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2010

Zhao, Y. L., Shveyd, A. K., & Stoddart, J. F. (2011). Solid-state structures and superstructures of two charged donor-acceptor rotaxanes. *Tetrahedron Letters*, 52, 2044-2047.

<https://hdl.handle.net/10356/91151>

<https://doi.org/10.1016/j.tetlet.2010.09.140>

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Solid-state structures and superstructures of two charged donor-acceptor rotaxanes

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ARTICLE INFO

Article history:

Received

Received in revised form

Accepted

Available online

Keywords:

conformation

crystal structure

hydrogen bonding

pseudorotaxane

rotaxane

ABSTRACT:

Two [2]rotaxanes and also a [2]pseudorotaxane containing 1,5-dioxynaphthalene recognition sites located in the middle of their dumbbell and thread components, respectively, and encircled by single cyclobis(paraquat-*p*-phenylene) rings have been synthesized under template control and their solid-state (super)structures have been solved. The investigations revealed that the stoppers on the dumbbell components, the solvents, and the counterions can affect the conformations adopted by the [2]rotaxanes and [2]pseudorotaxane in the solid state.

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Since the first report¹ of the synthesis of cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) in 1988, CBPQT⁴⁺ ring-containing catenanes and rotaxanes have attracted² the attention of chemists, physicists, materials scientists and engineers, on account of the fact that these mechanically interlocked molecules can be harnessed in molecular muscle-activated cantilevers,³ macroscopic sol-gel and liquid-crystalline switches,⁴ molecular electronic devices,⁵ mechanized mesoporous silica nanoparticles,⁶ and metal-organic frameworks.⁷ In particular, bistable [2]rotaxanes have commonly consisted of π -electron-rich tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) units located in the rod portions of their dumbbell components encircled by single CBPQT⁴⁺ rings. The geometries and switching characteristics of these bistable [2]rotaxanes have been investigated⁸ in solution in order to obtain an understanding of the intramolecular interactions between the ring and dumbbell components. It is also instructive, however, to obtain solid-state structures of these [2]rotaxanes in order to understand their switching properties. A systematic search (Fig. 1) of the literature has revealed a total of 91 crystal structures of cyclophane-based donor-acceptor catenanes already reported⁹ by ourselves and others to date. By contrast, as a result of the difficulties encountered during attempts to crystallize cyclophane-based donor-acceptor [2]rotaxanes, there are only 15 of their solid-state structures reported in literature. Bistable [2]rotaxanes have been synthesized which incorporate DNP, TTF, and HQ (hydroquinone) units along with the CBPQT⁴⁺ ring and stoppers such as monoaza-18-crown-6,¹⁰ triisopropylsilane,¹¹ (1*R*,2*S*,5*R*)-menthyl groups,¹² 2,6-diisopropylbenzene,¹³ 3,5-di(*tert*-butyl)benzene,¹⁴ adamantane,¹⁵ anthracene,¹⁶ and ferrocene.¹⁶ Herein, we report the preparation and characterization, by single crystal X-ray crystallography, of two donor-acceptor [2]rotaxanes

1R•4PF₆ and **2R•4PF₆** and one [2]pseudorotaxane [**DcCBPQT**]**4PF₆**.

Figure 1. A histogram summarizing the solid-state structures of charged donor-acceptor catenanes (blue) and rotaxanes (red) recorded in the literature from 1989 to the present day. There are 91 of the former and 15 of the latter.

The preparation of the [2]rotaxanes **1R•4PF₆** and **2R•4PF₆**, and the [2]pseudorotaxane [**DcCBPQT**]**4PF₆** is presented in the Supplementary Data (SD). The dumbbell compounds were prepared from the appropriate ditosylated DNP diethylene glycol derivatives¹⁷ and 4-[4-isopropylphenyl bis-(4-*tert*-butylphenyl)methyl]phenol,¹⁸ 2,6-diisopropylphenol, or thymol. The [2]rotaxanes **1R•4PF₆** and **2R•4PF₆** and the [2]pseudorotaxane [**DcCBPQT**]**4PF₆** were obtained subsequently by a template-directed synthetic approach from their corresponding dumbbell

compound, 1,1'-[1,4-phenylenebis(methylene)]bis-4,4'-bipyridinium bis(hexafluorophosphate),^{11a} and 1,4-bis(bromomethyl benzene) in DMF under 10 kbar pressure at room temperature for 3 days. The two [2]rotaxanes and one [2]pseudorotaxane were isolated as analytically pure solids in yields ranging from 57 % to 66 %, after SiO₂ column chromatography with Me₂CO / NH₄PF₆ (100:1 v/w) as eluent. Although [D<CBPQT]4PF₆ is a [2]pseudorotaxane, it is very stable during the processes involved in its preparation and characterization. The [2]rotaxanes **1R**•4PF₆ and **2R**•4PF₆ and the [2]pseudorotaxane [D<CBPQT]4PF₆ were characterized by NMR spectroscopy, electrospray ionization mass spectrometry, and X-ray crystallography.

