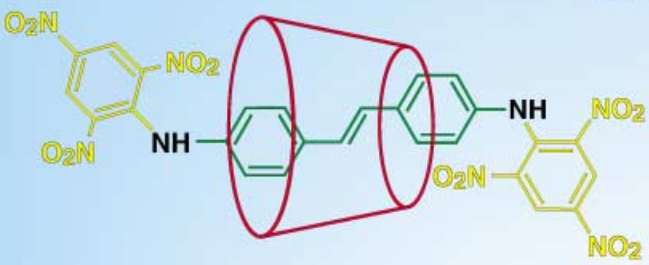
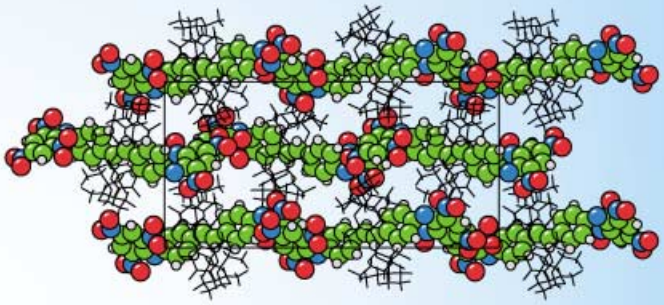
Self-assemblies of cyclodextrin rotaxanes form insulated and aligned molecular fibres resembling co-axial cables

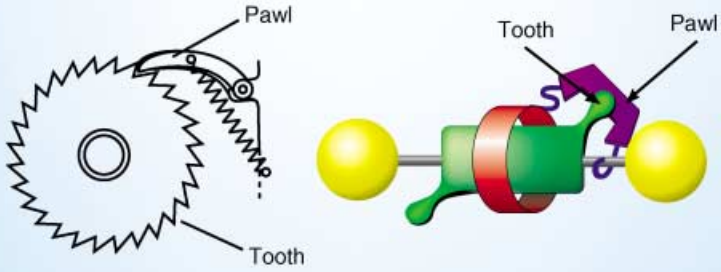


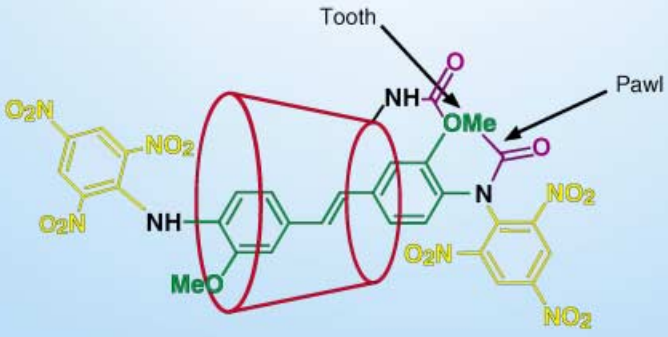
Molecular structure



Solid-state structure

Installation of a ratchet tooth and pawl restricts rotation in a cyclodextrin rotaxane





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Separated and Aligned Molecular Fibres in Solid State Self-Assemblies of Cyclodextrin [2]Rotaxanes

Hideki Onagi,[a] Benedetta Carrozzini,[b] Giovanni L. Cascarano,[b] Christopher J. Easton,*[a] Alison J. Edwards,[a] Stephen F. Lincoln,[c] and A. David Rae[a]

Abstract: The conformations of two [2]rotaxanes, each comprising α-cyclodextrin as the rotor, a stilbene as the axle and 2,4,6-trinitrophenyl substituents as the capping groups, have been examined in solution and in the solid state, using ^{1}H NMR spectroscopy and X-ray crystallography, respectively. In solution, introducing substituents onto the stilbene prevents the cyclodextrin from being localized over one end of the axle. Instead the cyclodextrin moves back and forth along the substituted stilbene. In the solid state, the axles of the rotaxanes form extended molecular fibres that are separated from each other and aligned along a single axis. The molecular fibres are strikingly similar to those formed by the axle component of one of the rotaxanes in the absence of the cyclodextrin, but in the latter case they are neither separated nor all aligned.

