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The Solid State Structures of a [3]Rotaxane and its [3]Pseudorotaxane Precursor

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Abstract: The solid state structures of a [3]pseudorotaxane — formed from a bis(azidomethyl)-substituted *p*-xylene-α,α'-dibenzylammonium dication and two dibenzo-24-crown-8 rings — and a [3]rotaxane derived from it — by two dipolar cycloadditions of the azidomethyl groups with di-*t*-butyl acetylenedicarboxylate — are described. The (super)structures are remarkably similar in their geometries and packing.

We have reported recently[1] that [2]- and [3]-rotaxanes[2] may be self-assembled[3] by template-directed syntheses based upon the stabilising noncovalent bonding interactions that exist between secondary dialkylammonium ions and suitably sized macrocyclic polyethers which result[4–7] in the formation of pseudorotaxane-like[8] supramolecular architectures. This self-assembly process utilises a threading-followed-by-stoppering approach (Figure 1). For example, the bis(azidomethyl)-substituted *p*-xylene-α,α'-dibenzylammonium dicationic salt **1**·2PF$_6$ was complexed with the crown ether, dibenzo-24-crown-8 (**DB24C8**), forming a single-stranded, doubly encircled [3]pseudorotaxane intermediate [(**DB24C8**)$_2$· **1**][PF$_6$]$_2$, which was converted into the corresponding [3]rotaxane **2**·2PF$_6$ by the formation of the two bulky stoppering groups using two dipolar cycloadditions with di-*t*-butyl acetylenedicarboxylate.[1] The [3]rotaxane — created by the assembly of five molecules into one — was isolated in an acceptable 10% yield. In this communication, we describe the solid state (super)structures of (a) the [3]pseudorotaxane intermediate [(**DB24C8**)$_2$· **1**][PF$_6$]$_2$ and (b) the [3]rotaxane **2**·2X.

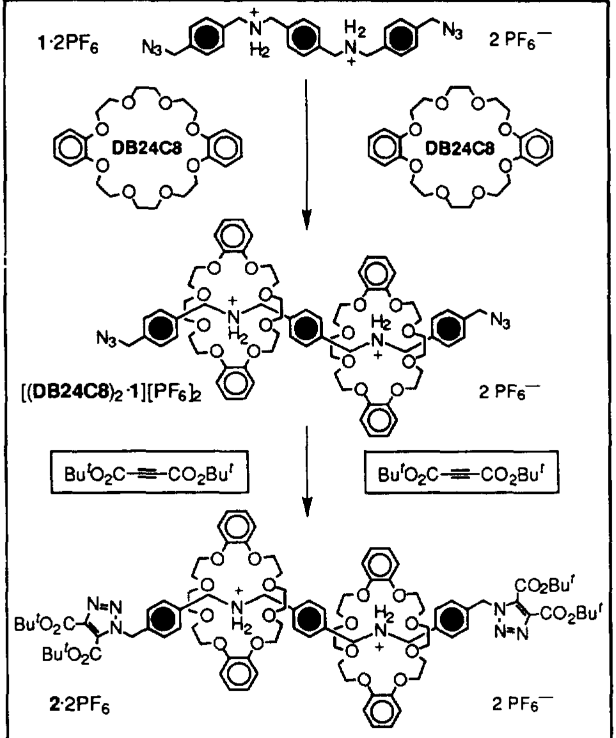
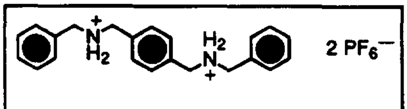


Figure 1. The self-assembly of the [3]pseudorotaxane [(**DB24C8**)$_2$·**1**][PF$_6$]$_2$ by threading — and the [3]rotaxane **2**·2PF$_6$ by stoppering of the [3]pseudorotaxane — in CH$_2$Cl$_2$/MeCN.

