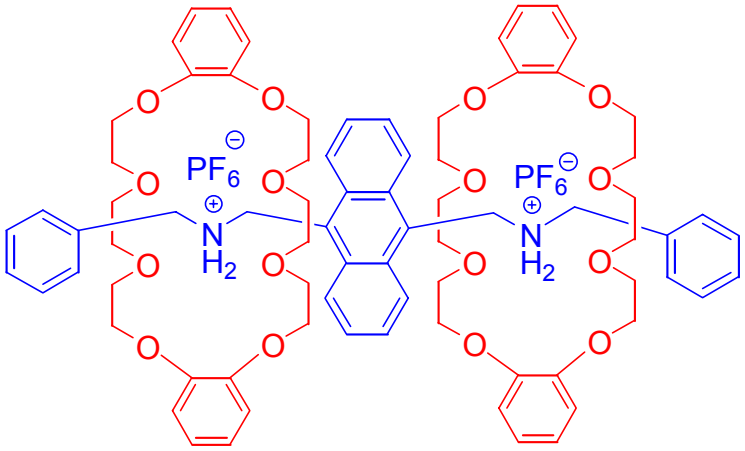


Figure 10. A [3]pseudorotaxane containing two dibenzo-24-crown-8 macrocycles and one linear scaffold.

The inclusion of two or more guest molecules in a molecular host is attractive because it provides unique opportunities to study new forms of stereoisomerism[27], bimolecular reactions[28], and molecular recognition[29] in microenvironments.[30] Kim and coworkers[30] made some [3] pseudorotaxanes (Figure 9). Two different guests were threaded into the cavity of cucurbit[8]uril under the driving force of electron transfer interaction between the two guests and hydrogen bonding interaction between guests and the host (Figure 11). These [3]pseudorotaxanes are very stable, which allowed them to be isolated and characterized by X-ray crystallography.

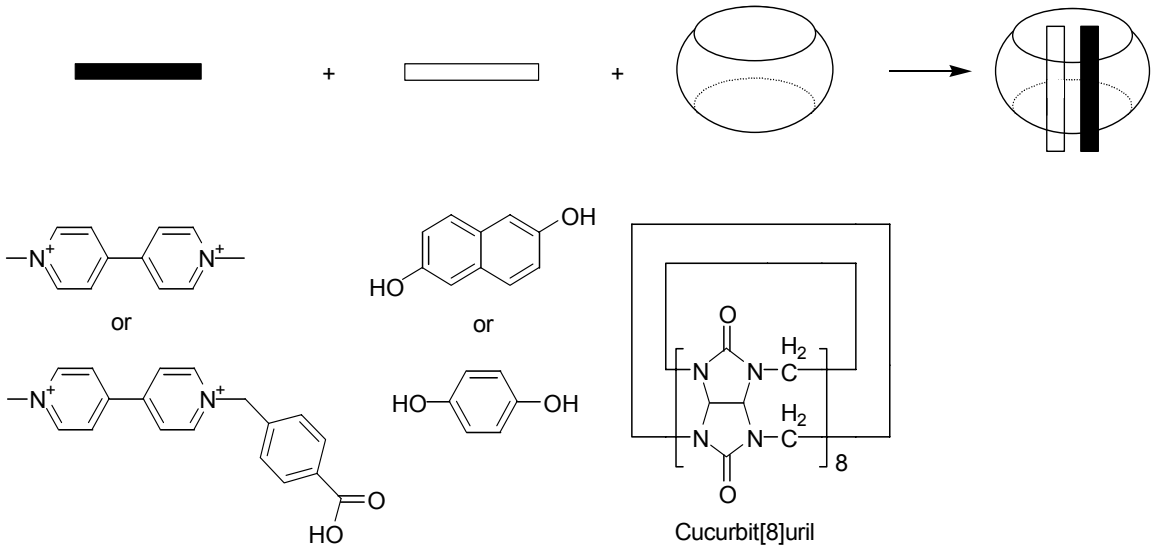
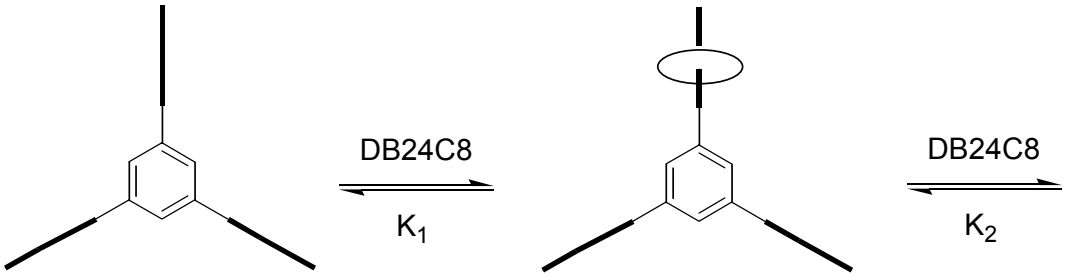


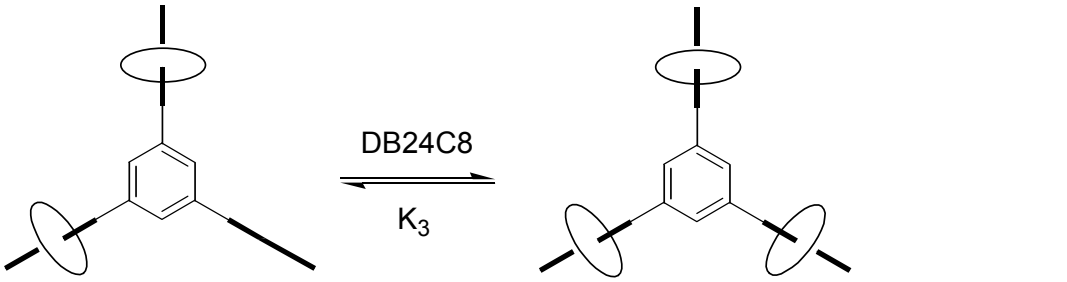
Figure 11. Threading of a hetero-guest pair into the cavity of cucurbit[8]uril.

