

Push–Pull [2]Pseudorotaxanes. Electronic Control of Threading by Switching ON/OFF an Intramolecular Charge Transfer

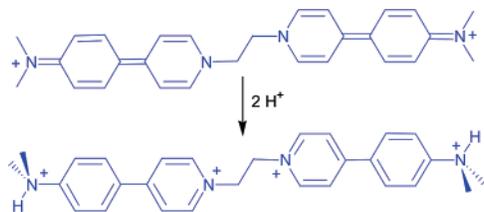
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Received April 28, 2006

ABSTRACT



Addition of acid and base allows switching between two different structures in a push–pull bis(pyridinium)ethane axle, controlling its ability to form [2]pseudorotaxanes with a dibenzo-24-crown-8 ether wheel.

Control over the relative position and motion of components in interpenetrated or interlocked molecules can impart machine-like properties at the molecular level. Examples include threading and unthreading of a [2]pseudorotaxane,¹ translation of the macrocycle in a [2]rotaxane molecular shuttle,² rotation of the rings in a [2]catenane,³ or reorientation (flipping, pirouetting) of the cyclic wheel in [2]rotaxanes.⁴

Previously, we demonstrated the synthetic value of 1,2-bis(pyridinium)ethane cations as templates for the construction of interpenetrated and interlocked molecules, such as [2]pseudorotaxanes,⁵ [2]rotaxanes,⁶ [n]polyrotaxanes,⁷ and [3]catenanes.⁸ The interaction between a cationic 1,2-bis(pyridinium)ethane axle and a dibenzo-24-crown-8 ether

(DB24C8) wheel occurs by three sets of complementary interactions: (i) ion–dipole interactions between the N⁺-pyridinium and the oxygen atoms on the crown ether, (ii) a set of eight weak C–H···O hydrogen bonds between the α -N⁺ hydrogen atoms and the oxygen atoms on the crown ether, and (iii) π -stacking between the electron-rich catechol rings of the crown ether and the electron-poor pyridinium rings of the axle.

During a systematic study of [2]pseudorotaxane formation between 1,2-bis(pyridinium)ethane axles and crown ether wheels, we noted that the presence of an electron-donating

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NH₂ group at the 4-position of the pyridinium group dramatically reduced the observed association constant.⁹ This was attributed to a reduction in the acidity of the participating hydrogen bonding groups on the axle but also to a reduction in the charge at the pyridinium nitrogen due to contributions from an unfavorable resonance form. We reasoned that it should be possible to fine-tune the strength of a [2]pseudo-rotaxane interaction and control the threading–unthreading process using these different resonance structures.

To this end, we designed the new axle molecule **1**²⁺, which can be represented by two possible resonance forms having dramatically different structures and charge distributions; see Figure 1. This molecule has the structure of an organic D-π-

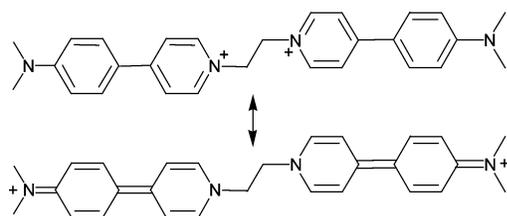


Figure 1. Dicationic axle **1**²⁺ can be represented by two possible resonance forms.

A-π-D chromophore with two terminal donor groups (*N,N*-dimethylamino) and an inner acceptor group (bis-pyridinium). In principle, this should give rise to an intramolecular charge transfer (ICT) observable in the electronic spectrum, and we reasoned that it should be possible to turn *OFF* the ICT by addition of a Lewis acid, such as BF₃ or H⁺.

The new axle **1**²⁺ was synthesized from the reaction of 1,2-dibromoethane with 4'-(*N,N*-dimethylamino) phenyl-4-