Keywords: cyclodextrins · nanostructures · rotaxanes · self-assembly · supramolecular chemistry

Introduction

Supramolecular chemistry is a key aspect of the growing interest in nanotechnology, and the associated development of nanomaterials, molecular machines and microelectronic devices.[1–7] It provides access to novel and complex structures, and allows for the prefabrication of molecular entities. In this regard, rotaxanes and catenanes are of particular interest since they comprise multiple species that are physically inter-locked and unable to dissociate.[8–12] For the full potential of such supramolecular species to be realised, it will be necessary to understand and be able to control their self-assembly in the solid state.[13] To this end, X-ray crystallography has been used to examine the structures of several catenanes,[8,14–18] rotaxanes,[8,19–26] pseudorotaxanes and pseudopolyrotaxanes.[18,27–31]

Cyclodextrins are particularly versatile building blocks for supramolecular chemistry, since they occur naturally in a range of sizes and are readily modified.[32,33] Many cyclodextrin-based rotaxanes have been synthesized,[34–38] and a number of crystal structures of cyclodextrin inclusion complexes have been reported,[39] but to the best of our knowledge there have been only two reports of crystal structures of cyclodextrin pseudopolyrotaxanes[40,41] and one of a cyclodextrin [2]rotaxane.[42] Previously we reported the synthesis of the rotaxane **1a** and an analysis of its conformation in solution.[43] In order to manipulate the conformation, we have now modified the stilbene moiety and synthesized the dimethoxystilbene derivative **1b**. We have also examined the solid-state structures of both the rotaxanes **1a** and **1b**, as well as that of the dumbbell component **2a** of the former, in order to explore the effects of cyclodextrin complexation and guest modification on self-assembly.

Results and Discussion

In our previous report, the yield of the rotaxane **1a** was given as 10%.[43] This has now been increased to 79%, mainly by improving the isolation procedure. The conformation of **1a** was determined using a variety of ^{1}H NMR ex-

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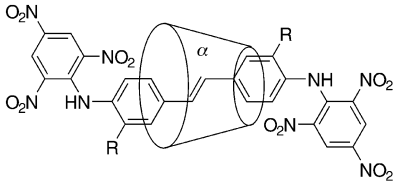
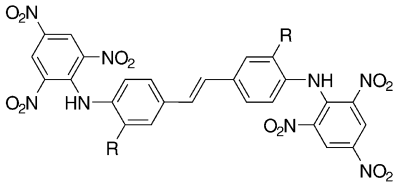


1a R = H
1b R = OMe



2a R = H
2b R = OMe

material revealed a single component, showing the characteristic ultraviolet absorbance of the dumbbell, and pink colouration of a cyclodextrin on exposure to acidic naphthalene-1,3-diol. The deprotonated molecular ion of the product was found at *m*/*z* 1663 by ESI-MS operated in the negative ion mode. These data clearly show that the isolated material is the mechanically interlocked molecule **1b**.

The conformation of the rotaxane **1b** was determined by employing 2D DQF-COSY and ROESY experiments, as outlined previously for the rotaxane **1a**.[43] As found for **1a**, with **1b** the simplicity of the resonances of the cyclodextrin protons in the 1D NMR spectrum shows that the cyclodextrin is freely rotating around the stilbene moiety. Figure 1b is a portion of the ROESY spectrum, which shows that, unlike the case with the rotaxane **1a**, the cyclodextrin of the dimethoxy-substituted rotaxane **1b** is not localized over one

periments, and is illustrated in Figure 1a together with a portion of the key ROESY NMR spectrum. With this rotaxane, the cyclodextrin is freely rotating around, but localized over, one end of the stilbene moiety. The free rotation is evident from the simplicity of the resonances of the cyclodextrin protons, and the localization is apparent through the observation of NOEs between the cyclodextrin protons and protons H(1)–H(5) of the stilbene, and the absence of any NOE between stilbene protons H(6) and the cyclodextrin protons.

It was considered that incorporation of a substituent in place of a stilbene H(1) proton would alter the conformation, due to buttressing between the substituent and the rim of secondary hydroxy groups of the cyclodextrin. To examine this, the rotaxane **1b** was prepared as outlined in Scheme 1. A mixture of the stilbene **6** and α-cyclodextrin, in aqueous buffer at room temperature and pH 10, was allowed to equilibrate for 2 h. 2,4,6-Trinitrobenzene-1-sulfonate (**7**) was then added and the mixture was stirred for a further 10 h. The crude product mixture was subjected to a Diaion HP-20 column to isolate the rotaxane **1b**, which was obtained in 27% yield as an orange powder. TLC of this