Recently, Gibson's group[31] studied the equilibrium formation of [2]-, [3]- and [4]-pseudorotaxanes (Figure 12) from a homotritopic guest molecule and a complementary macrocycle host. When the macrocycle host was DB24C8, [2]-, [3]- and [4]-

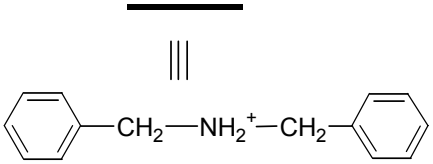
pseudorotaxanes A were obtained.[31a] They found that the three ammonium sites of the homotritopic guest acted independently in complexation with DB24C8 in CD_3COCD_3. Therefore the three individual association constants for the three pseudorotaxanes followed the expected statitistical ratios, that is, $K_1:K_2:K_3 = 9:3:1$. When the macrocyclic host was changed to crown-functionalized dendron, [2]-, [3]- and [4]-pseudorotaxanes B (Figure 12) were obtained.[31b] However, this time they found the three ammonium sites acted not independently but cooperatively in CD_3COCD_3. The three individual association constants exceeded the expected statistical ratios because of the thermodynamically favorable encapsulation of the ionic species. These were believed to be the first evaluations of association constants for [3]- and [4]-pseudorotaxanes.[31a]



Homotritopic guest [2]pseudorotaxane A



[3]pseudorotaxane A [4]pseudorotaxane A



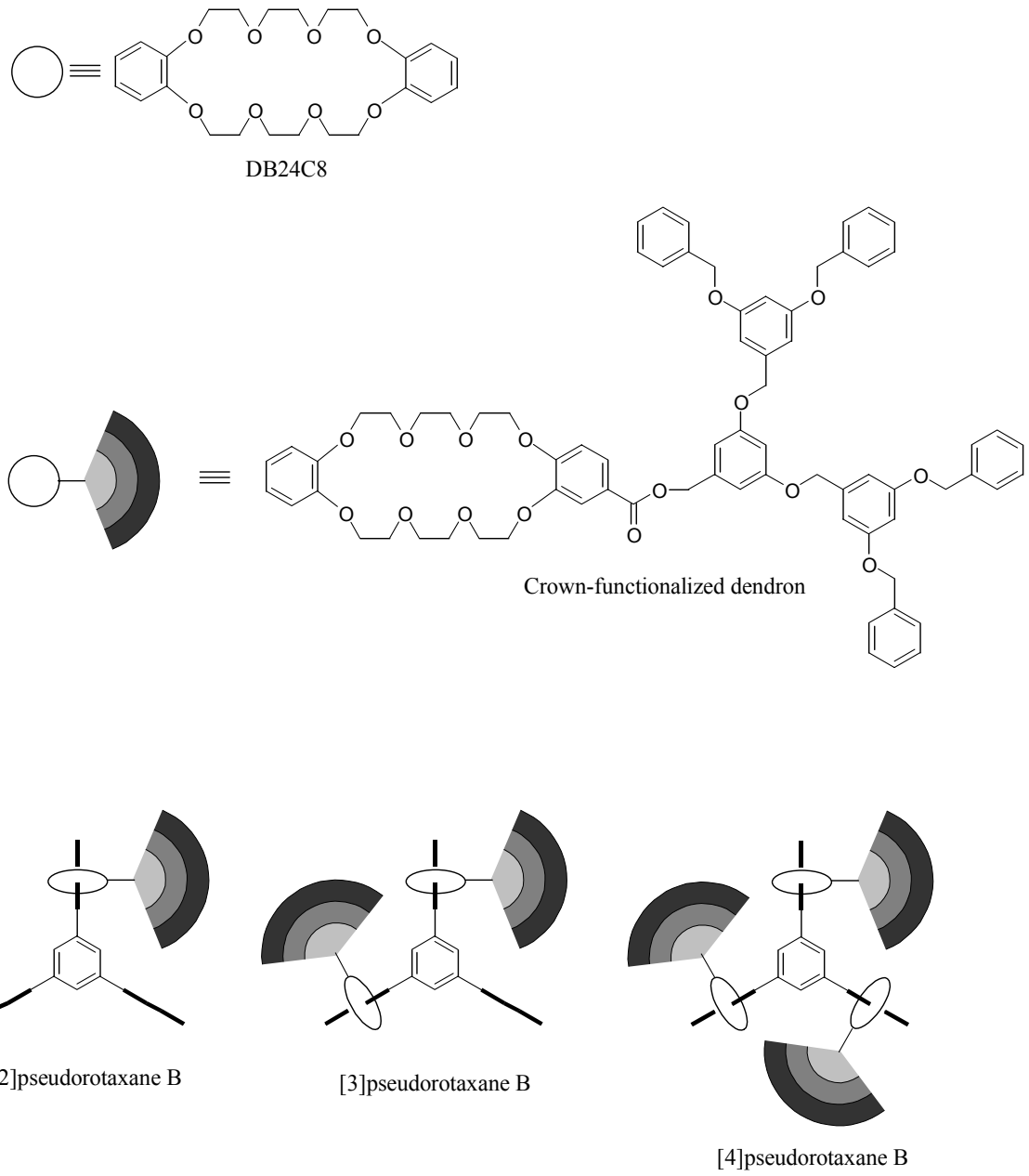


Figure 12. The equilibrium formation of [2]-, [3]- and [4]-pseudorotaxanes from a homotritopic guest molecule and a complementary macrocycle host.