Crystals of the [3]pseudorotaxane, suitable for X-ray crystallographic analysis, were grown by liquid-liquid diffusion of *n*-hexane into a MeCN-$CHCl_3$ solution of a 2:1 mixture of **DB24C8** and **1**·$2PF_6$. Analysis of one such crystal by liquid secondary-ion mass spectrometry suggested that the [3]pseudorotaxane superstructure exists in the 'gas phase', as evidenced by a strong peak at *m/z* 1470 corresponding to the ion [(**DB24C8**)$_2$·**1**·PF_6]$^+$. A similarly intense peak for a termolecular complex had previously been observed[5,6] for the corresponding [3]pseudorotaxane formed between the analogous unsubstituted dicationic salt **3**·$2PF_6$ with **DB24C8** in the 'gas phase'. The X-ray crystal structure analysis of [(**DB24C8**)$_2$·**1**][PF_6]$_2$ reveals[9,10] the expected [3]pseudorotaxane in which the bis(azidomethylbenzylammonium)xylene dication **1**$^{2+}$ is threaded through two **DB24C8** macrocycles in a C_i symmetric arrangement. Both **DB24C8** molecules have a conventional extended conformation and host-guest stabilisation is achieved *via* a combination of [N-H···O] and [C-H···O] hydrogen bonding and π-π stacking interactions (Figure 2). The overall geometry of the [3]pseudorotaxane is very similar[5,6] to that of its unsubstituted analogue, [(**DB24C8**)$_2$·**3**][PF_6]$_2$, with the central and terminal *p*-xylene rings being oriented approximately orthogonally with respect to each other, though with the C-CH_2-NH_2^+-CH_2-C chain in this instance being non-planar. The packing of the [3]pseudorotaxanes in the crystallographic *b* direction is stabilised by pairs of [C-H···π] interactions involving one of the phenoxymethylene C-H groups of one **DB24C8** and the catechol ring of another, and *vice versa* (the [H···π] distances and [C-H···π] angles are 2.72 Å, and 143°, and 2.76 Å and 145°, respectively). There are no significant intermolecular interactions involving the azidomethyl groups.



3·$2PF_6$

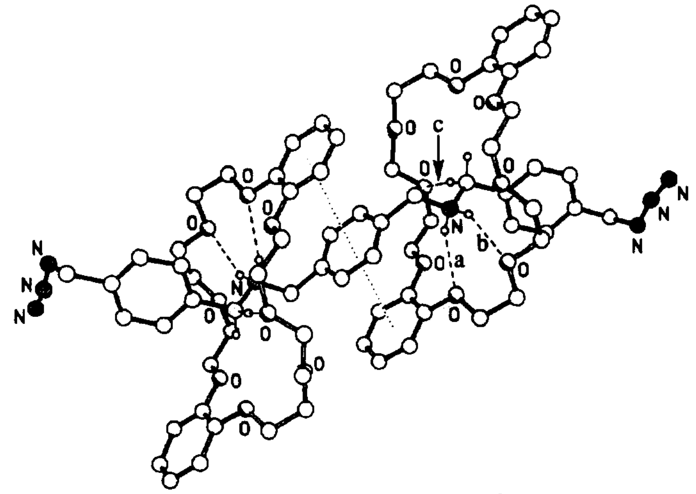


Figure 2. The superstructure of the [3]pseudorotaxane [(**DB24C8**)$_2$·**1**]$^{2+}$ in the solid state. The hydrogen bonding geometries: [X···O] and [H···O] distances (Å) and [X-H···O] angles (°) are (a) 3.04, 2.26, 145, (b) 3.00, 2.22, 145, and (c) 3.20, 2.26, 166. The π-π stacking geometries: centroid-centroid separations 3.70 Å, interplanar separations 3.47 Å.

Crystals of the [3]rotaxane were grown[11] by slow evaporation of a CH_2Cl_2-Et_2O solution of **2**·$2PF_6$. The X-ray analysis of the [3]rotaxane **2**$^{2+}$ reveals[10,12] a C_i symmetric structure that is remarkably similar to that observed for [(**DB24C8**)$_2$·**1**][PF_6]$_2$, showing that the presence of the bulky bis(*t*-butoxycarbonyl)triazoyl units has little influence on the mode of complexation of the dicationic unit by the two **DB24C8** macrocycles. The [3]rotaxane is again stabilised by a combination of [N-H···O], [C-H···O] and π-π stacking interactions (Figure 3). The central and outer *p*-xylyl rings are oriented approximately orthogonally with respect to each other, but here the C-CH_2-NH_2^+-CH_2-C linking chain is essentially planar, with a geometry that is essentially the same as that observed[5,6] for [(**DB24C8**)$_2$·**3**][PF_6]$_2$. The triazole rings and their adjacant *p*-xylyl units are essentially orthogonal to each other and there is a noticeable enlargement from tetrahedral of the angle at the linking methylene carbon atom (114°). This bond angle bending is a consequence of the non-bonded repulsion between one of the ortho-C-H hydrogen atoms of the *p*-xylyl ring and the π-system of the triazole ring.[13] Investigation of the packing of the [3]rotaxanes reveals a juxtaposition of the phenoxymethylene C-H group in one molecule and the π-system of one of the catechol rings of another, analogous to that observed in the structures of both [(**DB24C8**)$_2$·**1**][PF_6]$_2$ and [(**DB24C8**)$_2$·**3**][PF_6]$_2$, although, in this instance, the [H···π] distance is 3.1 Å and thus can only represent a very weak [C-H···π] interaction. A closer approach of catechol units of symmetry-related molecules is inhibited by the steric interaction between one of the *t*-butyl substituents in one molecule and the outer *p*-xylyl ring of another.