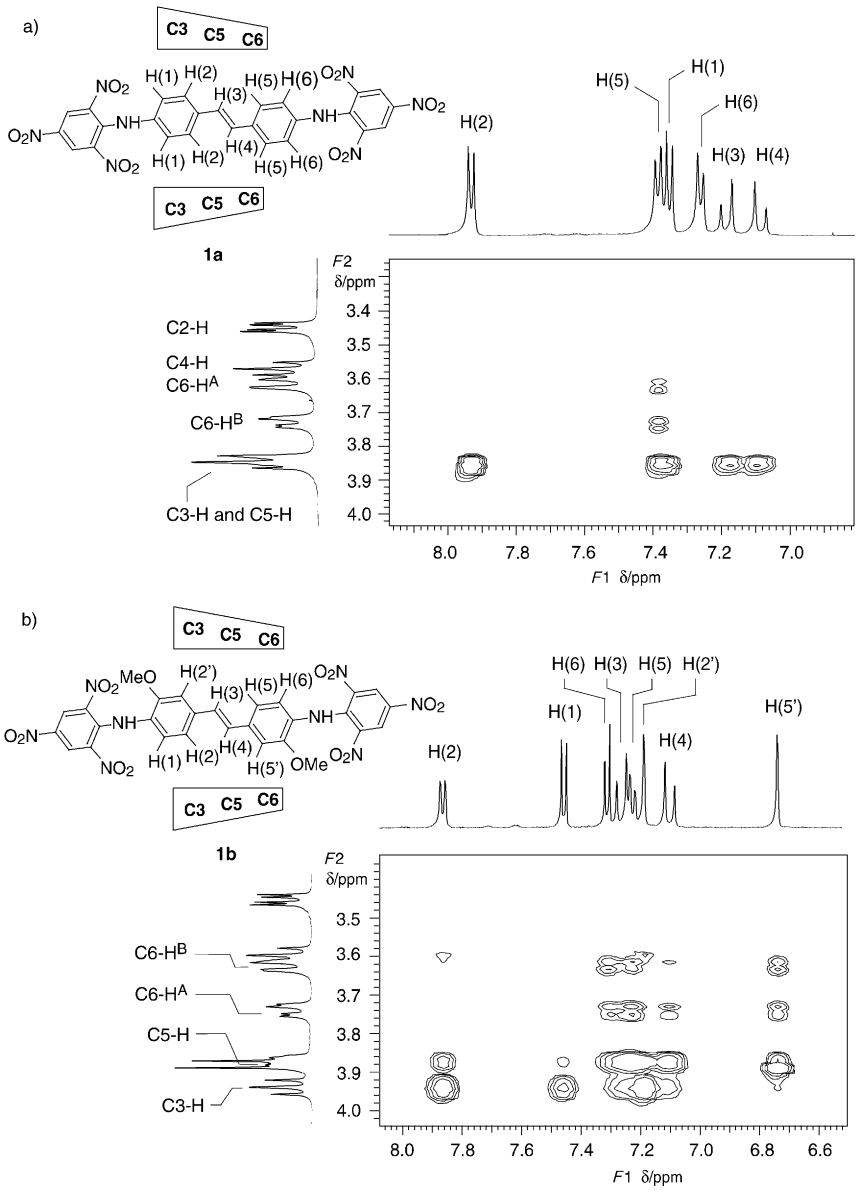
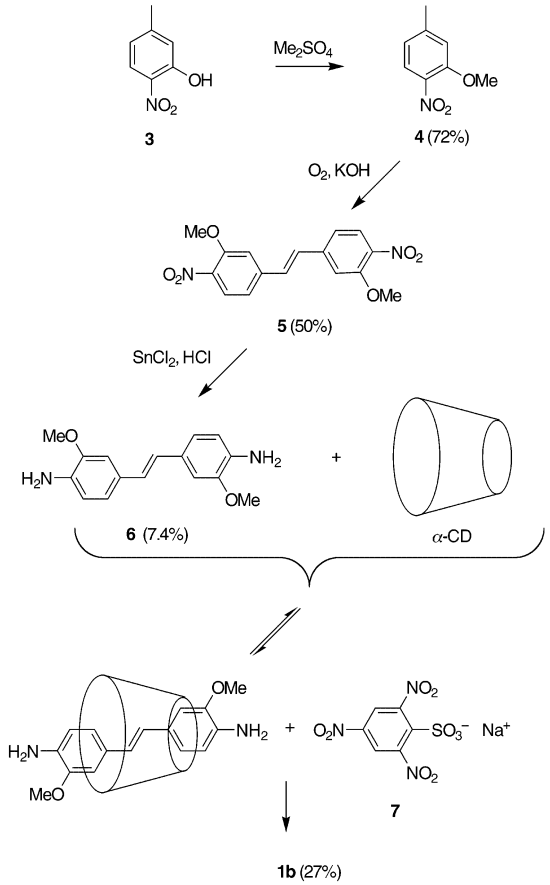


