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Path Selection for Conformational Interconversions in [2]Catenanes

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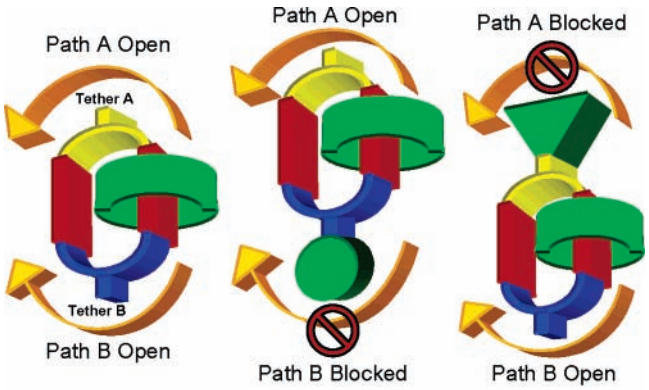
ABSTRACT



Cartoon of blocked and open paths for interconversions

The conformational interconversions of several [2]catenanes containing a dibenzo-34-crown-10 ether (BPP34C10) interlocked with rings containing two 4,4′-dipyridyls tethered by different aryl spacers have been studied. Blocking groups on the tethers enabled the two pathways for circumrotation of the BPP34C10 to be open or blocked. The activation barrier for migration along the open tethers varied from 11 to 13 kcal/mol. This study demonstrates an ability to select the pathway for conformational interconversions in [2]catenanes.

Noncovalent interactions are of central importance in determining the properties of novel materials[1] and biological systems.[2] To better detail the role of nonbonding interactions during conformational changes or reactions, we have undertaken a study of conformational interconversions in bistable [2]catenane systems. The low-energy conformations of [2]catenanes comprised of π-electron-rich dibenzo-34-crown-10 ether (BPP34C10) mechanically interlocked with rings containing two π-electron-deficient 4,4′-dipyridyls are well-established and are based on electrostatic and π,π-stacking interactions.

Such catenanes form bistable complexes where the crown ether prefers to π-stack over either of the dipyridyl groups.[3] Stoddart has reported activation barriers for conformational interconversions of several [2]catenanes where the two tethers between the dipyridyl groups are identical, and thus the energy barrier for migration of the crown ether along either pathway would be the same.[3,4] As part of our developing program to control the energetic pathway for changes in noncovalent interactions, we report herein our initial findings

† Undergraduate research participants.

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on the conformational interconversions of asymmetrically tethered [2]catenanes.

To determine the extent to which translation could be restricted to a predetermined path of our choosing, we designed a series of [2]catenanes in which sterically bulky groups could be appended to either of the two different phenyl ring spacers connecting the two dipyridyl groups. With a blocking group attached to tether **B** in Figure 1,

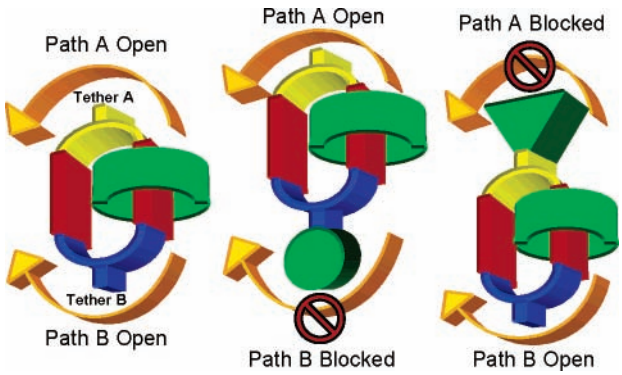
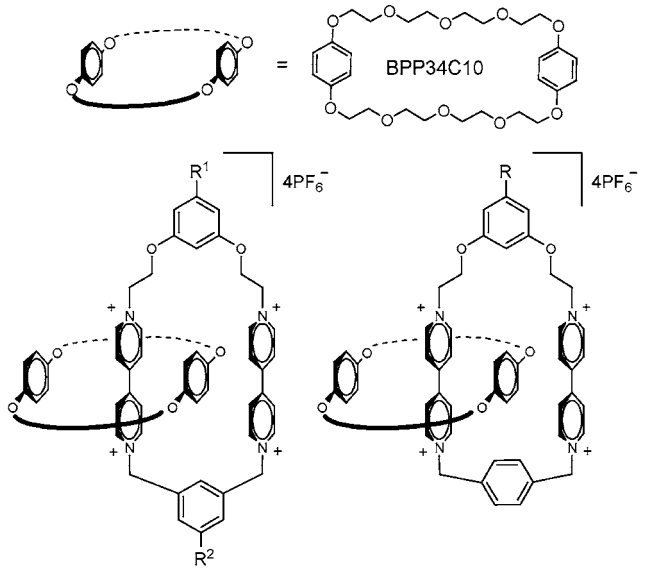