A dendrimer-like three-armed rotaxane, where each arm was threaded through a cycle, was prepared by Stoddart's group.[32]

There are other driving forces used for the construction of pseudorotaxanes and rotaxanes. Anderson et al.[33] reported the synthesis and characterization of an azo dye [2]rotaxane (Figure 13). The driving forces for this rotaxane are hydrophilic-hydrophobic interactions and edge-to-face interactions between the four central hydrogens of the biphenyl and the cyclophane aromatic rings. Its X-ray crystal structure proved the existence of these H-aromatic ring interactions. Further analysis revealed that there were no face-to-face stacking π-π interactions between the biphenyl and the cyclophane.

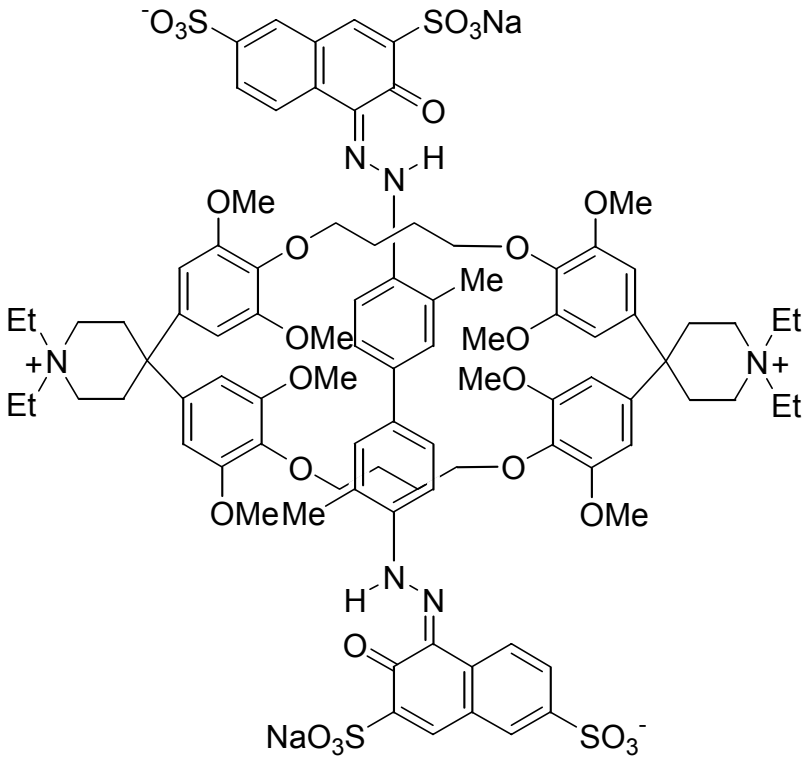


Figure 13. An azo dye [2]rotaxane.

Fujimoto and coworkers[34] prepared the first Janus [2]rotaxane (Figure 14) from the self-assembly dimerization of a lipophilic α-CD monomer bearing a diazotizable 4-aminoazobenzene. The feature of this α-CD monomer is that it contains not only a guest site but a host site.

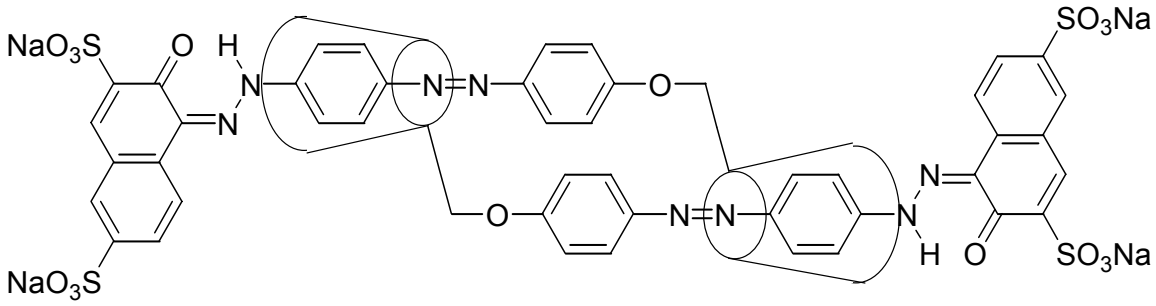


Figure 14.[34] The first Janus [2]rotaxane.

Stoddart's group[35] designed a [2]pseudorotaxane (Figure 15) made up of a homotritopic guest molecule and a homotritopic host molecule driven by hydrogen bonding interactions. This [2]pseudorotaxane is very stable in $CDCl_3/CD_3CN$ solution, but it will dissociate completely via doubly and singly threaded intermediates when CD_3SOCD_3 is added progressively to the $CDCl_3/CD_3CN$ solution.