Figure 1. Resonance assignments and portions of the 500 MHz ROESY NMR spectra recorded in [D_4]-methanol with a mixing time of 250 ms for a) the rotaxane **1a** and b) the rotaxane **1b**.



Scheme 1.

end of the stilbene. Instead, the NOE cross-peaks indicate that the cyclodextrin is moving on the NMR time-scale, back-and-forth on the axle, from one end of the stilbene to the other. This accounts for the observation of: i) NOE cross-peaks between each of the stilbene protons and at least one type of the interior cyclodextrin-C3, C5 and C6 protons; ii) interactions of many of the stilbene protons with more than one type of cyclodextrin proton; and iii) NOEs between the cyclodextrin C6-H^A protons and H(4)–H(6) of the stilbene. The latter and their similar intensities in particular show that the cyclodextrin must be mobile, otherwise the H(4)–H(6) stilbene protons are too far apart to show NOEs with one type of cyclodextrin proton, given the inverse-dependence of NOE intensity on the sixth power of the distance between interacting protons.[44] This argument is based on the assumption that the axis delineated by the 4- and 4′-carbons of the stilbene is close to parallel to the C6 axis of symmetry of the cyclodextrin. In principle, the NOEs observed, including those between the cyclodextrin C6-H^A protons and H(4)–H(6) of the stilbene, could be explained if these axes were substantially out of alignment. Then the stilbene H(4), H(5) and H(6) protons could each rotate in a circle at a similar distance from the cyclodextrin C6-H^A protons. However, such a deviation of the axes from parallel is very unlikely considering the sizes and shapes of the cyclodextrin and stilbene. Thus the methoxy substituents of the rotaxane **1b** appear to affect its conformation in solution, increasing the mobility of the cyclodextrin along the stilbene axle.

The solid-state structures of the rotaxanes **1a** and **b** were also examined, through X-ray crystallographic analysis. For comparison, the solid-state structure of the stilbene derivative **2a** was also determined. The dumbbell **2a** had been prepared, in 85 % yield, through reaction of 4,4′-diaminostilbene with 2,4,6-trinitrobenzene-1-sulfonate (**7**).[43] In a similar manner, the dimethoxy-substituted dumbbell **2b** was obtained from the dimethoxystilbene **6**. However, repeated attempts to obtain crystals of the dumbbell **2b** suitable for analysis were not successful. Crystals of the analogue **2a** were obtained from *N*,*N*-dimethylformamide. Crystals of each of the rotaxanes **1a** and **b** were also prepared, by slow diffusion of methanol into saturated aqueous solutions, in sealed containers.

The crystallographic analysis of compounds **1a**, **1b** and **2a** was not straightforward and the procedures that were used are described in the Supporting Information. The structures thus determined are illustrated in Figure 2. Across all three structures there is a remarkable similarity in the mode of packing of the substituted stilbenes. This packing is dominated by a chain-like motif as shown in Figure 3. Each of the chains is inherently centrosymmetric. In the case of the dumbbell **2a**, each molecule is located about a crystallographic centre of inversion and adjacent molecules are likewise crystallographically related. In the rotaxanes **1a** and **1b**, the presence of the cyclodextrin precludes the occurrence of crystallographic centres of inversion. Nevertheless, the centrosymmetric relationship within the chains holds locally and is strictly followed.

The chains in the dumbbell **2a** are formed by molecules related by the translation $^1/_2+x$, $^3/_2+y$, z, and these chains then pack alongside equivalent chains to form layers lying parallel to the *ab* plane of the unit cell. Alternate layers are rotated about the crystallographic two-fold axis so that chains in adjacent layers are not parallel. By contrast, the chains formed from the rotaxanes **1a** and **1b** are separated from each other and all aligned parallel, along the crystallographic *b* axis. In the case of the rotaxane **1a**, the two crystallographically independent but quite similar conformations of the dumbbell component found in the asymmetric unit alternate along each chain. The cyclodextrins form head-to-head/tail-to-tail and head-to-tail/tail-to-head hydrogen-bonded columnar networks in the rotaxanes **1a** and **1b**, respectively. Each accommodates the chains of aligned and separated dumbbell components.

