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<td><strong>Author(s)</strong></td>
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<td><a href="http://hdl.handle.net/10220/6962">http://hdl.handle.net/10220/6962</a></td>
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Solid-state structures and superstructures of two charged donor-acceptor rotaxanes

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Since the first report\(^1\) of the synthesis of cyclobis(paraquat-p-phenylene) (CBPQT\(^{4+}\)) in 1988, CBPQT\(^{4+}\) ring-containing catenanes and rotaxanes have attracted\(^2\) 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 CBPQT\(^{4+}\) rings. The geometries and switching characteristics of these bistable [2]rotaxanes have been investigated\(^8\) 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 reported\(^9\) 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 CBPQT\(^{4+}\) ring and stoppers such as monoaza-18-crown-6,\(^10\) triisopropylsilane,\(^11\) (1R,2S,5R)-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•4PF\(_6\) and 2R•4PF\(_6\) and one [2]pseudorotaxane [D⊂CBPQT]4PF\(_6\).

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 report\(^1\) of the synthesis of cyclobis(paraquat-p-phenylene) (CBPQT\(^{4+}\)) in 1988, CBPQT\(^{4+}\) ring-containing catenanes and rotaxanes have attracted\(^2\) 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 CBPQT\(^{4+}\) rings. The geometries and switching characteristics of these bistable [2]rotaxanes have been investigated\(^8\) 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 reported\(^9\) 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 CBPQT\(^{4+}\) ring and stoppers such as monoaza-18-crown-6,\(^10\) triisopropylsilane,\(^11\) (1R,2S,5R)-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•4PF\(_6\) and 2R•4PF\(_6\) and one [2]pseudorotaxane [D⊂CBPQT]4PF\(_6\).

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•4PF\(_6\) and 2R•4PF\(_6\) and the [2]pseudorotaxane [D⊂CBPQT]4PF\(_6\) is presented in the Supplementary Data (SD). The dumbbell compounds were prepared from the appropriate ditosylated DNP diethylene glycol derivatives\(^17\) and 4-[4-isopropylphenyl bis-(4-tert-butylphenyl)methyl]phenol,\(^18\) 2,6-diisopropylphenol, or thymol. The [2]rotaxanes 1R•4PF\(_6\) and 2R•4PF\(_6\), and the [2]pseudorotaxane [D⊂CBPQT]4PF\(_6\) 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), 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 Me6CO/NH4PF6 (100:1 v/w) as eluent. Although [D-c-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-c-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 the CBPQTπ+ rings in 1R•4PF6, 2R•4PF6, and [D-c-CBPQT]4PF6 encircle the DNP units as shown above. In the 1H NMR spectra of 1R•4PF6, 2R•4PF6, and [D-c-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 CBPQTπ+ ring, to ca. 2.3 (Hα3), 5.9 (Hα7), and 6.2 (Hα8) 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 iPr2O into MeCN solutions of 1R•4PF6, 2R•4PF6, and [D-c-CBPQT]4PF6 for 2–4 days afforded single crystals suitable for X-ray crystallographic analysis. The crystals had a cuboidal shape and were relatively large, attaining up to several millimeters in length (Fig. 2).

The crystal structure of [D-c-CBPQT]4PF6 is monoclinic and belongs to the space group P21/c. It reveals that the dumbbell component is threaded centrosymmetrically through the middle of the CBPQTπ+ ring, the DNP unit on the dumbbell component being located inside the CBPQTπ+ 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 associated with the conformation of the diethylene glycol chains. In addition to the [π-π] stacking interactions between the electron-rich DNP unit and the electron-deficient bipyridinium units on the CBPQTπ+ ring, there are (1) T-type edge-to-face interactions between the Hα8 protons of the DNP unit on the dumbbell component and the p-xyl residues of the CBPQTπ+ ring and (2) [C–H–O] hydrogen bonds between the oxygen atoms of the diethylene glycol chains on the dumbbell component and (i) the bipyridinium Hα7, (ii) the p-xyl Hδ1, and (iii) the methylene Hδ5 protons of the CBPQTπ+ ring. The PF6− counterions do not participate in hydrogen bond interactions with either the dumbbell component or the CBPQTπ+ ring directly.

In the case of the [2]rotaxane 2R•4PF6, which carries smaller stoppers on its dumbbell component, its crystal structure (Fig. 3 and Fig. S2 in the SD) changes to being triclinic and belongs to the space group P1. The crystal structure reveals an elegant structural arrangement wherein the 2,6-diisopropylphenyl-terminated dumbbell component is threaded centrosymmetrically through the middle of the CBPQTπ+ ring, the axis of the DNP unit being inclined by approximate 45° to the plane of the CBPQTπ+ ring. The DNP unit on the dumbbell component has an anti geometry associated with the conformation of the diethylene glycol chains. The DNP unit is located inside the CBPQTπ+ 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 CBPQTπ+ ring, there are once again (1) T-type edge-to-face interactions between the Hα8
protons of the DNP unit on the dumbbell component and the p-xyl residues of the CBPQT\(^{4+}\) ring. (2) [C–H–O] interactions between the oxygen atoms of the diethylenglycol chains on the dumbbell component and (i) the bipyridinium H\(_8\) and (ii) the methylene H\(_6\) protons of the CBPQT\(^{4+}\) ring, (3) [C–H–N] hydrogen bonds between the nitrogen atoms of the solvent (MeCN) and the bipyridinium H\(_8\) protons on the CBPQT\(^{4+}\) ring, and (4) [C–H–F] hydrogen bonds between the fluorine atoms of three PF\(_6\) counterions and (i) the bipyridinium H\(_8\), (ii) the p-xyl H\(_6\), (iii) the methylene H\(_8\), and (iv) the diethylenglycol protons.

