Donor-Acceptor Pretzelanes and a Cyclic Bis[2]Catenane Homologue

Yi Liu, Paul A. Bonvallet, Scott A. Vignon, Saeed I. Khan and J. Fraser Stoddart*

[*] Prof. J. F. Stoddart, Dr. Y. Liu, Dr. P. A. Bonvallet,† Dr. S. I. Khan, Scott A. Vignon
    California NanoSystems Institute and
    Department of Chemistry and Biochemistry
    University of California, Los Angeles
    405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
    Fax: (+1) 310-206-1843

[+] Present Address:
    Prof. P. A. Bonvallet
    Department of Chemistry
    College of Wooster
    943 College Mall, Wooster, OH 44691-2363 (USA)

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Supporting Information
Experimental Section

**General Methods:** Reagents were purchased from Aldrich or synthesized as described. The compounds 1, 4, 6•2PF₆, and 8 were prepared according to literature procedures. Solvents were purified according to literature procedures. Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV-light, prior to development with iodine vapor. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. Proton and carbon nuclear magnetic resonance spectra (¹H-NMR and ¹³C-NMR) were recorded on a Bruker Avance500, Avance 600 or ARX500, using the deuterated solvent as lock and the residual protiated solvent as internal standard. All chemical shifts are quoted using the δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Electrospray mass spectra (ESI-MS) were measured on a VG ProSpec triple focusing mass spectrometer.

3: A mixture of the carboxylic acid derivative 1 (0.50 g, 0.79 mmol), diethylene glycol (2) (0.42 g, 3.97 mmol), 1,3-dicyclohexylcarbodiimide (DCC) (0.33 g, 1.59 mmol) and 4-dimethylaminopyridine (DMAP) (cat. amount) in CH₂Cl₂ (20 mL) was stirred for 1 h at room temperature. The resulting suspension was filtered, the filtrate was evaporated and the residue was subjected to column chromatography (SiO₂: CH₂Cl₂/MeOH 30:1) to give the alcohol 3 (0.54 g, 95%). ¹H NMR (CD₃OD, 600 MHz, 298 K): δ = 7.82 (d, J = 8.4 Hz, 2 H), 7.29 (t, J = 8.4 Hz, 2 H), 7.09 (d, J = 2.2 Hz, 2 H), 6.80 (d, J = 7.8 Hz, 2 H), 6.41 (t, J = 2.2 Hz, 1 H), 4.45 (t, J = 4.5 Hz, 2 H), 4.20 (t, J = 4.5 Hz, 4 H), 3.96 (t, J = 4.5 Hz, 4 H), 3.84–3.81 (m, 6 H), 3.77–3.76 (m, 4 H), 3.70–3.68 (m, 8 H), 3.67–3.65 (m, 4 H), 3.63–3.61 (m, 6 H), 3.33 (m, 2 H); ¹³C NMR (CD₃OD, 150 MHz, 298 K): δ = 166.3, 159.9, 154.3, 131.6, 126.7, 124.8, 114.2, 107.7, 105.5, 105.4, 72.4, 70.5, 70.5,
70.4, 70.3, 69.4, 69.2, 68.8, 67.8, 67.4, 64.2, 60.8; MS (ESI): 719.4 [M + H]⁺, 741.3 [M + Na]⁺, 757.2 [M + K]⁺.

5: A mixture of the alcohol 3 (0.50 g, 0.70 mmol), the carboxylic acid derivative 4[1] (0.30 g, 0.77 mmol), DCC (0.22 g, 1.0 mmol) and DMAP (cat. amount) in CH₂Cl₂ (20 mL) was stirred for 1 h at room temperature. The resulting suspension was filtered, the filtrate was evaporated, and the residue was subjected to column chromatography (SiO₂: hexanes/EtOAc 1:3) to give the dibomide 5 as a sticky solid (0.57 g, 75%). ¹H NMR (CDCl₃, 500 MHz, 298 K): δ = 7.83 (d, J = 8.4 Hz, 2 H), 7.69 (s, 2 H), 7.29 (t, J = 8.4 Hz, 2 H), 7.14 (d, J = 2.2 Hz, 2 H), 6.76 (d, J = 7.8 Hz, 2 H), 6.43 (t, J = 2.2 Hz, 1 H), 4.92 (s, 4 H), 4.44 (s, 2 H), 4.43 (t, J = 4.5 Hz, 2 H), 4.30 (t, 2 H), 4.25 (t, J = 4.5 Hz, 4 H), 3.98 (m, 6 H), 3.88 (t, J = 4.5 Hz, 4 H), 3.80–3.78 (m, 4 H), 3.76–3.74 (m, 2 H), 3.72–3.62 (m, 16 H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ = 167.0, 166.4, 166.1, 159.6, 154.2, 137.0, 136.5, 129.7, 128.3, 127.9, 126.6, 125.0, 114.5, 108.1, 105.6, 70.9, 70.8, 70.7, 70.6, 69.6, 69.4, 69.1, 69.1, 68.0, 67.5, 64.8, 64.0, 33.9, 25.5; MS (ESI): 1114.5 [M + Na]⁺, 1130.5 [M + K]⁺.