In summary, comparison with the structure of the stilbene derivative **2a** indicates that in the solid state the cyclodextrins of the rotaxanes **1a** and **1b** align and separate the chains formed by the dumbbell components. They do so without substantially altering the conformations of the dumbbell components or their intermolecular interactions along the chains. The result is self-assembled structures that resemble co-axial cables, with the cyclodextrins insulating but not otherwise affecting molecular fibres formed by the axles. Although the properties of the rotaxanes **1a** and **1b** as electrical conductors have not yet been examined, in

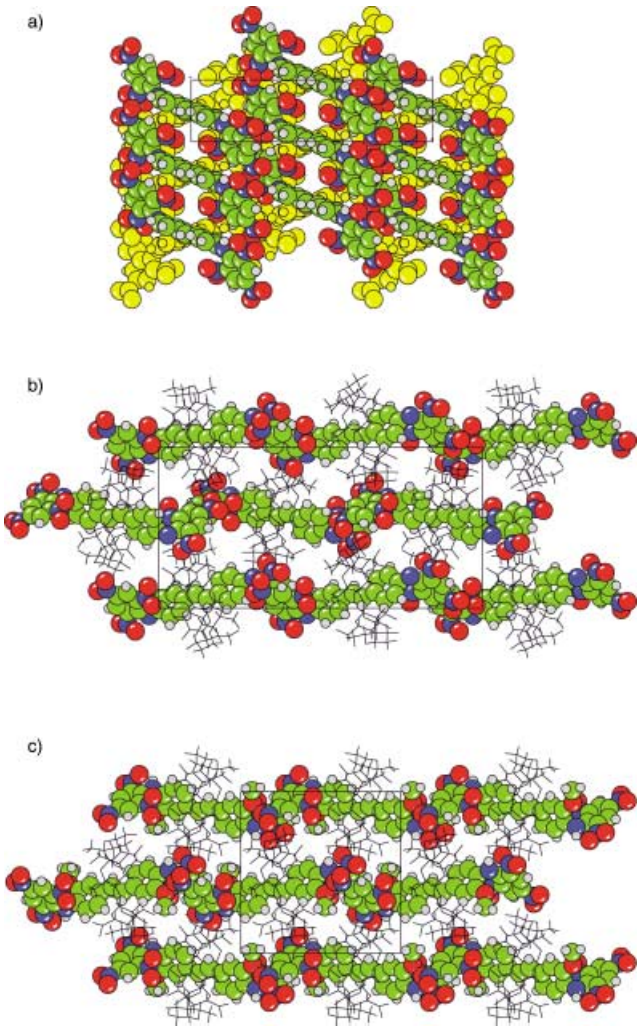


Figure 2. Solid-state structures of a) the dumbbell **2a**, and b) and c) the rotaxanes **1a** and **1b**, respectively, where the trinitrophenylamino-substituted stilbenes are represented by spheres and the cyclodextrins by lines.

analogous systems, Cacialli and co-workers[45] have recently demonstrated the insulating properties of the cyclodextrins of β-cyclodextrin-poly(*p*-phenylene) polyrotaxanes, to preserve the semiconducting properties of the *p*-phenylene polymer in the solid state. This supports speculation that such species might one day find applications in new-generation microelectronics.

Experimental Section

General: ^{1}H NMR spectra were recorded at 500 MHz using a Varian Inova 500 spectrometer or at 300 MHz using a Varian Mercury 300 spectrometer, and ^{13}C NMR spectra were recorded at 75.5 MHz using a Varian Inova 300 spectrometer. Rotating frame ^{1}H,^{1}H nuclear overhauser effect spectroscopy (ROESY) was performed with a mixing time of 250 ms. [D_4]Methanol with an isotopic purity of 99.8 % and [D_6]DMSO with an isotopic purity of 99.9 % were purchased from Cambridge Isotope Laboratories Inc., MA., and were referenced to $\delta = 3.31$ for ^{1}H and 49.15 for ^{13}C (CD_3OD) and $\delta = 2.50$ for ^{1}H ([D_6]DMSO) with respect to the resonance of Me_4Si. Electrospray ionization (ESI) mass spectrometry was carried out with a Micromass VG Quattro II mass spectrometer.