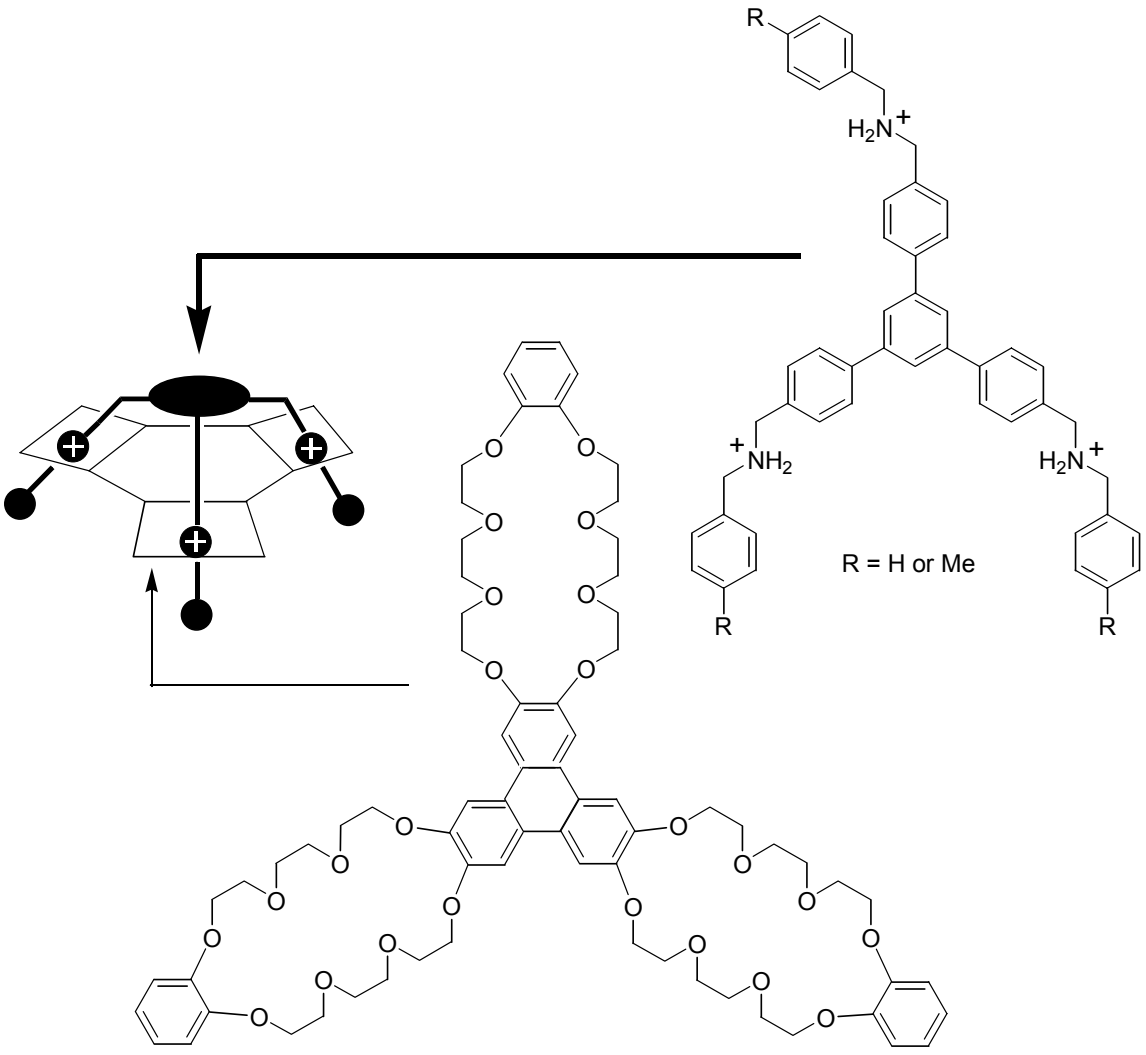


Figure 15. A [2]pseudorotaxane made from a homotritopic guest molecule and a homotritopic host molecule.

Zhao and coworkers[36] synthesized a novel [3]rotaxane (Figure 16) containing one linear component, a neutral tetraamide cyclophane, and a tetracationic cyclophane. Variable-temperature proton NMR investigation shows that the activation energy associated with the shuttling process of the tetracationic cyclophane between the two hydroquinone sites is remarkably reduced by the presence of the neutral cyclophane because of the spatial repulsion between the two cyclophanes. No shuttle behavior of the neutral ring was observed within the investigated temperature range. Furthermore, for the first time, the rotation of the dipyridinium subunit around the axis was investigated by variable-temperature proton NMR spectroscopy.

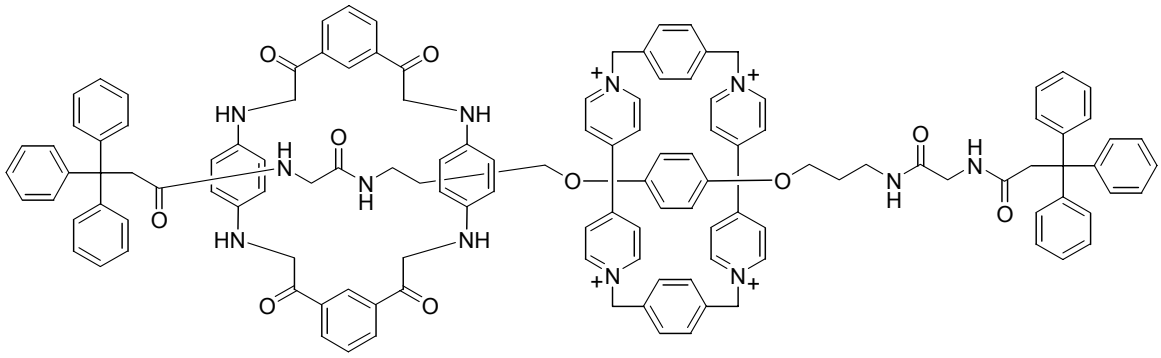


Figure 16. A novel [3]rotaxane containing one linear component, a neutral tetraamide cyclophane, and a tetracationic cyclophane.