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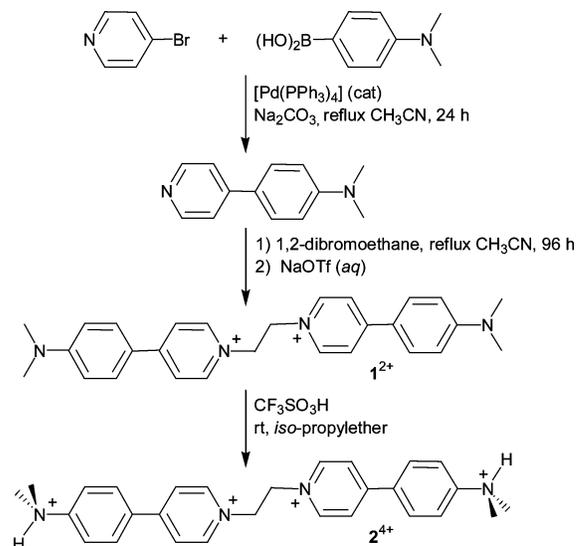
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pyridine obtained by a Suzuki coupling between 4-*N,N*-dimethylaminophenylboronic acid and 4-bromopyridine. The protonated version **2**⁴⁺ was generated by the addition of CF₃SO₃H; see Scheme 1.

Scheme 1. Synthesis of Axles **1**²⁺ and **2**⁴⁺



The X-ray crystal structures of **1**²⁺ and **2**⁴⁺ reveal that there are significant differences in their solid-state structures; see Figure 2.¹⁰ There is evidence that axle **1**²⁺ adopts a

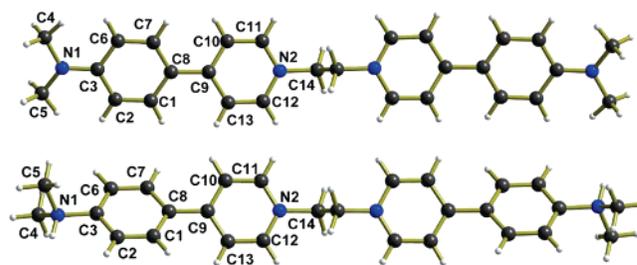


Figure 2. X-ray structures of **1**²⁺ (top) and **2**⁴⁺ (bottom) showing the atom labeling scheme and bond distances.

pseudo-quinoid form with, for example, reduced N1–C3 and C8–C9 distances (1.367(3), 1.466(4) Å, respectively) and a small dihedral angle between aromatic rings of 18.4° supporting delocalization of the positive charge. In contrast, the bonding parameters for **2**⁴⁺ are indicative of the more common bis(pyridinium)ethane form with longer N1–C3 and C8–C9 distances (1.483(5), 1.473(5) Å, respectively) and a more substantial dihedral angle of 55.4°; see Table 1.

For both **1**²⁺ and **2**⁴⁺, DFT (B3LYP) calculations localized the HOMO on the aniline ring and the LUMO on the

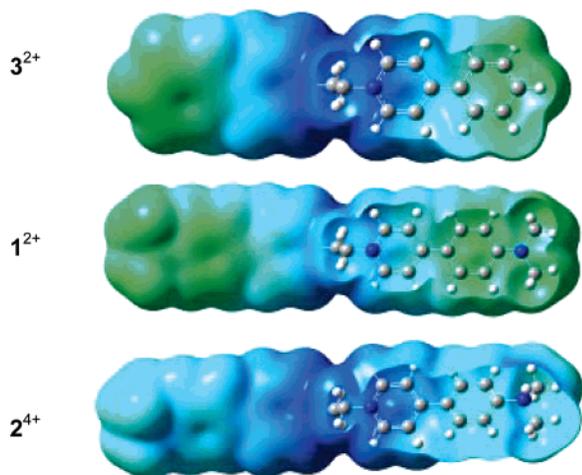
(10) *DIAMOND 3.1*; CRYSTAL IMPACT, Postfach 1251, D-53002, Bonn, Germany 2005.

Table 1. Comparison of Bond Distances in 1^{2+} and 2^{4+} ^a

| bond | distance for 1^{2+} (Å) | distance for 2^{4+} (Å) |
|---------|---------------------------|---------------------------|
| N1–C3 | 1.367(3) | 1.483(5) |
| C1–C2 | 1.376(4) | 1.381(5) |
| C2–C3 | 1.415(4) | 1.382(5) |
| C3–C6 | 1.406(4) | 1.368(5) |
| C6–C7 | 1.374(4) | 1.380(5) |
| C7–C8 | 1.403(4) | 1.388(5) |
| C8–C9 | 1.466(4) | 1.473(5) |
| C9–C10 | 1.401(4) | 1.390(5) |
| C10–C11 | 1.365(4) | 1.372(5) |
| C11–N2 | 1.348(3) | 1.337(5) |
| N2–C12 | 1.349(3) | 1.344(5) |
| C12–C13 | 1.365(4) | 1.363(5) |
| C9–C13 | 1.410(4) | 1.396(5) |
| N2–C14 | 1.471(3) | 1.491(4) |