Thin-layer chromatography (TLC) was performed on Kieselgel 60 F_{254} coated plates (Merck). Developed plates were visualized by UV light and/or dipping the plate into a solution of 0.1 % naphthalene-1,3-diol in ethanol/water/H_2SO_4 200:157:43, followed by heating with a heat-gun. Elemental analyses were performed by the Australian National University Microanalytical Service. Melting points were performed on a Reichert hot-stage apparatus and are uncorrected.

α-Cyclodextrin was the generous gift of Nihon Shokuhin Kako Co., Japan. It was recrystallized from water and dried in vacuo over P_2O_5 to constant weight before use. 2,4,6-Trinitrobenzene-1-sulfonic acid sodium salt dihydrate (TNBS) (**7**) was purchased from Tokyo Kasei. 5-Methyl-2-nitrophenol (**3**) was purchased from Aldrich Chemical Company. Diaion HP-20 resin was purchased from Supelco, PA, USA.

[(*E*)-4,4′-Bis(2,4,6-trinitrophenylamino)stilbene]-[α-cyclodextrin]-[rotaxane] (1a): The [2]rotaxane **1a** was prepared as reported previously[43] except that the crude product was dissolved in water and the solution was loaded onto a Diaion HP-20 column (310 × 25 mm). The column was flushed with water until no more unreacted α-cyclodextrin was detected

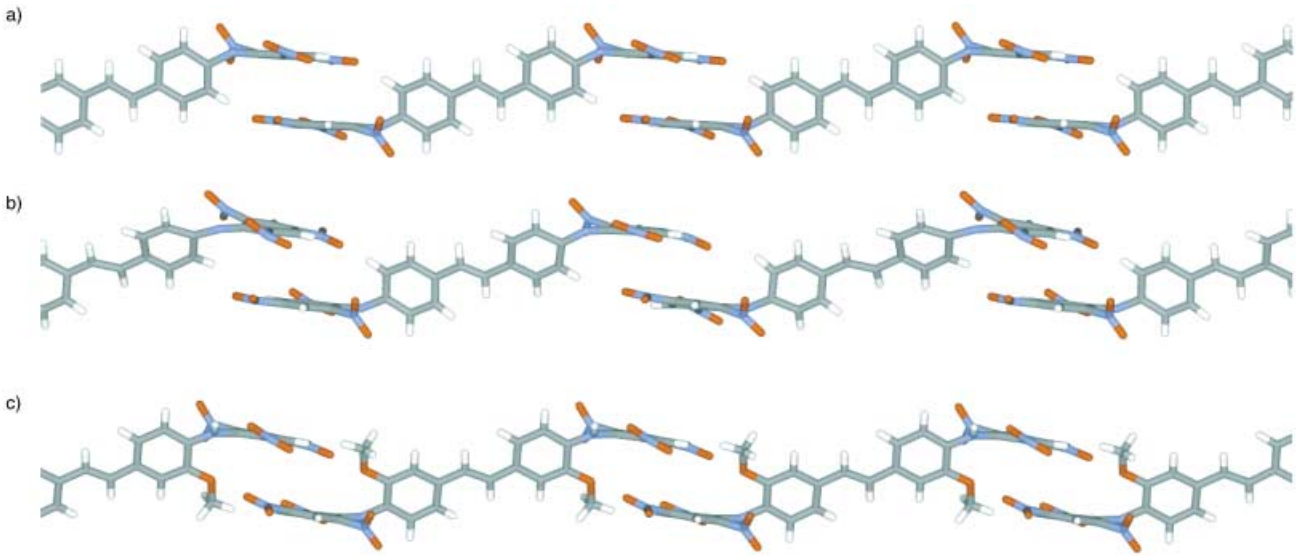


Figure 3. The chain-like motif formed by the trinitrophenylamino-substituted stilbenes in the solid state structures of a) the dumbbell **2a**, and b) and c) the rotaxanes **1a** and **1b**, respectively.

in the eluent by TLC (ca. 2.5 dm^3). The column was then eluted with a water/methanol gradient. The rotaxane **1a** was obtained when the column was eluted with 50–70% methanol. The fractions containing this material were concentrated under reduced pressure and the residue was lyophilized to give a red powder in 79% yield, with physical and spectroscopic properties consistent with those reported previously.[43]