Figure 1. Cartoon representation of [2]catenanes.

translation occurs along pathway **A**. With **A** blocked, interconversion occurs via pathway **B**. With neither blocking group present, free translocation would be observed. Extending the work of Stoddart,[5] we have prepared catenanes **1**−**6** having either the resorcinol-based tether blocked or not blocked and the xylene-based tether blocked or not blocked (Figure 2).

The preparation of the two blocking groups is shown in Scheme 1. Grignard addition of 4-methylphenylmagnesium bromide to the available ester **7**[6] gave the tertiary alcohol **8** which was reduced[7] and then deprotected[8] to give substituted resorcinol **9**. Following a known sequence,[9] diester **10** was prepared by a Suzuki coupling, then reduced, and brominated to give substituted 1,3-bis(bromomethyl)-5-(4-*tert*-butylphenyl)benzene (**11**).

The preparation of the previously unreported unsubstituted [2]catenane **1** was accomplished as depicted in Scheme 2. Resorcinol (**12a**) or 5-substituted resorcinol **9** was converted to 1,3-bis(2-hydroxylethyl)benzenes **13a**,**b** which were brominated to the 1,3-bis(2-bromoethyl)benzenes **14a**,**b** whose treatment with excess 4,4′-dipyridyl[6] gave bis(pyridiniums) **15a** and **15b**. Catenanes **1**−**6** were formed through three component reactions between 1 equiv of bis(pyridiniums)

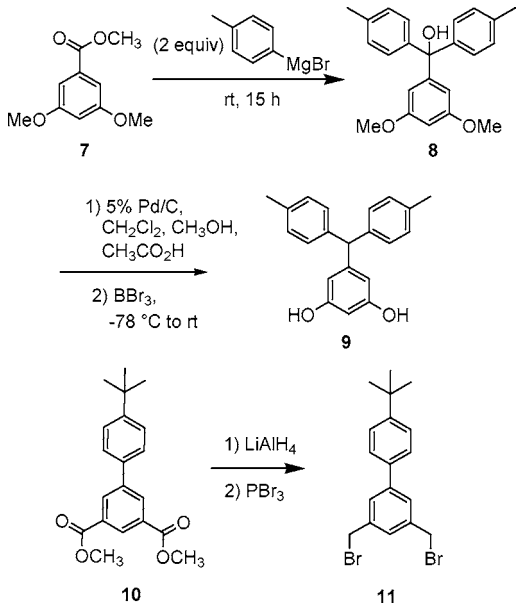


1 R^1 = H , R^2 = H
2 R^1 = H , R^2 = 4-*tert*-butylphenyl
3 R^1 = bis(4-methylphenyl)methyl , R^2 = H
4 R^1 = bis(4-methylphenyl)methyl , R^2 = 4-*tert*-butylphenyl
5 R = H
6 R = bis(4-methylphenyl)methyl

Figure 2. [2]Catenanes in study.

15a or **15b**, 1.2 equiv of 1,3-xylenes or 1,4-xylenes, or **11** and 3 equiv of BPP34C10 in acetonitrile at room temperature under 1 atm of nitrogen for 4 days. Catenanes **5** and **6** were similarly prepared using 1,4-di(bromomethyl)benzene. After solvent removal, the catenanes were isolated by preparative TLC on silica, initially at 50 °C with 1:1 methanol−ethyl

Scheme 1. Synthesis of Blocking Groups



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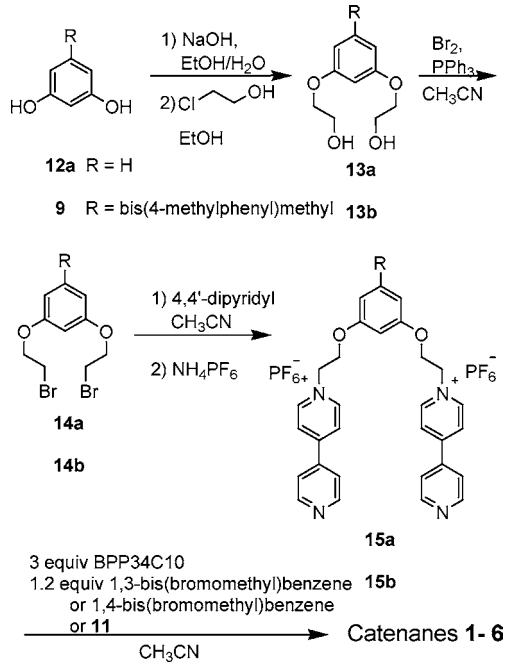
Scheme 2. [2]Catenane Synthesis