^a The dihedral angle between the pyridine ring and the aniline ring is 18.4° for 1^{2+} and 55.4° for 2^{4+} . Both molecules have a crystallographically imposed center of symmetry.

pyridinium ring, with important contributions from the N atoms in each case (see Supporting Information). Figure 3

**Figure 3.** DFT calculated (B3YLP) electron distributions for (top to bottom) the dication bis(4-phenylpyridinium)ethane 3^{2+} , axle 1^{2+} , and protonated axle 2^{4+} .

shows a comparison of the electron distribution in 1^{2+} and 2^{4+} along with the unsubstituted axle 1,2-bis(4-phenylpyridinium)ethane, 3^{2+} . It is clear that the protonated axle 2^{4+} and the model compound 3^{2+} have a similar electron-poor distribution (dark blue color) at the central recognition site, whereas 1^{2+} is quite different (lighter blue), which supports the notion of different resonance forms for these axles.

Mixing 1 equiv of axle with 1 equiv of **DB24C8** yields a [2]pseudorotaxane that undergoes slow exchange on the NMR time scale. The new push–pull axle, 1^{2+} , binds **DB24C8** in CD_3CN solution with a very small association constant ($34 M^{-1}$). This *OFF* scenario can be switched *ON*

by the addition of 2 equiv of acid to yield 2^{4+} , which can then act as a standard 1,2-bis(pyridinium)ethane axle for [2]-pseudorotaxane formation. A substantial increase in association constant was observed for 2^{4+} (~5-fold) to a value ($156 M^{-1}$) that is comparable to that observed for 3^{2+} ($172 M^{-1}$) for which there is no substituent on the phenyl ring and no ICT.¹¹

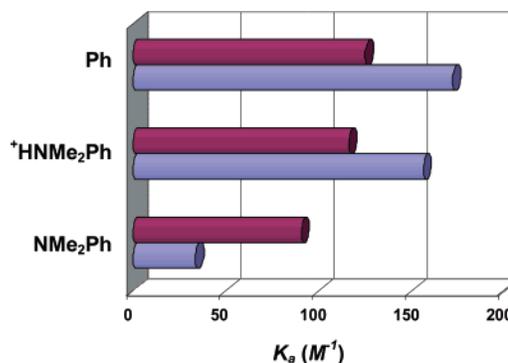
To further assess this system, an analogous series of axle molecules, 4^{2+} , 5^{4+} , and 6^{2+} , were synthesized with the *N,N*-dimethylaniline, *N,N*-dimethylanilinium, and phenyl groups moved to the 3-position of the pyridinium ring. Complexation with **DB24C8** in CD_3CN was studied, and although axle 4^{2+} containing the *N,N*-dimethylaniline group has a lower association constant, the effect is far less pronounced. Table 2 summarizes the association constants for

Table 2. Association Constants, K_a , and ΔG° Values for 1^{2+} – 6^{2+} with **DB24C8** in CD_3CN ($2 \times 10^{-3} M$) at 298 K

| axle | K_a (M^{-1}) ^a | ΔG° ($kJ mol^{-1}$) |
|----------|---------------------------------|------------------------------------|
| 1^{2+} | 34 | 8.7 |
| 2^{4+} | 156 | 12.5 |
| 3^{2+} | 172 | 12.8 |
| 4^{2+} | 91 | 11.2 |
| 5^{4+} | 116 | 11.8 |
| 6^{2+} | 125 | 12.0 |

^a Values were determined using the single point method by direct integration of the appropriate resonances. Error estimated at <5%.

axles 1^{2+} – 6^{2+} with **DB24C8**, and these results are depicted graphically in Figure 4.

**Figure 4.** Comparison of the association constants for the formation of [2]pseudorotaxanes between **DB24C8** and the six axles in this study (blue = 4-position, purple = 3 position).

The difference in association constants, the X-ray metrical parameters, and the DFT calculated structures all support

(11) CD_3CN was used for this study because of solubility limitations. Measurements for 1^{2+} and 2^{4+} in CD_3NO_2 resulted in larger association constants (65 and $251 M^{-1}$) but show that the relative 5-fold increase holds. Thus it is likely this difference will be a consistent factor regardless of solvent.

the idea that it is a major contribution from a pseudo-quinoid resonance form for axle 1^{2+} that results in its anomalously poor ability to interpenetrate **DB24C8** and form significant noncovalent interactions with the crown ether. Moreover, protonation of 1^{2+} to give 2^{4+} restores the pyridinium character of the axle and significantly enhances its ability to interact noncovalently and form a [2]pseudorotaxane. This feature can then be used as a methodology to control threading and unthreading by turning *ON* and *OFF* the interaction.