3-Methoxy-4-nitrotoluene (4): Dimethyl sulfate (80 g, 0.63 mol) was added to a stirred mixture of 5-methyl-2-nitrophenol (**3**) (25.0 g, 0.16 mol) and potassium carbonate (36 g) in xylenes (100 mL) which was heated under reflux. After 20 h at reflux, additional dimethyl sulfate (25 g, 0.20 mol) was added. After a further 4 h at reflux, the mixture was cooled and aqueous sodium hydroxide (0.75 mol L^{-1}, 1.0 L) was added. The solvent was then removed by distillation. Water (100 mL) was added to the residue and the solution was extracted with diethyl ether. The ether extracts were dried over $MgSO_4$ and concentrated under reduced pressure to yield the toluene **4** as a tan solid (37.7 g, 72%). M.p. 58–61 °C [lit.:[46] 61 °C]; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.76 (d, J = 8.2 Hz, 1H; ArH), 6.86 (s, 1H; ArH), 6.79 (d, J = 8.2 Hz, 1H; ArH), 3.92 (s, 3H; OMe), 2.39 (s, 3H; Me); MS (EI): m/z (%): 167 (100) [M^+], 137 (22), 120 (72), 91 (37), 78 (15).

(*E*)-3,3′-Dimethoxy-4,4′-dinitrostilbene (5): A solution of the toluene **4** (3.0 g, 0.018 mol) in acetone (4.5 mL) was added to a stirred solution of KOH (50 g) in methanol (150 mL) maintained at 10 °C. Oxygen was bubbled through the mixture while it was stirred at 10 °C for 2 h, then the mixture was poured into water (500 mL). The resultant precipitate was collected by filtration, and washed with water, then methanol and then dichloromethane. The solid residue was recrystallized from chlorobenzene to yield the stilbene **5** as a tan solid (1.5 g, 50%). M.p. 215–240 °C [lit.:[47] 190–240 °C]; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.94 (d, J = 8.5 Hz, 2H; ArH), 7.59 (s, 2H), 7.58 (d, J = 1.5 Hz, 2H; ArH), 7.37 (dd, J = 1.5 and 8.5 Hz, 2H; ArH), 3.99 (s, 6H; OMe); MS (EI): m/z (%): 330 (100) [M^+], 300 (7), 175 (11), 165 (17), 152(7).

(*E*)-4,4′-Diamino-3,3′-dimethoxystilbene (6): A mixture of the dinitrostilbene **5** (1.5 g, 9.0 mmol) and $SnCl_2$ (7 g, 7.2 mmol) in conc. HCl (7 mL) and acetic acid (6 mL) was heated at reflux for 4 h, then it was cooled, and poured into ice-cold water (150 mL). The resultant precipitate was collected by filtration. Recrystallization from ethanol yielded the stilbene **6** as tan flakes (180 mg, 7.4%). M.p. 157 °C [lit.:[47] 148–150 °C]; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 6.97 (d, J = 1.6 Hz, 2H; ArH), 6.81 (dd, J = 1.6 and 8.2 Hz, 2H; ArH), 6.79 (s, 2H), 6.56 (d, J = 8.2 Hz, 2H; ArH), 4.80 (s, 4H; NH_2), 3.79 (s, 6H; OMe); MS (EI): m/z (%): 270 (100) [M^+], 238 (6), 223 (8), 210 (7), 195 (8), 135 (7).