acetate to promote dethreading of any pseudorotaxanes and rapid elution of the crown ether to the top of the plate. A second elution at room temperature with 7:2:1 methanol−10% aqueous ammonium chloride−nitromethane[4] moved the catenanes to about 0.3−0.4 R_f and left uncoordinated pyridyls near the origin of the plate. The silica gel with the catenanes was removed and extracted with the 7:2:1 solvent system. The filtrate was concentrated, and aqueous NH_4PF_6 was added to precipitate the catenanes as orange to red solids in 19−32% yield.

Two rotational temperature-dependent isomerizations of related catenanes have been established by Stoddart.[3] Typically, the rotation of a BPP34C10 about a single dipyridyl group has an energy barrier of approximately 16 kcal/mol determined using established NMR techniques.[10] The energy barrier for the translocation or circumrotation of the crown ether from one dipyridyl group to the other typically requires several kilocalories per mole less energy. Consistent with these prior findings, catenanes **1**−**6** exhibited ^{1}H NMR spectra at room temperature that were in the fast exchange region for translocation of the crown ether around the second ring but in an intermediate exchange region for the rotation of the crown ether about its center. At higher temperatures, both processes were fast and a single set of averaged signals was observed for the protons at the 2 and 2′ dipyridyl positions. Below −40 °C, the 1:1 set of dipyridyl signals indicated that both exchange processes were in the slow exchange region. The coalescence temperature and frequency difference of exchanging sets of signals were used to calculate the activation barrier for the translocation of the crown ether between the bistable states.[10] The data are summarized in Table 1.

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Table 1. Summary of Data and Calculation of Activation Energy

catenane	coalescence temp (K)[a]	frequency difference (Hz)	energy of activation (kcal/mol)[b]
1	240	15.5	12.5
2	255	22.2	13
3	255	39.3	12.5
4	>335	25.5	>18[c]
5	220	19.5	11
6	240	64.8	12

[a] Approximated to the nearest 5 °C. [b] An error of 5 °C in determining the coalescence temperature corresponds to an error of 0.2 kcal/mol in the activation energy. [c] No exchange observed by 2D ^{1}H NMR exchange experiments.

Catenane **1** having unsubstituted resorcinol and 1,3-xylyl linkers gave an activation barrier of 12.5 kcal/mol. When both the resorcinol and xylene groups were substituted in **4**, both pathways were blocked. Because no line broadening was observed in the ^{1}H NMR spectra up to 60 °C nor was any evidence for exchange seen in 2D EXSY spectra,[11] the activation barrier for passing over either of these blocking groups should be significantly higher than 18 kcal/mol. When just the resorcinol ring was blocked in **3**, passage over the 1,3-xylyl ring required 12.5 kcal/mol, whereas a 13 kcal/mol barrier was measured for passage over the 1,3-bis-(ethyloxy)benzene tether in **2**. Passage along the 1,4-xylyl linker was significantly more facile than the 1,3-xylyl group as indicated by the 12 kcal/mol barrier in **6**. Apparently, BPP34C10 has a more difficult time passing over the tighter, more constricted turn in the 1,3-xylyl tether in **3** than over the longer, narrower 1,4-xylyl tether in **6**. Passage over the long 3-bis(ethyloxy)benzene in **2** demanded energy requirements similar to that of the 1,3-xylyl tether, and both are significantly more difficult than turning over the 1,4-xylyl tether.

In summary, through the appropriate incorporation of blocking groups on one or both of the phenyl linkers, it was possible to block one or both of the two pathways for circumrotation in bistable catenanes **1**−**6**. The energy barrier for passage along a 1,3-bis(ethyloxyl)benzene tether was 13 kcal/mol, more than that for the 1,4-xylyl tether which was 12 kcal/mol and for the 1,3-xylyl tether which was 12.5 kcal/mol. This study points out an ability to choose different pathways for conformational changes in noncovalently linked systems.

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Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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