The UV-Vis spectra of the [2]rotaxanes and the [2]pseudorotaxane, recorded in MeCN, show charge transfer (CT) absorption bands in the 450–600 nm region, an observation which indicates that the CBPQT⁴⁺ rings in **1R**•4PF₆, **2R**•4PF₆, and [D<CBPQT]4PF₆ encircle the DNP units as shown above. In the ¹H NMR spectra of **1R**•4PF₆, **2R**•4PF₆, and [D<CBPQT]4PF₆ recorded in CD₃CN at 298 K, the resonances of the DNP units experience large upfield shifts, on account of the shielding effect of the encircling CBPQT⁴⁺ ring, to ca. 2.3 (H_{4/8}), 5.9 (H_{3/7}), and 6.2 (H_{2/6}) ppm as compared with those for the same protons in the corresponding dumbbell compounds where the resonances appear in the region δ = 7–8 ppm.

Slow vapor diffusion of *i*Pr₂O into MeCN solutions of **1R**•4PF₆, **2R**•4PF₆, and [D<CBPQT]4PF₆ for 2–4 days afforded single crystals suitable for X-ray crystallographic analysis.¹⁹ The crystals had a cuboidal shape and were relatively large, attaining up to several millimeters in length (Fig. 2).

The crystal structure²⁰ (Fig. 3 and Fig. S1 in the SD) of the [2]rotaxane **1R**•4PF₆ is monoclinic and belongs to the space group *P*2₁/*c*. It reveals that the dumbbell component is threaded centrosymmetrically through the middle of the CBPQT⁴⁺ ring, the DNP unit on the dumbbell component being located inside the CBPQT⁴⁺ ring with interplanar separations of ca. 3.5 Å between the average mean planes of the π -donor and π -acceptors. The DNP unit on the dumbbell component has an *anti* geometry

Figure 2. Photographs (a and b) of the single crystals grown by vapor diffusion of *i*Pr₂O into a solution of **2R**•4PF₆ in MeCN at room temperature.

associated with the conformation of the diethyleneglycol chains. In addition to the [π - π] stacking interactions between the electron-rich DNP unit and the electron-deficient bipyridinium units on the CBPQT⁴⁺ ring, there are (1) T-type edge-to-face interactions between the H_{4/8} protons of the DNP unit on the dumbbell component and the *p*-xylyl residues of the CBPQT⁴⁺ ring and (2) [C–H...O] hydrogen bonds between the oxygen atoms of the diethyleneglycol chains on the dumbbell component and (i) the bipyridinium H_α, (ii) the *p*-xylyl H_a and (iii) the methylene H_b protons of the CBPQT⁴⁺ ring. The PF₆[−] counterions do not participate in hydrogen bond interactions with either the dumbbell component or the CBPQT⁴⁺ ring directly.

In the case of the [2]rotaxane **2R**•4PF₆, which carries smaller stoppers on its dumbbell component, its crystal structure²¹ (Fig. 3 and Fig. S2 in the SD) changes to being triclinic and belongs to the space group *P*1̄. The crystal structure reveals an elegant structural arrangement wherein the 2,6-diisopropylphenyl-terminated dumbbell component is threaded centrosymmetrically through the middle of the CBPQT⁴⁺ ring, the axis of the DNP unit being inclined by approximate 45° to the plane of the CBPQT⁴⁺ ring. The DNP unit on the dumbbell component has an *anti* geometry associated with the conformation of the diethyleneglycol chains. The DNP unit is located inside the CBPQT⁴⁺ ring with interplanar separations of ca. 3.5 Å between the π -donor and π -acceptors. In addition to the [π - π] stacking interaction between the electron-rich DNP unit and the electron-deficient bipyridinium units on the CBPQT⁴⁺ ring, there are once again (1) T-type edge-to-face interactions between the H_{4/8}

Figure 3. Ball-and-stick representations of the crystal structures of the [2]rotaxanes **1R**⁴⁺ and **2R**⁴⁺. Hydrogen atoms, solvent molecules, and counterions are omitted for the sake of clarity. The DNP unit is colored red, the CBPQT⁴⁺ ring blue, and the remainder gray.