9: A mixture of the alcohol 8[1] (0.50 g, 0.81 mmol), the carboxylic acid derivative 4 (0.35 g, 0.89 mmol), DCC (0.25 g, 1.2 mmol) and DMAP (cat. amount) in CH₂Cl₂ (20 mL) was stirred for 1 h at room temperature. The resulting suspension was filtered, the filtrate was evaporated, and the residue was subjected to column chromatography (SiO₂: hexanes/EtOAc 1:3) to give the dibomide 9 as a sticky solid (0.42 g, 52%). ¹H NMR (CDCl₃, 600 MHz, 298 K): δ = 7.89 (d, J = 8.4 Hz, 2 H), 7.73 (s, 2 H), 7.33 (t, J = 8.4 Hz, 2 H), 6.80 (d, J = 8.4 Hz, 2 H), 6.46 (d, J = 2.2 Hz, 2 H), 6.263 (t, J = 2.2 Hz, 1 H), 5.13 (s, 2 H), 4.97 (s, 4 H), 4.51 (s, 2 H), 4.43 (t, J = 4.5 Hz, 2 H), 4.29 (t, 2 H), 4.03 (t, J = 4.5 Hz, 4 H), 3.89 (t, J = 4.5 Hz, 4 H), 3.85–3.83 (m, 4 H), 3.77–3.74 (m, 8 H), 3.80–3.78 (m, 4 H), 3.76–3.74 (m, 2 H), 3.72–3.62 (m, 16 H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ = 167.0, 166.4, 166.1, 159.6, 154.2, 137.0, 136.5, 129.7, 128.3, 127.9, 126.6, 125.0, 114.5, 108.1, 105.6, 70.9, 70.8, 70.7, 70.6, 69.6, 69.4, 69.1, 69.1, 68.0, 67.5, 64.8, 64.0, 33.9, 25.5; MS (ESI): 1114.5 [M + Na]⁺, 1130.5 [M + K]⁺.
3.73–3.72 (m, 4 H), 3.70–3.68 (m, 4 H); \(^{13}\)C NMR (CDCl\(_{3}\), 150 MHz, 298 K): \(\delta = 166.9, 166.5, 160.1, 154.4, 137.3, 136.6, 128.5, 126.8, 125.2, 114.7, 106.8, 105.8, 101.3, 71.1, 71.0, 70.9, 70.8, 69.8, 69.6, 68.2, 67.6, 67.5, 39.0, 25.6; MS (ESI): 987.1695 [\(M^+\)].

12•4PF\(_6\): A mixture of crown ether 8 (0.63 g, 1.02 mmol), the dicationic salt 6•2PF\(_6\)\(^{[3]}\) (0.72 g, 1.02 mmol) and the dibromide 4 (0.40 g, 1.02 mmol) in DMF (15 mL) was stirred at room temperature for 5 days. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO\(_2\): MeOH/NH\(_4\)Cl (2M)/MeNO\(_2\) 7:2:1). The purple fractions containing the product were combined and concentrated to a residue. Solid NH\(_4\)PF\(_6\) was added to precipitate the [2]catenane 12•4PF\(_6\) as a purple solid (1.05 g, 56%). M.p. 219°C (dec.); \(^1\)H NMR (CD\(_3\)CN/D\(_2\)O, 500 MHz, 298 K): \(\delta = 9.10\) (d, \(J = 6.1\) Hz, 2 H), 9.01 (d, \(J = 6.1\) Hz, 2 H), 8.70 (d, \(J = 6.1\) Hz, 2 H), 8.57 (d, \(J = 6.1\) Hz, 2 H), 8.48 (s, 2 H), 8.04 (s, 2 H), 7.94 (s, 2 H), 7.30–7.24 (m, 8 H), 6.68 (d, \(J = 13.6\) Hz, 2 H), 6.28 (d, \(J = 7.7\) Hz, 1 H), 6.21 (s, 1 H), 6.17 (s, 1 H), 5.96 (t, \(J = 7.7\) Hz, 1 H), 5.86 (d, \(J = 13.6\) Hz, 2 H), 5.79 (d, \(J = 7.7\) Hz, 1 H), 5.76 (d, \(J = 13.6\) Hz, 4 H), 5.72 (t, \(J = 7.7\) Hz, 1 H), 5.29 (s, 1 H), 4.52 (s, 2 H), 4.44 (s, 2 H), 4.30 (br. s, 2 H), 4.25 (br. s, 2 H) 4.20 (br. s, 2 H), 4.16 (br. s, 2 H), 4.09–3.93 (m, 8 H), 3.84 (br. s, 2 H), 3.80 (br. s, 2 H), 3.67 (br. s, 2 H), 3.64 (br. s, 2 H), 3.50 (m, 4 H), 3.33 (br. s, 2 H), 3.25 (br. s, 2 H), 2.48 (d, \(J = 7.7\) Hz, 1 H), 2.39 (d, \(J = 7.7\) Hz, 1 H); HRMS (ESI) C\(_{77}\)H\(_{81}\)F\(_{22}\)N\(_5\)O\(_{17}\)P\(_4\): [\(M – PF_6\)]\(^+\), calcd 1698.4336, found 1698.4597; [\(M – 2PF_6\)]\(^2+\), calcd 776.7344, found 776.7347.

