

Helical Chirality in Donor-Acceptor
Catenanes[†]

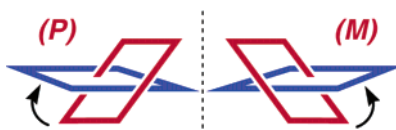
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ABSTRACT



A [2]catenane in which the macrocyclic polyether, bisraphenylene[34]crown-10, is interlocked with the tetracationic cyclophane, cyclobis-(paraquat-*p*-phenylene), is shown by dynamic ¹H NMR spectroscopy, using (i) neutral and (ii) anionic chiral shift reagents (CSRs), to exist at low temperatures (197 K) in acetone-*d*₆ solutions as 1:1 and 2:1 mixtures of diastereoisomeric complexes and salts, respectively, as a consequence of the helical chirality associated with the [2]catenane interacting with the CSRs.

Stereochemistry has been at the center of the development of host-guest¹ and supramolecular² chemistry for three decades now. Thus, chiral crown ethers³ have been used to resolve⁴ racemic substrates as well as to serve⁵ as asymmetric catalysts in reactions of prochiral substrates. Chirality has been introduced into host molecules in the form of chiral

axes,^{3,6} and planes,^{3,7} as well as stereogenic centers.^{3,8} More recently, there have been elegant examples reported⁹ of the induction of helical chirality in complex supermolecules. Meanwhile, molecular recognition and self-assembly processes¹⁰ have given a remarkable fillip¹¹ to the template-directed synthesis¹² of mechanically interlocked compounds,¹³ e.g., catenanes,¹⁴ rotaxanes,¹⁵ knots,¹⁶ and Borromean links.¹⁷

[†] Dedicated to the life and works of Norma Stoddart (1944–2004).

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One of the most productive molecular recognition systems to have been employed¹⁸ for the template-directed synthesis¹² of catenanes and rotaxanes relies upon the donor-acceptor interactions that exist between π -electron-rich ring systems (e.g., hydroquinone, 1,5-dioxynaphthalene, tetrathiafulvalene, etc.) and π -electron deficient units (e.g., bipyridinium, diazapyrenium, etc.). Perhaps the most highly investigated [2]catenane¹⁹ with these recognition units is one, specifically **1**⁴⁺, wherein (Figure 1) a bisparaphenylene[34]crown-10 (BPP34C10) ring is interlocked with the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺). An inherent structural feature of **1**⁴⁺ is the tilt of approximately 45° between the mean planes of the BPP34C10 and the CBPQT⁴⁺ in order to maximize the geometries and strengths of the [C–H···O]²⁰ and [C–H··· π]²¹ interactions between the tetracationic cyclophane and the macrocyclic polyether. This

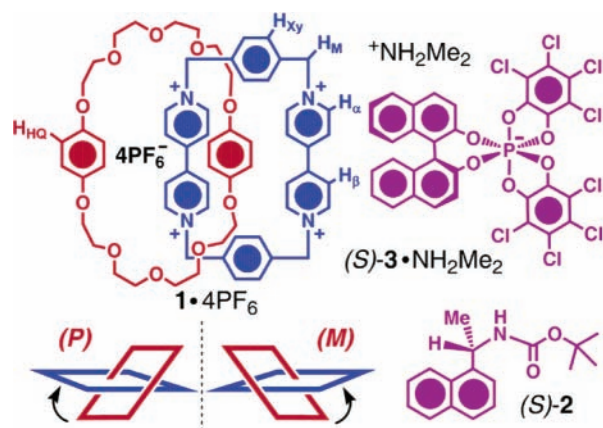


Figure 1. Structural formulas of the [2]catenane **1**·4PF₆ and of the chiral shift reagent (S)-**2** and the chiral anion (S)-**3**·NH₂Me₂, together with a schematic representation of the helical enantiomers, (P) and (M), resulting from the 45° tilt angle between the rings of the donor-acceptor catenane.

geometrical arrangement (coconformation²²) between the two rings generates an element of helical chirality in the [2]catenanes such that enantiomers with (P) and (M) helicities can be identified. The inversion of these two enantiomers can be achieved by a rocking process that requires the breaking of both the [C–H···O] and [C–H··· π] interactions^{20,21} while maintaining the [π ··· π] stacking interactions²³ between the π -donating and π -accepting aromatic ring systems. Previously, we have demonstrated²⁴ that this rocking process, with an energy barrier of 9 kcal mol^{−1}, is the fastest of three processes, the other two being circumrotations of one ring through the other, that can be investigated¹⁹ in solution by dynamic ¹H NMR spectroscopy (DNMR).