protons of the DNP unit on the dumbbell component and the *p*-xylyl residues of the CBPQT⁴⁺ ring, (2) [C–H···O] interactions between the oxygen atoms of the diethyleneglycol chains on the dumbbell component and (i) the bipyridinium H_α and (ii) the methylene H_b protons of the CBPQT⁴⁺ ring, (3) [C–H···N] hydrogen bonds between the nitrogen atoms of the solvent (MeCN) and the bipyridinium H_β protons on the CBPQT⁴⁺ ring, and (4) [C–H···F] hydrogen bonds between the fluorine atoms of three PF₆[−] counterions and (i) the bipyridinium H_{α/β}, (ii) the *p*-xylyl H_a, (iii) the methylene H_b and (iv) the diethyleneglycol protons.

In the packing of **1R**•4PF₆ and **2R**•4PF₆, the [2]rotaxanes are connected by intermolecular [π–π] stacking interactions aided and abetted by a hydrogen bonding network associated with intervening PF₆[−] counterions and solvent molecules. The [2]rotaxane **1R**•4PF₆ assumes a cluster-like packing mode (Fig. 4a), while **2R**•4PF₆ adopts a sheet-like packing mode (Fig. 4b).

Figure 4. Packing superstructures of the [2]rotaxanes **1R**•4PF₆ (a) and **2R**•4PF₆ (b). Hydrogen atoms are omitted for the sake of clarity.

Replacing a 2- or 6-isopropyl group with a 5-methyl group on the stoppers of the [2]rotaxane **2R**•4PF₆ yields the [2]pseudorotaxane [**D**⊂**CBPQT**]4PF₆. The crystal superstructure²² (Fig. 5 and Fig. S3 in the SD) of the [**D**⊂**CBPQT**]4PF₆ is also triclinic and belongs to the space group *P* $\bar{1}$. The dumbbell (**D**) is threaded centrosymmetrically through the middle of the CBPQT⁴⁺ ring. The DNP unit on the dumbbell has an *anti* geometry associated with the conformation of the diethyleneglycol chains. The DNP unit is located inside the CBPQT⁴⁺ ring with interplanar separations of ca. 3.5 Å between the π-donor and π-acceptors, associated with the [π–π] stacking interactions. In spite of the T-type edge-to-face interactions between the H_{4/8} protons of the DNP unit on the dumbbell and the *p*-xylyl residues of the CBPQT⁴⁺ ring, there are some differences between the solid-state (super)structures of **2R**•4PF₆ and [**D**⊂**CBPQT**]4PF₆ in terms of the hydrogen bonding donors and acceptors. In the crystal superstructure of [**D**⊂**CBPQT**]4PF₆, only one type of [C–H···O] interaction exists between the oxygen atoms of the diethyleneglycol chains on the dumbbell and the bipyridinium H_α protons of the CBPQT⁴⁺ ring, while there are

[C–H···F] hydrogen bonds between the fluorine atoms of two PF₆[−] counterions and (i) the bipyridinium H_β, (ii) the DNP H_{2/4} and (iii) the diethyleneglycol protons, and there are [C–H···N] hydrogen bondings between the nitrogen atoms of the solvent MeCN and (i) the bipyridinium H_α and (ii) the *p*-xylyl H_a protons of the CBPQT⁴⁺ ring. In analogy with the [2]rotaxane **2R**•4PF₆, the [2]pseudorotaxane adopts a sheet-like packing mode.

Figure 5. Ball-and-stick representations of the crystal superstructure of the [2]pseudorotaxane [**D**⊂**CBPQT**]⁴⁺. Hydrogen atoms, solvent molecules, and counterions are omitted for the sake of clarity. The DNP unit is colored red, the CBPQT⁴⁺ ring blue, and the remainder gray.

In summary, two [2]rotaxanes and one [2]pseudorotaxane have been prepared and their solid-state (super)structures have been obtained. Close examination of these (super)structures indicates that the geometries of the [2]rotaxanes and [2]pseudorotaxane in the solid state are stabilized, not only by the [π–π], [C–H···π], and [C–H···O] interactions between the dumbbells and the CBPQT⁴⁺ rings, but also by the participation of solvent molecules and counterions in hydrogen bonding. Yet again, the importance²³ of counterions in dictating the solid-state superstructures of rotaxanes and pseudorotaxanes is clearly evident.

Acknowledgments

The research was supported by the US National Science Foundation (NSF) under grant number CHE-0924620.