1.9. DETERMINATION OF STOICHIOMETRY

In the study of host-guest complexes, including pseudorotaxanes, it is always necessary to determine the stoichiometry of the complexation. Among the several methods to determine stoichiometries, the Job plot method[37] and the mole ratio method[38] are widely

used. We will use a complex $\mathbf{H}_m\mathbf{G}_n$, where **H** is the host and **G** is the guest while *m* and *n* are the numbers of hosts and guests in the complex respectively, as an example to show how these two methods work.

For the Job plot method, two solutions of **H** and **G** at the same molar concentration are prepared. Then different volumes of these two solutions are mixed to obtain a series of solutions for which the ratio of $[\mathbf{H}]_0$ to $[\mathbf{G}]_0$, initial concentrations of **H** and **G** in each solution, is changing continually in small steps while the total concentration of $[\mathbf{H}]_0 + [\mathbf{G}]_0$ is kept constant. Then a plot of the product of the change of a suitable property, for example, the chemical shift of a hydrogen, of **H** or **G** and $[\mathbf{H}]_0$ or $[\mathbf{G}]_0$ against the molar fraction of **H**, $[\mathbf{H}]_0/([\mathbf{H}]_0 + [\mathbf{G}]_0)$, yields a curve having a maximum at $[\mathbf{H}]_0/([\mathbf{H}]_0 + [\mathbf{G}]_0) = m/(m + n)$ and zero values for $[\mathbf{H}]_0/([\mathbf{H}]_0 + [\mathbf{G}]_0) = 0$ and 1. A Job plot for a 2:1 ($m = 2$ and $n = 1$) complexation is shown in Figure 17 as an example.

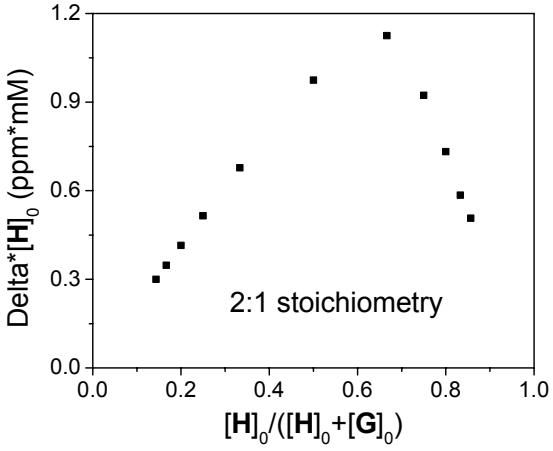


Figure 17. A Job plot for 2:1 complexation of **H** with **G**.

For the mole ratio method, a series of solutions for which $[\mathbf{H}]_0$ is kept at a constant while $[\mathbf{G}]_0$ is systematically changed so that $[\mathbf{H}]_0/[\mathbf{G}]_0$ can be varied in small steps. Then a plot of a suitable property of **H** against $[\mathbf{H}]_0/[\mathbf{G}]_0$ is made to yield a curve. The break point of the curve corresponds to the composition, *m*/*n*, in the complex. A mole ratio plot for a 1:1 complexation is shown in Figure 18 as an example.

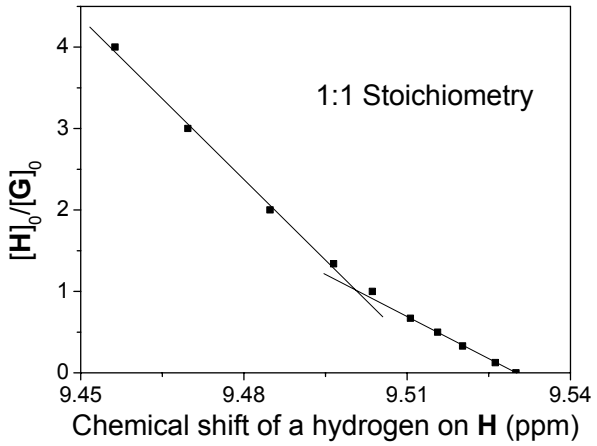
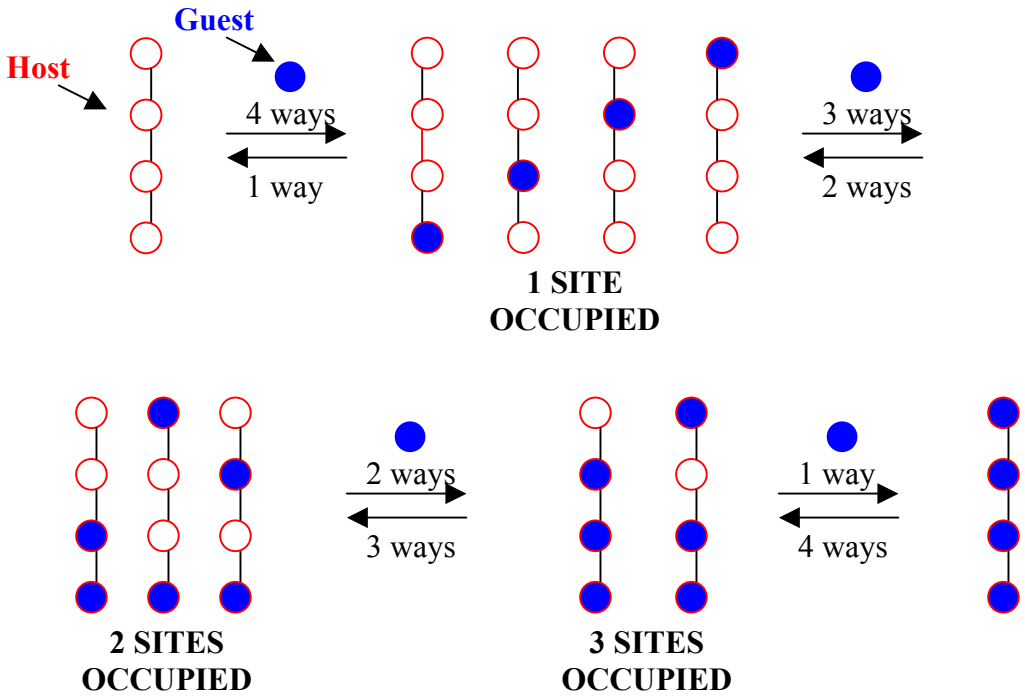