During a much more recent variable-temperature ¹H NMR spectroscopic investigation²⁵ into the dynamic processes that characterize a series of analogous bipyridinium-containing [2]catenanes with noninvertible axial chirality, two different species in unequal amounts were detected at low temperatures. Since they interconvert rapidly at higher temperatures on the ¹H NMR time scale, it is believed that these two species are diastereoisomers resulting from the helical chirality generated by the mutual ring tilts in the presence

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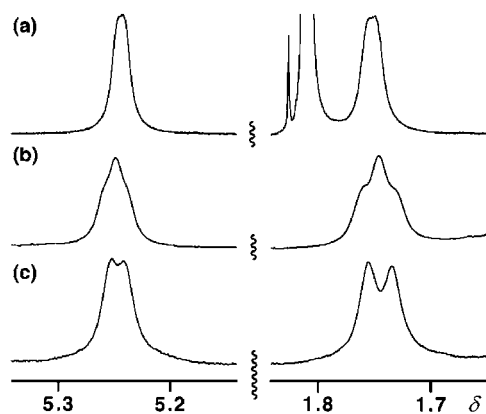


Figure 2. Partial ^1H NMR spectra, recorded in CD_3COCD_3 , showing (a) the signals for the inside hydroquinone protons in $1\cdot 4\text{PF}_6$ at 197 K, (b) the change upon addition of 1.2 equiv of the chiral shift reagent (S)-2, and (c) on ^1H decoupling of the A_2B_2 system.

of the axial chirality present in the bipycolinium unit. To be able to investigate this element of helical chirality without interference from any other stereoelement, we decided to carry out a more detailed investigation of the [2]catenane

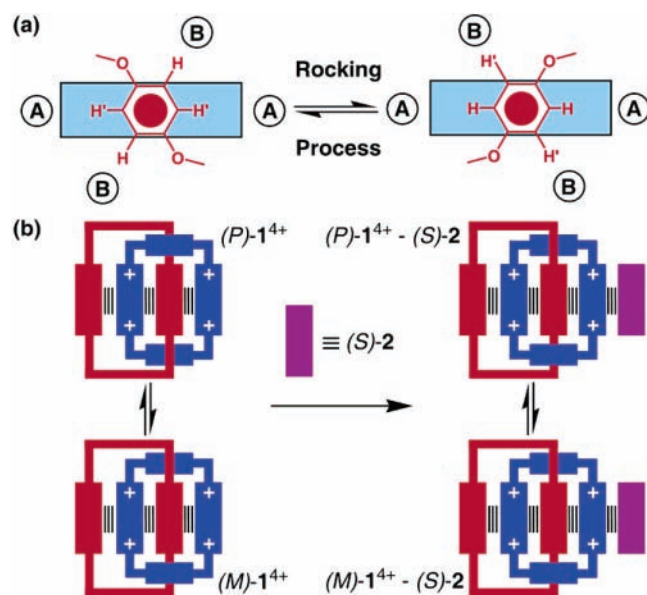


Figure 3. (a) Schematic representation of the proton exchanges that occur during the ring rocking process. H and H' exchange between the A and B sites, differentiated by either participating in a $[\text{C}-\text{H}\cdots\pi]$ interaction with the *p*-xylylene ring of the CBPQT^{4+} cyclophane (site A) or pointing up out of the cavity of the CBPQT^{4+} cyclophane (site B). (b) Schematic representation depicting binding of the chiral shift reagent (S)-2 by an alongside $[\pi\cdots\pi]$ stacking interaction with a bipyridinium unit of the CBPQT^{4+} cyclophane in 1^{4+} . Note that the diastereoisomeric complexes (P)- $1^{4+}-(\text{S})-2$ and (M)- $1^{4+}-(\text{S})-2$ are present in CD_3COCD_3 solution in equimolar amounts. They are also in rapid equilibrium on the ^1H NMR time scale.