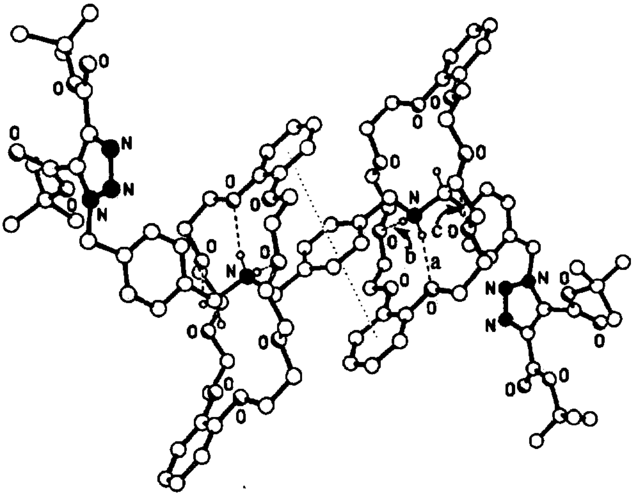


Figure 3. The structure in the solid state of the [3]rotaxane **2**$^{2+}$. The hydrogen bonding geometries: [X···O] and [H···O] distances (Å) and [X-H···O] angles (°) are (a) 3.14, 2.25, 170, (b) 2.95, 2.05, 177, and (c) 3.16, 2.49, 127. The π-π stacking geometries: centroid-centroid separations 3.94 Å, interplanar separations 3.53 Å.

The solid state structures reported in this communication represent important additions to the understanding of the noncovalent bonding interactions which stabilise pseudorotaxanes and rotaxanes[14] formed between secondary dialkylammonium ions and crown ethers. The fact that the structures of the [3]pseudorotaxanes [(**DB24C8**)$_2$·**1**]$^{2+}$ and [(**DB24C8**)$_2$·**3**]$^{2+}$ and the [3]rotaxane **2**$^{2+}$ resemble each other so closely in their complexing geometries and packing arrays suggests that the interactions between these complementary species should provide a reliable synthon[15] for the self-assembly of even more complex supramolecular arrays and molecular assemblies.

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9. Crystal data for [(**DB24C8**)$_2$·**1**][PF$_6$]$_2$: [$C_{72}H_{92}N_8O_{16}$][PF$_6$]$_2$, $M = 1615.48$, triclinic, space group $P\bar{1}$, $a = 11.424(2)$, $b = 11.580(3)$, $c = 14.865(3)$ Å, $\alpha = 84.20(1)$, $\beta = 83.72(1)$, $\gamma = 88.57(1)°$, $V = 1944.5(7)$ Å^3, $Z = 1$ (the superstructure has crystallographic C_i symmetry), $D_c = 1.380$ g cm^{-3}, μ(Cu-K$_\alpha$) = 1.364 mm^{-1}, $F(000) = 846$. A crystal with the dimensions 0.33 x 0.15 x 0.15 mm was used for data collection. Data were measured on a Siemens P4/RA diffractometer with Cu-K$_\alpha$ radiation (graphite monochromator) using ω-scans. The compound appears to be radiation sensitive and decayed rapidly in the X-ray beam. Repeated attempts to grow another suitable crystal were unsuccessful. The data set was thus severely restricted comprising 2216 unique reflections of which 1384 had $|F_o| > 4\sigma(|F_o|)$. The structure was solved by direct methods and refinement on F^2 with only the PF$_6$ anion anisotropic gave $R_1 = 0.1022$ and $wR_2 = 0.2944$ for 232 parameters. Despite the above limitations, the gross details of the superstructure are definitive.
10. Further details of the crystal structure investigations can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation.
11. During the several months taken to obtain crystals suitable for structural determination, a counterion exchange occurred such that the crystal of the [3]rotaxane contained a mixture of chloride and nitrate anions. This situation was not unexpected, since a similar event occurred during crystallisation of an analogous [2]rotaxane. See reference 1.
12. Crystal data for [**2**·1.7Cl·0.3NO$_3$]: [$C_{96}H_{128}N_8O_{24}$][Cl]$_{1.7}$[NO$_3$]$_{0.3}$·2CH$_2$Cl$_2$, $M = 2026.8$, monoclinic, space group $P2_1/c$, $a = 12.718(1)$, $b = 19.684(2)$, $c = 21.174(2)$ Å, $\beta = 92.89(1)°$, $V = 5294(1)$ Å^3, $Z = 2$ (the molecule has crystallographic C_i symmetry), $D_c = 1.27$ g cm^{-3}, μ(Cu-K$_\alpha$) = 20.2 cm^{-1}, $F(000) = 2148$. A clear platy needle of dimensions 0.37 x 0.37 x 0.10 mm was used. 7212 Independent reflections were measured on a Siemens P4/RA diffractometer with Cu-K$_\alpha$ radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and all the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give $R_1 = 0.075$ and $wR_2 = 0.189$ for 4684 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 115°$] and 649 parameters.
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