[(*E*)-4,4′-Bis(2,4,6-trinitrophenylamino)-3,3′-dimethoxystilbene]-[α-cyclodextrin]-[rotaxane] (1b): A mixture of α-cyclodextrin (1.8 g, 1.85 mmol) and the diaminostilbene **6** (100 mg, 0.37 mmol) in carbonate buffer (0.2 mol L^{-1}, pH 10, 25 mL) was stirred at room temperature for 2 h. TNBS **7** (260 mg, 0.74 mmol) was then added and the mixture was stirred at room temperature for 10 h. The resulting dark red solution was washed with ethyl acetate (5 × 25 mL), then it was concentrated under reduced pressure. The residue was dissolved in water (50 mL) and the solution was applied to a Diaion HP-20 column (310 × 25 mm). The column was flushed with water until no more unreacted α-cyclodextrin was detected in the eluent by TLC (ca. 2.5 L). The column was then eluted with a water–methanol gradient. The rotaxane **1b** was obtained when the column was eluted with 50–70% methanol. The fractions containing this material were concentrated under reduced pressure and the residue was lyophilized to give a red powder (165 mg, 27%), TLC (*n*-butanol/ethanol/H_2O 5:4:3): R_f = 0.65 (relative to the solvent front); ^{1}H NMR (500 MHz, CD_3OD): δ = 9.09 (s, 2H; trinitrophenyl), 8.99 (s, 2H; trinitrophenyl), 7.85 (d, J = 8.5 Hz, 1H; stilbene), 7.44 (d, J = 8.5 Hz, 1H; stilbene), 7.28 (d, J = 8.5 Hz, 1H; stilbene), 7.24 (d, J_{trans} = 16.0 Hz, 1H; stilbene), 7.21 (d, J = 8.5 Hz, 1H; stilbene), 7.17 (s, 1H; stilbene), 7.08 (d, J_{trans} = 16.0 Hz, 1H; stilbene), 6.72 (s, 1H; stilbene), 4.92 (d, $J_{1,2}$ = 3.5 Hz, 6H; cyclodextrin-C1-H), 3.91 (apparent t, J = 9.5 Hz, 6H; cyclodextrin-C3-H), 3.87–3.84 (m, 6H; cyclodextrin-C5-H), 3.87 (s, 3H; OMe), 3.85 (s, 3H; OMe), 3.73 (m, 6H; cyclodextrin-C6-H), 3.61 (m, 6H; cyclodextrin-C6-H′), 3.58 (apparent t, J = 8.5 Hz, 6H; cyclodextrin-C4-H), 3.44 (dd, J = 3.5 and 9.5 Hz, 6H; cyclodextrin-C2-H); ^{13}C NMR (75.5 MHz, CD_3OD): δ = 153.9, 153.7 140.2, 140.0, 139.8, 139.6, 137.9, 137.1, 136.7, 136.6, 131.0, 129.5, 128.0, 127.5, 127.4, 127.2, 126.1, 124.3, 120.0, 117.9, 113.6, 113.5, 104.2, 83.3, 75.2, 74.0, 74.0 (two coincident resonances), 61.8, 57.5, 57.4; MS (ESI, −ve): m/z: 1663 [$M-H^+$]; elemental analysis calcd (%): for $C_{64}H_{80}N_8O_{44}\cdot 5H_2O$: C 44.24, H 5.11, N 6.45, found C 44.29, H 5.24, N 6.42.

Crystallographic analysis of the rotaxanes 1a and 1b, and the dumbbell 2a: Crystals of the rotaxanes **1a** and **1b** suitable for single crystal X-ray diffraction studies were grown by slow diffusion of methanol into saturated aqueous solutions. Those of the dimethoxystilbene derivative **1b** were of a remarkably uniform tetrahedral morphology and size. Crystals of the dumbbell **2a**[43] were obtained from *N*,*N*-dimethylformamide. None of the crystals was strongly diffracting. At the 3σ level, **1a** had less than 50% of reflections to $2\Theta = 45°$ observable, **1b** had 70% observable to $2\Theta = 48°$ and **2a** had 80% to $2\Theta = 46°$. Data were collected by means of CCD images on a Nonius KappaCCD single crystal diffractometer,[48] with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), and extracted using routine methods,[49] before being corrected for absorption.[50] The principal crystallographic data are shown in Table 1. Procedures used to solve[51,52] and refine[53] the structures are described in Supporting Information.

Table 1. Principal crystallographic data for the rotaxanes **1a** and **1b** and the dumbbell **2a**.

	1a	**1b**	**2a**
formula	$C_{62}H_{76}N_8O_{42}$	$C_{64}H_{80}N_8O_{44}$	$C_{26}H_{16}N_8O_{12}\cdot 2C_3H_7NO$
M_r	1605.30	1665.36	778.66
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$C2/c$
a [Å]	13.4291(2)	13.4266(5)	29.2792(6)
b [Å]	17.6940(3)	17.8128(8)	6.8221(2)
c [Å]	35.7701(7)	18.4482(7)	18.7367(6)
β [°]	95.0575(7)	107.410(3)	114.7760(11)
V [Å^3]	8466.4(3)	4210.0(3)	3398.1(3)
Z	4	2	4
T [K]	200	125	200

CCDC-213579 (**1a**), -213578 (**1b**) and -213580 (**2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Acknowledgements

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