Figure 18. A mole ratio plot for 1:1 complexation of **H** with **G**.

1.10. GRAPHICAL ANALYSES OF COMPLEXATION INVOLVING MULTIFUNCTIONAL SPECIES

The interactions between binding sites of multifunctional species can be divided into cooperative complexation, anticooperative complexation, and satatistical complexation. Let us use a complex based on a guest and a host which has four binding sites as an example. If all sites of the host behave independently and are identical, statistical binding will be observed, i.e. the observed ratio of K_1:K_2:K_3:K_4 will be 4 : 3/2 : 2/3 : 1/4 (Scheme 4). If the ratios

of the K values are greater than statistical, the system exhibits cooperative binding. For example, If the observed ratio K_1:K_2 = 4, which is greater than the statistical ratio, 4/(3/2) = 8/3, the complexation from one-site occupied situation to two-site occupied situation is cooperative. If the ratios are less than statistical, the system exhibits anti-cooperative binding. For example, If the observed ratio K_1:K_2 = 1, which is less than the statistical ratio, 4/(3/2) = 8/3, the complexation from one-site occupied situation to two-site occupied situation is anticooperative.



Scheme 4. Complexation between a guest and a host with four binding sites.

The interactions between binding sites of multifunctional species can be analyzed by the Scatchard plot.[39] Let us suppose the multifunctional species is the guest **G**. In order to make this plot, first, it is necessary to prepare a series of solutions for which $[\mathbf{G}]_0$ is kept constant while $[\mathbf{H}]_0$ is systematically changed. Then a plot of $p/[G]_{uc}$ against p is made to

yield a curve (Figure 19), the Scatchard plot. If this curve is nonlinear and has a maximum, the interactions between different binding sites of **G** during its complexation with the host are cooperative. If it is nonlinear and has a minimum, an anticooperative complexation is obtained. If it is linear, the complexation is statistical, that is, the binding sites behave independently during their complexation to the host. The intercept and the negative of the slope are equal to the average association constant for two steps.

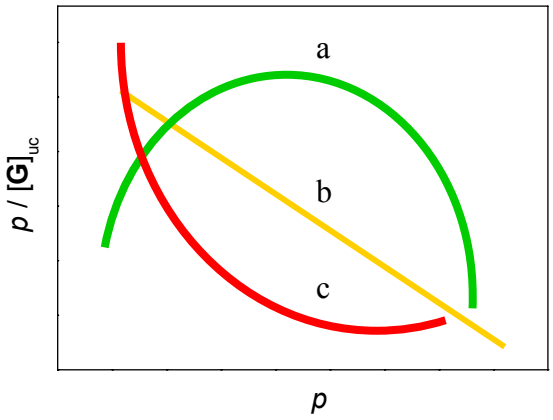


Figure 19. Scatchard plots for complexation involving a multifunctional guest **G**: (a) cooperative complexation, (b) statistical complexation, and (c) anticooperative complexation. p is the complexed fraction of **G**. $[\mathbf{G}]_{uc}$ is the concentration of uncomplexed **G**.

1.11. CALCULATIONS OF ASSOCIATION CONSTANTS

The association constant K_a is an important parameter to measure the stability of the complex between linear and cyclic species in pseudorotaxanes. Up to now most calculations of association constants of pseudorotaxanes are based on the data obtained

from NMR spectra though other methods such as UV-Vis absorption spectra, and *p*H titration.[1] There are two ways to use the NMR spectral data to get the value of K_a: one is by using integrals of peaks, and the other is by using the change of chemical shift. Here let us discuss the calculation of K_a of a 1:1 complex, [A•B], which is made from cyclic component, A, and linear component, B.