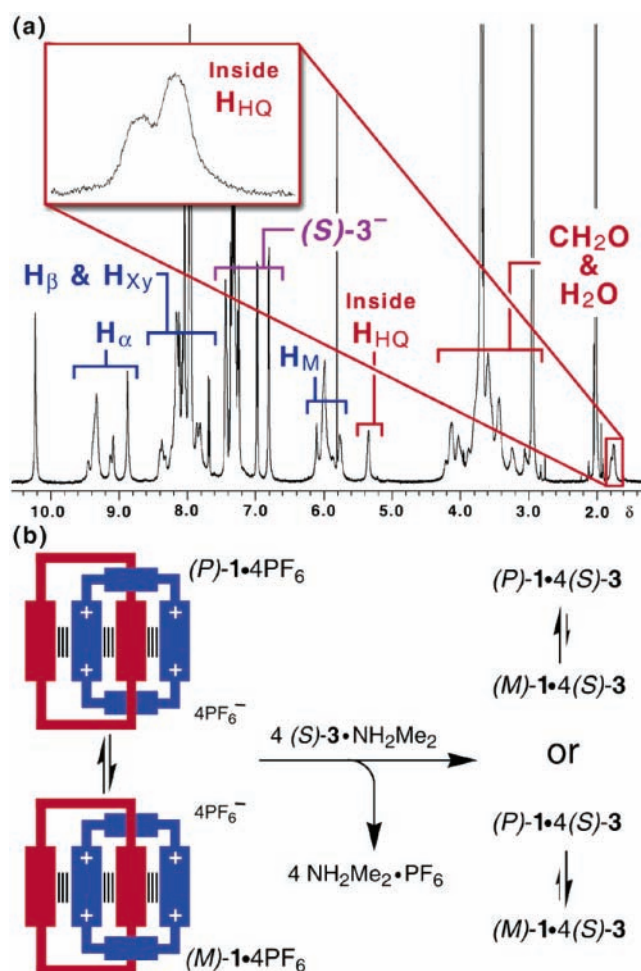


Figure 4. (a) ^1H NMR spectrum, recorded in CD_3COCD_3 of $1\cdot 4\text{PF}_6$ after addition of 4.0 equiv of the chiral anion (S)- $3\cdot \text{NH}_2\text{Me}_2$ at 197 K. The inset shows an expansion of the peaks centered around $\delta = 1.76$ ppm, corresponding to the "resonance" for the two "equivalent inside" hydroquinone ring protons of BPP34C10 involved in $[\text{C}-\text{H}\cdots\pi]$ interactions with the bridging *p*-phenylene groups in CBPQT^{4+} . (b) Schematic representation of the formation of diastereoisomeric salts (P)- $1\cdot 4(\text{S})-3$ and (M)- $1\cdot 4(\text{S})-3$. Twice as much of one of these salts is formed under the inherent equilibrium conditions as the other. The ion-exchanged catenane has not been isolated, and no attempt has so far been made to isolate the anion-exchanged diastereoisomeric salts.

1^{4+} by DNMR. Here, we report some DNMR studies carried out on 1^{4+} in the presence (Figure 1) of (i) a neutral²⁶ chiral shift reagent (CSR) (S)-2 and (ii) an anionic²⁷ CSR, (S)- 3^- .

The ^1H NMR spectrum of $1\cdot 4\text{PF}_6$ was recorded (Figure 2a) in CD_3COCD_3 at 197 K. Resonances corresponding to the "inside" hydroquinone protons that are involved in $[\text{C}-\text{H}\cdots\pi]$ interactions²¹ with the two *p*-phenylene groups in CBPQT^{4+} , as well as the hydroquinone protons that are pointing above and below (Figure 3a) the CBPQT^{4+} component, are observed at $\delta = 1.75$ and 5.25 ppm, respectively, i.e., the ring rocking process is slow on the ^1H NMR time scale. To identify the two enantiomers with (P) and (M) helicities associated with the rocking process, a CSR (S)-2 was chosen such that it would bind with 1^{4+} by $[\pi\cdots\pi]$