As predicted, the D- π -A- π -D nature of axle 1^{2+} provides a chromophore with two terminal donor groups and two inner acceptor groups and results in an ICT band with λ_{max} at 447 nm in CH_3CN solution. The resulting intense yellow-orange coloration of the naked axle can be completely eliminated upon the addition of H^+ to give the axle 2^{4+} ; see Figure 5.

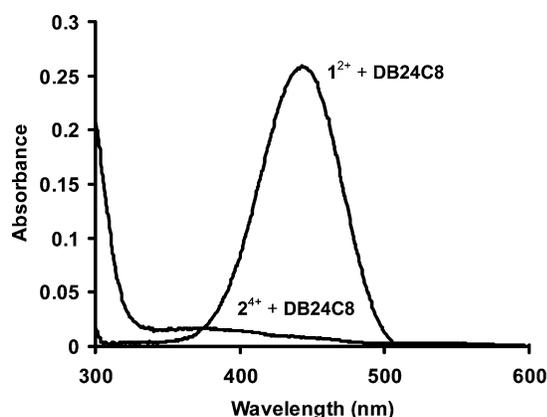


Figure 5. UV-vis absorption spectra of [2]pseudorotaxanes recorded in CD_3CN solution at a concentration of 1.0×10^{-3} M.

The colorless, protonated axle 2^{4+} can then form a [2]pseudorotaxane with **DB24C8**, which gives rise to a pale yellow coloration due to a weak charge-transfer interaction between the electron-rich catechol rings of **DB24C8** and the electron-poor pyridinium rings of the axle.

In summary, the push-pull effect reduces the ability of the bis(pyridinium)ethane unit to act as a recognition site toward **DB24C8**, by decreasing the positive charge on the pyridinium nitrogen atom, reducing the acidity of the hydrogen atoms adjacent the pyridinium N^+ , and increasing the electron density in the pyridinium rings. This induces a

reduction of the association constant with **DB24C8** in CD_3CN compared to 1^{2+} and 3^{2+} or 4^{2+} , 5^{4+} , and 6^{2+} and is an effective *OFF* state for [2]pseudorotaxane formation.¹²

When a Lewis acid such as H^+ is added, protonation of the aniline nitrogen atom occurs and the resulting 1,2-bis-(pyridinium)ethane axle threads through **DB24C8** and converts to the *ON* state. The linking of this mechanical action of [2]pseudorotaxane formation to a significant color change can be described as a *NOT* logic gate since the threading of the two components to form the interpenetrated molecule is signaled by the loss of the bright orange color. We have successfully used alternating equivalents of trifluoromethanesulfonic acid and triethylamine to cycle this protonation-deprotonation in the presence of **DB24C8** five times with no evidence of decomposition or loss of color intensity. Incorporation of this switchable component into other mechanically linked systems is in progress.

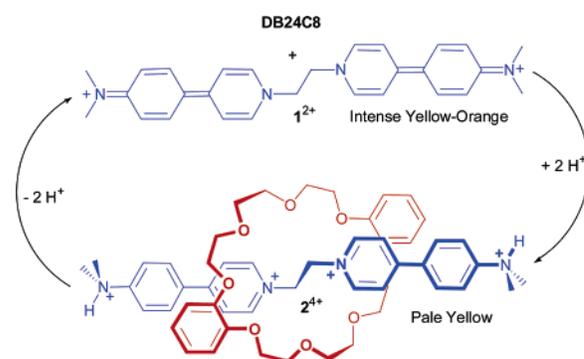


Figure 6. Schematic representation of the threading and dethreading process initiated by alternating acid and base.

Acknowledgment. S.J.L. and J.W.G. thank NSERC of Canada for support of this research in the form of Discovery Grants.

Supporting Information Available: Experimental details, NMR spectra, and depictions of HOMO and LUMO, including files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL0610338

(12) For a recent ICT example, see: Das, S.; Nag, A.; Goswami, D.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2006**, *128*, 402–403.