	A	+	B	⇌	[A•B]
Initial Concentraion:	$[A]_0$		$[B]_0$		0
Equilibrium Concentration:	[A]		$[B]=[B]_0-([A]_0-[A])$		$[A]_0-[A]$

$$K_a = ([A]_0 - [A])/([A][B])$$

(a) By using integrals of peaks

This method is used to calculate association constants of slow exchange systems. Let us suppose that the integration of uncomplexed peak of a hydrogen atom on A is I_{uc} and that of complexed peak of this hydrogen atom is I_c in the NMR spectrum of the complex solution. Furthermore, $[B]_0 \geq [A]_0$. Then

$[A] = [I_{uc} / (I_{uc} + I_c)]\ [A]_0$ and $[B] = [B]_0 - ([A]_0 - [A]) = [B]_0 - [I_c / (I_{uc} + I_c)]\ [A]_0$.

Therefore $K_a = ([A]_0 - [A])/([A][B]) = ([A]_0 - [A])/\{[A]\{\ [B]_0 - [I_c / (I_{uc} + I_c)]\ [A]_0\}\}$

$= ([A]_0/[A] - 1)/\{[B]_0 - [I_c / (I_{uc} + I_c)]\ [A]_0\}$

$=(I_c / I_{uc})/\{[B]_0 - [I_c / (I_{uc} + I_c)]\ [A]_0\}$

(b) By using the change of chemical shift

This method is used to calculate association constant of fast exchange systems. Suppose that the change of the chemical shift of a hydrogen atom on A is Δ when not all A is complexed, for example, when $[A]_0 = [B]_0$. The change of the chemical shift of a hydrogen atom is Δ_0 when A is completely complexed, such as, when $[A]_0 << [B]_0$. Then $[A] = (1 - \Delta/\Delta_0)\,[A]_0$ and $[B] = [B]_0 - ([A]_0 - [A]) = [B]_0 - (\Delta/\Delta_0)\,[A]_0$.

Therefore $K_a = ([A]_0 - [A])/([A][B]) = (\Delta/(\Delta_0 - \Delta))/([B]_0 - (\Delta/\Delta_0)\,[A]_0)$.

In order to get the value of Δ_0, proton NMR characterizations are done on a series of solutions for which $[A]_0$ is kept at a constant while $[B]_0$ is changed. Then Δ_0 can be determined by extrapolation of a plot of $1/\Delta = 1/(\delta - \delta_u)$ vs. $1/[B]_0$. This is called the Benesi-Hildebrand method.[40]

Weber pointed out that the most precise information about the complex is obtained from data that has a Δ/Δ_0 value between 0.2 and 0.8.[41] Therefore the appropriate concentrations should be chosen for the calculation of K_a.

1.12. DETERMINATION OF THE EXISTENCE OF HYDROGEN-BONDING

Hydrogen bonding is one of important stabilization forces for pseudorotaxanes. It happens between the hydrogen atom covalently connected to a strongly electronegative

atom (hydrogen bonding donor) such as oxygen, fluorine, or nitrogen, or even a carbon atom in some systems such as chloroform and paraquat derivatives, and an electronegative atom (hydrogen bonding acceptor), such as oxygen, chlorine, and fluorine, which have at least one lone electron pair. A hydrogen bond can be represented as D-H···A, where D and A represent hydrogen bonding donor and acceptor, respectively. The strength of the hydrogen bond depends on the angle of D-H···A and the distance between H and A. In order for hydrogen bonding to arise, traditionally it is thought that the distance between H and A should be less than the sum of van der Waals radii of the hydrogen atom and the acceptor atom. The van der Waals radius of an atom is the radius of an imaginary hard sphere and can be determined from measurements of atomic spacing between pairs of unbonded atoms in crystals.[42] The Van der Waals radii of C, F, H, and O are 1.70, 1.47, 1.20, 1.52 Å respectively.[43] Therefore for C-H···O hydrogen bonding, the distances between C and O and between H and O should be less then 4.42 (1.70 + 1.20 + 1.52) and 2.72 (1.20 + 1.52) Å, resepectively. In the same way for C-H···F, the distances between C and F and between H and F should be less then 4.37 (1.70 + 1.20 + 1.47) and 2.67 (1.20 + 1.47) Å, resepectively. Recently this van der Waals cutoff method was challenged by Berg and Seddon et al. in their C-H···X study.[44] However, it is widely accepted that the D-H···A angle should be greater than 90º.[44,45] A wealth of structural[46] and spectroscopic[47] data revealed that C-H···O hydrogen bonds have H···O distances from 2.0 to 3.0 Å, C···O distances from 3.0 to 4.0 Å, and C-H···O angles from 90 to 180º.[45]

1.13. INFLUENCE OF RESONANCE AND INDUCTIVE EFFECTS ON ACIDITY OF VARIOUS PROTONS OF PARAQUAT DERIVATIVES AND DIBENZYLAMMONIUMS

The inductive effect is the polarization of one bond caused by the polarization of an adjacent bond.[48] Resonance always results in a different distribution of electron density than would be the case if there were no resonance. This decrease in electron density at one position (and corresponding increase elsewhere) is called the resonance effect.[49] These two effects have important influence on the acidity of some protons of paraquat derivatives and dibenzylammonium salts. In the following discussion, we will take dimethyl paraquat and dibenzylammonium as examples. All hydrogens on dimethyl praquat are more acidic than usual aliphatic or aromatic hydrogens due to effects produced by the two positive charges. However, methyl and α-pyridinium hydrogens are more acidic than β-pyridinium hydrogens not only because they are closer to the positive charge centers (induction) but also due to resonance effects shown in Figure 20.