Supplementary Data

Supplementary data (detailed synthetic procedures, characterization, crystal figures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.XXX.

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- 19 The crystal structures were solved by direct methods and refined by full-matrix least squares against $|F_o|$. Absorption corrections were based on multiple and symmetry-equivalent reflections in the data sets using the SADABS program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library. CCDC 784687 for **1R•4PF₆**, CCDC 784688 for **2R•4PF₆**, and CCDC 784689 for **[D₂CBPQT]4PF₆** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.
- 20 Crystal data for **1R•4PF₆**: $C_{14}H_{16}F_{24}N_4O_{12}P_4$, $M_r = 2702.68$, monoclinic, space group $P2_1/c$, $a = 27.0538(11)$, $b = 12.0145(5)$, $c = 21.2433(9)$ Å, $\alpha = 90^\circ$, $\beta = 95.957(3)^\circ$, $\gamma = 90^\circ$, $V = 6867.6(5)$ Å³, $Z = 2$, $\lambda = 1.54178$ Å, $\rho_{\text{calcd}} = 1.307$ g cm⁻³, $\mu(\text{Cu K}\alpha) = 1.301$ mm⁻¹, $F(000) = 2840$, $T = 100(2)$ K, crystal size $0.24 \times 0.18 \times 0.09$ mm³, θ range 3.28 – 64.72° , index ranges $-31 \leq h \leq 30$, $-14 \leq k \leq 12$, $-22 \leq l \leq 24$, 33786 reflections collected and 11314 unique reflections, $R_{\text{int}} = 0.0354$, data/restraints/parameters 11314/413/1024, goodness-of-fit on $F^2 = 1.024$, $R_1 = 0.0571$ [$I > 2\sigma(I)$], $wR_2 = 0.1575$ (all data), $\Delta\rho$ max/min 0.680 – -0.450 e Å⁻³.
- 21 Crystal data for **2R•4PF₆**: $C_{86}H_{104.88}F_{24}N_8O_{7.33}P_4$, $M_r = 1947.56$, triclinic, space group $P\bar{1}$, $a = 12.1214(10)$, $b = 12.1650(10)$, $c = 16.3414(2)$ Å, $\alpha = 88.095(10)^\circ$, $\beta = 82.200(10)^\circ$, $\gamma = 72.65^\circ$, $V = 2278.7(4)$ Å³, $Z = 1$, $\lambda = 0.71073$ Å, $\rho_{\text{calcd}} = 1.416$ g cm⁻³, $\mu(\text{Cu K}\alpha) = 0.189$ mm⁻¹, $F(000) = 1009$, $T = 100(2)$ K, crystal size $0.51 \times 0.38 \times 0.19$ mm³, θ range 1.26 – 30.13° , index ranges $-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-23 \leq l \leq 23$, 99746 reflections collected and 13354 unique reflections, $R_{\text{int}} = 0.0319$, data/restraints/parameters 13354/24/623, goodness-of-fit on $F^2 = 1.046$, $R_1 = 0.0428$ [$I > 2\sigma(I)$], $wR_2 = 0.1252$ (all data), $\Delta\rho$ max/min 0.683 – -0.574 e Å⁻³.
- 22 Crystal data for **[D₂CBPQT]4PF₆**: $C_{90}H_{104}F_{24}N_{12}O_6P_4$, $M_r = 2029.73$, triclinic, space group $P\bar{1}$, $a = 12.8216(2)$, $b = 12.8607(2)$, $c = 15.3121(2)$ Å, $\alpha = 102.208(10)^\circ$, $\beta = 105.452(10)^\circ$, $\gamma = 93.893(10)^\circ$, $V = 2357.8(6)$ Å³, $Z = 1$, $\lambda = 0.71073$ Å, $\rho_{\text{calcd}} = 1.429$ g cm⁻³, $\mu(\text{Cu K}\alpha) = 0.187$ mm⁻¹, $F(000) = 1052$, $T = 113(2)$ K, crystal size $0.66 \times 0.44 \times 0.28$ mm³, θ range 1.42 – 30.43° , index ranges $-14 \leq h \leq 18$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$, 34179 reflections collected and 13899 unique reflections, $R_{\text{int}} = 0.0424$, data/restraints/parameters 13899/0/620, goodness-of-fit on $F^2 = 1.077$, $R_1 = 0.0521$ [$I > 2\sigma(I)$], $wR_2 = 0.1627$ (all data), $\Delta\rho$ max/min 0.932 – -0.640 e Å⁻³.
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