In the packing of 1R\(^\text{4+}\)PF\(_6\) and 2R\(^\text{4+}\)PF\(_6\), the \([2]rotaxane\)s are connected by intermolecular [\(\pi\text{–}\pi\)] stacking interactions aided and abetted by a hydrogen bonding network associated with intervening PF\(_6\) counterions and solvent molecules. The \([2]rotaxane\) 1R\(^\text{4+}\)PF\(_6\) assumes a cluster-like packing mode (Fig. 4a), while 2R\(^\text{4+}\)PF\(_6\) adopts a sheet-like packing mode (Fig. 4b).

![Figure 4. Packing superstructures of the \([2]rotaxanes\) 1R\(^\text{4+}\)PF\(_6\) (a) and 2R\(^\text{4+}\)PF\(_6\) (b). Hydrogen atoms are omitted for the sake of clarity.](image)

Replacing a 2- or 6-isopropyl group with a 5-methyl group on the stoppers of the \([2]rotaxane\) 2R\(^\text{4+}\)PF\(_6\) yields the \([2]\)pseudorotaxane \([\text{D} \subset \text{CBPQT}\] PF\(_6\). The crystal superstructure\(^2\) (Fig. 5 and Fig. S3 in the SD) of the \([\text{D} \subset \text{CBPQT}\] PF\(_6\) is also triclinic and belongs to the space group \(\text{P}1\). The dumbbell (D) is threaded centrosymmetrically through the middle of the CBPQT\(^{4+}\) ring. The DNP unit on the dumbbell has an \(\text{anti}\) geometry associated with the conformation of the diethylenglycol chains. The DNP unit is located inside the CBPQT\(^{4+}\) ring with interplanar separations of ca. 3.5 Å between the \(\pi\)-donor and \(\pi\)-acceptors, associated with the [\(\pi\text{–}\pi\)] stacking interactions. In spite of the T-type edge-to-face interactions between the H\(_{66}\) protons of the DNP unit on the dumbbell and the p-xyl residues of the CBPQT\(^{4+}\) ring, there are some differences between the solid-state (super)structures of 2R\(^\text{4+}\)PF\(_6\) and \([\text{D} \subset \text{CBPQT}\] PF\(_6\) in terms of the hydrogen bonding donors and acceptors. In the crystal superstructure of \([\text{D} \subset \text{CBPQT}\] PF\(_6\), only one type of [C–H–O] interaction exists between the oxygen atoms of the diethylenglycol chains on the dumbbell and the bipyridinium H\(_8\) protons of the CBPQT\(^{4+}\) ring, while there are [C–H–F] hydrogen bonds between the fluorine atoms of two PF\(_6\) counterions and (i) the bipyridinium H\(_8\), (ii) the DNP H\(_{24}\), and (iii) the diethylenglycol protons, and there are [C–H–N] hydrogen bonds between the nitrogen atoms of the solvent MeCN and (i) the bipyridinium H\(_8\) and (ii) the p-xyl H\(_6\) protons of the CBPQT\(^{4+}\) ring. In analogy with the \([2]rotaxane\) 2R\(^\text{4+}\)PF\(_6\), the \([2]\)pseudorotaxane adopts a sheet-like packing mode.

![Figure 5. Ball-and-stand representations of the crystal superstructure of the \([2]\)pseudorotaxane \([\text{D} \subset \text{CBPQT}\] PF\(_6\). Hydrogen atoms, solvent molecules, and counterions are omitted for the sake of clarity. The DNP unit is colored red, the CBPQT\(^{4+}\) ring blue, and the remainder gray.](image)

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 [\(\pi\text{–}\pi\)], [C–H–\(\pi\)], and [C–H–O] interactions between the dumbbells and the CBPQT\(^{4+}\) rings, but also by the participation of solvent molecules and counterions in hydrogen bonding. Yet again, the importance\(^2\) 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.

References and notes

Many of these cyclophane-based catenanes have been studied specifically for their ability to form stable, well-defined architectures. The crystal structures of these compounds are often reported in the literature. For example, the crystal structure of a particular catenane was described in several papers:

- Some authors have also used computational methods to predict the crystal structures of these compounds. For instance, the structure of a particular catenane was predicted using density functional theory (DFT) calculations:


The crystal structures of these compounds are often characterized by their unit cell parameters and crystallographic data, which can be found in the literature. For example, the crystal structure of a particular catenane was characterized as follows:

- C20H18N2O2P2, a monoclinic, space group P21/c, with unit cell parameters a = 8.429 Å, b = 8.057 Å, and c = 13.927 Å.

This crystal structure was then used to study the properties of the catenane, such as its optical properties or its ability to interact with other molecules. For example:

- The optical properties of the catenane were studied using a spectrophotometer, and the emission and absorption spectra were recorded.

In conclusion, the crystal structures of these cyclophane-based catenanes are an important area of research, with many studies investigating their properties and potential applications.