The hydrogens on the ammonium group of dibenzylammonium are acidic due to the resonance effects as shown in Figure 21. The hydrogens on methylene groups are weakly acidic due to inductive effect from the positive ammonium group. The aromatic protons are far from the positive charge, so their acidity is almost the same as usual aromatic hydrogens. Therefore, totally dimethyl paraquat has more acidic protons than dibenzyl ammonium due to more positive charges.

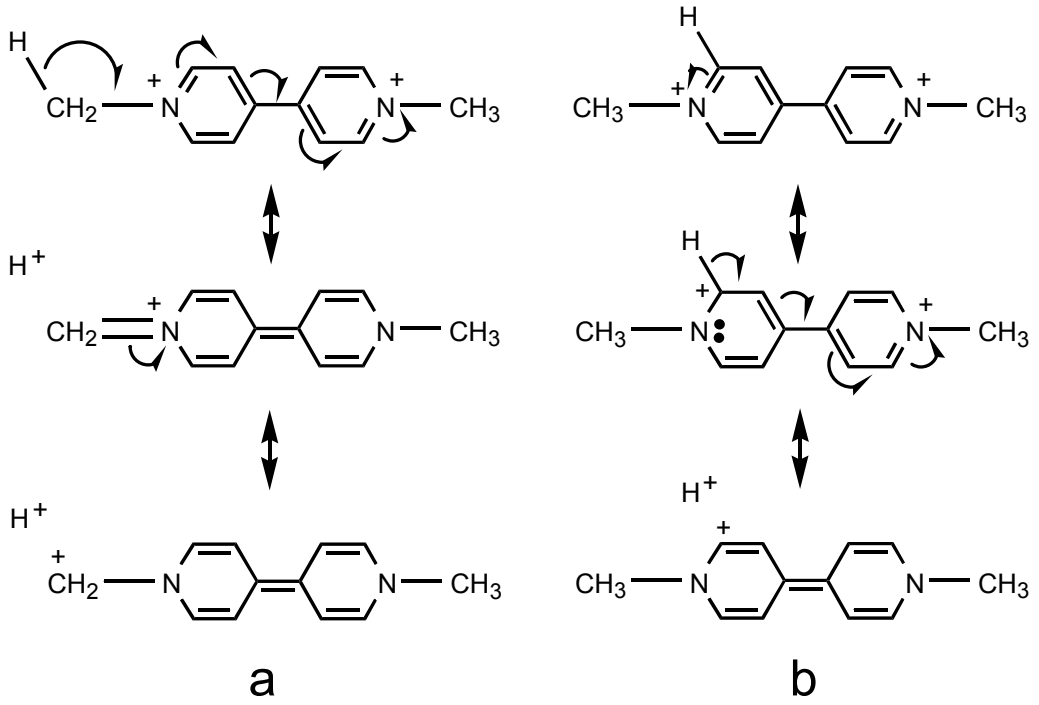


Figure 20. Resonance structures of dimethyl paraquat showing the acidity of methyl hydrogens (column a) and α–pyridinium hydrogens (column b).

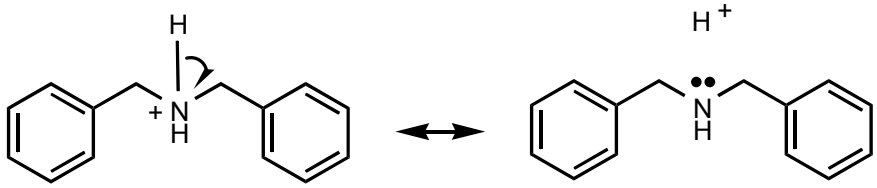


Figure 21. Resonance structures of dibenzylammoinium showing the acidity of ammonium hydrogens.

1.14. ERROR ANALYSES IN DETERMINING APPARENT ASSOCIATION CONSTANTS.

Errors in determining apparent association constants, K_a, arise mainly from the errors in weight measurements, volume measurement of solvents, and NMR chemical shifts. The error in weight is determined by the instrumental precision and the mass. For the instrument in our lab we usually use for the study of apparent association constants, the error is 0.05 mg. Therefore, for example, when you make a 5 mL dibenzo-24-crown-8 solution, the absolute error of the molar concentration will be [0.05 mg/(448.51 mg/mmol)]/5.00 mL = 0.0223 mM. Obviously, the higher concentration you make, the smaller relative error you will get. In our lab, we use to-deliver volumetric pipets to get the volume of the solvent for making a solution. For the 5.00 mL pipet, the error is ± 0.01 mL. For example, for making a 5.00 mL 5.00 mM solution of dibenzo-24-crown-8, the biggest error caused by volume measurement is (11.21 mg/448.51 mg/mmol)/4.99 mL - (11.21 mg/448.51 mg/mmol)/5.00 mL = 0.0100 mM. Take the mass and volume errors together, the total error in this example will be 0.0300 mM. Proton NMR characterizations bring errors to the values of apparent associations. Based on our numerous experiments, we have experimentally established ± 5% reproducibililty of Δ/Δ_0 values over the range 0.2 to 0.8. For example, in a 1.00 mM host and guest solution, if the observed fraction of complexation of the host is 0.520, the biggest error in the calculated value of K_a (2.27×10^3 M^{-1}) is {[0.546/(0.454*0.454)] × 10^3 M^{-1} - 0.494/(0.506*0.506) × 10^3 M^{-1}}/2 = 360 M^{-1}.

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