stacking with (Figure 3b) the “outside” π -electron-deficient bipyridinium unit of the CBPQT⁴⁺ component. The ¹H NMR spectrum, recorded at 197 K, of **1**·4PF₆ in the presence of (S)-**2** revealed (Figure 2b) two broad “triplets” centered on the same chemical shifts as the doublets had appeared (Figure 2a) in the absence of the CSR. The triplets were shown to be the result of two overlapping doublets in each case by decoupling those hydroquinone protons associated with signals centered on $\delta = 1.75$ and 5.25 ppm in turn and observing the signals for the other hydroquinone protons. In the decoupled spectrum (Figure 2c), two singlets of equal intensities are clearly evident for both pairs of hydroquinone protons. Clearly, two diastereoisomeric complexes, (P)-**1**⁴⁺–(S)-**2** and (M)-**1**⁴⁺–(S)-**2**, are present in solution in equimolar amounts, indicating that the CSR has little or no preference for binding to one helical enantiomer of **1**⁴⁺ over the other.

In a second set of low-temperature ¹H NMR experiments, the chiral anion (S)-**3**[–], as its Me₂NH₂⁺ salt was added to **1**·4PF₆ in CD₃COCD₃ solution in a 4:1 ratio. The ¹H NMR spectrum (Figure 4), recorded at 197 K, revealed a couple of broad singlets centered at $\delta = 1.76$ ppm, corresponding to the resonances for the pair of inside hydroquinone protons involved in [C–H··· π] interactions²¹ with CBPQT⁴⁺. On this occasion, however, the separation of the two singlets is larger

and the ratio of their relative intensities is almost 2:1, i.e., the anionic CSR forms diastereoisomeric salts with **1**⁴⁺ in such a manner that (S)-**3**[–] prefers to ion-pair two times more favorably with one, (P) or (M), of the enantiomeric helices of **1**⁴⁺ than with the other, and we do not yet know which one is which.

While the molecular chirality²⁸ associated with molecular knots and oriented molecular links (catenanes) is topological in origin, and that found in certain rotaxanes, which can be characterized in terms of cycloenantiomerism²⁹ (or even cyclodiastereoisomerism), is usually not easy to invert, the helical chirality present in the [2]catenane **1**⁴⁺ is dynamic, i.e., the (P) and (M) enantiomers invert very rapidly at room temperature in solution. The observation, however, of their forming diastereoisomeric complexes of substantially different ground-state energies in the appropriate chiral environments augurs well for the design of molecular switches³⁰ based on the inherent helical chirality of simple donor–acceptor catenanes.

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(26) Compound (S)-**2** was prepared by the Boc protection of the amine (S)-(–)-1-(1-naphthyl)ethylamine (250 mg, 1.46 mmol), with di-*tert*-butyl dicarbonate (480 mg, 2.20 mmol) and triethylamine (2 mL, 13.4 mmol) in a solution of CH₂Cl₂. The mixture was stirred at room temperature for 12 h and washed with aqueous 2 M HCl solution (2 × 100 mL) and H₂O (1 × 100 mL). The organic phase was dried (MgSO₄) and the solvent evaporated. Flash chromatography (SiO₂, MeCN/CH₂Cl₂, 1:9) yielded (S)-**2** as a white solid (271 mg, 69%). ¹H NMR (CD₃COCD₃): $\delta = 1.39$ (s, 9H), 1.57 (d, 3H), 5.61 (br, 1H), 6.55 (br, 1H), 7.44–7.59 (m, 3H), 7.61 (d, 1H), 7.80 (d, 1H), 7.92 (d, 1H), 8.22 (d, 1H). MS (ESI) *m/z* (%) 272.2 (M + H⁺, 100). Anal. Calcd for C₁₇H₂₁NO₂ (271.4): C, 75.25; H, 7.80; N, 5.16. Found: C, 74.81; H, 7.63; N, 5.09.

(27) Compound (S)-**3**·NH₂Me₂ [¹H NMR (CD₃OD): $\delta = 2.63$ (s, 6H), 6.66 (d, 2H), 7.36 (m, 4H), 7.49 (m, 2H), 7.92 (d, 2H), 8.05 (d, 2H), 8.26 (br, 2H)] was prepared according to procedures described in the literature. See: Lacour, J.; Londez, A.; Goujon-Ginglinger, C.; Buss, V.; Bernardinelli, G. *Org. Lett.* **2000**, 2, 4185–4188.

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