\(^1\)H NMR Spectroscopic Characterization of 10•4PF\(_6\) and 11•8PF\(_6\). The \(^1\)H NMR spectra of 10•4PF\(_6\) and 11•8PF\(_6\) recorded in CD\(_3\)CN are complicated and the proton resonances are broadened, almost certainly as a result of stereoisomers undergoing
equilibration at rates commensurate with the NMR timescale. Partial spectra of the resonances associated with the α-Bipy protons of $10\cdot4PF_6$ and $11\cdot8PF_6$ are illustrated in Figure S1a and c, respectively. Heating $10\cdot4PF_6$ and $11\cdot8PF_6$ in CD$_3$CN/D$_2$O solutions at 70 °C for one day in the presence of one drop HCl afforded a single product — corresponding to the [2]catenane $12\cdot4PF_6$ in each case — with four sharp doublets for the α-Bipy protons in its partial $^1$H NMR spectrum (Figure S1b). These observations provide chemical proofs of the mechanically interlocked topologies of $10\cdot4PF_6$ and $11\cdot8PF_6$.

**Figure S1**: Partial $^1$H NMR spectra showing the α-bipyridinium protons of a) $10^{4+}$ and c) $11^{8+}$ in CD$_3$CN at 298 K. Figure S1b shows the spectrum of hydrolyzed $10^{4+}$ and $11^{8+}$, which is identical to the spectrum of [2]catenane $12^{4+}$. 
Assignment of the Stereoisomers of the Pretzelane 7•4PF₆ in a CD₃CN Solution

Using 2D TROESY Spectroscopy. On the basis of a 2D TROESY spectrum of 7•4PF₆ recorded (Figure S2) at 298 K, the stereoisomers present in the solution can be assigned as (pR)-(P)-7⁺ and (pS)-(M)-7⁺. A triplet, centered on δ = 5.99 ppm, correlates to a doublet (H₈ of the DNP ring) at δ = 2.50 ppm and thus can be assigned to H₇ of the DNP ring. This triplet, in turn, exhibits (Figure S2) through-space correlation to the resonances for the xylylene protons (H₄ and H₄’) at δ = 7.94 ppm. This through-space correlation is the key to the assignment because it is only in the enantiomers (pR)-(P)-7⁺ and (pS)-(M)-7⁺ that such a correlation between DNP protons and xylylene protons could be present. By contrast, in the enantiomers (pS)-(P)-7⁺ and (pR)-(M)-7⁺, no such correlation should be observed since the DNP and xylylene protons are far apart, as illustrated in Figure S2. Thus, the present conformations are (pR)-(P)-7⁺ and (pS)-(M)-7⁺, which are the same as those in the solid state.

![Diagram](image-url)

**Figure S2:** The Partial 2D TROESY spectrum of 7•4PF₆ recorded in CD₃CN at 298 K. The correlation between the DNP proton (H₇) and the xylylene protons (H₄ and H₄’) in the pair of enantiomers (pR)-(P)-7⁺ and (pS)-(M)-7⁺ is highlighted (Box).
**Assignment of Absolute Chiralities to Helices and Planes.** In addition to planar chirality, the chiral element — that has been somewhat arbitrarily defined as helical chirality — present in these pretzelanes arises from the presence of the diimide functional group attached to one of the phenylene rings in the tetracationic cyclophane. Even in the absence of a tether, the loss of symmetry in two of the three symmetry planes of the parent cyclophane, cyclobis(paraquat-p-phenylene), results in the possibility (Figure S3) of forming two enantiomers, which are inverted by either pirouetting of the crown ether or rotation of the phthalimido unit. In order to assign descriptors to this chirality, we have chosen to draw arrows from the highest priority ring, which is determined by the ring that contains the largest number of the highest atomic number atoms ignoring the tether. The arrow is drawn toward the higher priority quadrant of the other ring, as

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*Figure S3:* Illustrations of assignment of absolute chiralities to helices and planes.
determined by bisecting the lower priority ring with the plane containing the high priority ring and the plane containing the lower priority ring, followed by comparing the four quadrants using standard atom priority rules. It is also important to note that the molecule has been oriented such that the higher priority ring is in front. The end result is an arrow that indicates either a positive \( (P) \) or negative \( (M) \) helicity on going from one ring to the other. For a discussion of both planar and helical chiralities, see: E. K. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994, Chapter 14.

**Formation of Diastereoisomeric Ion Pairs.** The following scheme illustrates the formation of diastereoisomeric ion pairs upon mixing of the chiral shift reagent \( \text{Me}_2\text{NH}_2\,*\,(R)-\text{BINPHAT}^{[6]} \) with the pretzelane \( 7\cdot4\text{PF}_6 \).

![Diagram of diastereoisomeric ion pairs](image)

**References:**


