Crystal structure of an azo dye rotaxane

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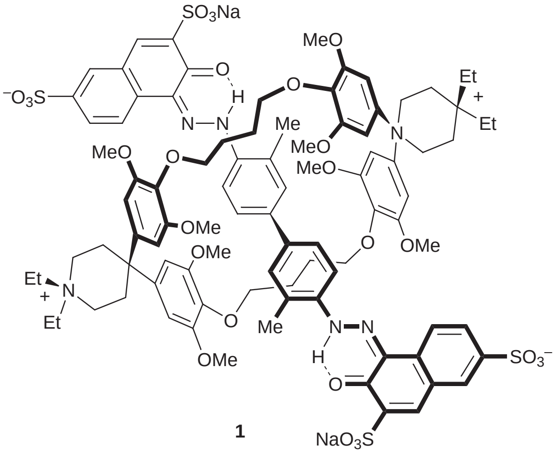
The crystal structure of an anionic azo dye rotaxane shows that the cyclophane embraces the centre of the dye; sodium coordinates to both the dye and the cyclophane, as well as DMSO solvent molecules, resulting in an infinite poly-rotaxane network.

Recently we prepared the first azo dye rotaxanes, by an azo-coupling reaction in water, using hydrophobic binding to ensure that the dye was formed threaded through the cyclophane.[1]



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Formation of rotaxane encapsulated dyes, such as **1**, allows the environment of the chromophore to be precisely controlled, which may lead to dyes with enhanced chemical and photochemical stability. Here we present the first crystal structure of a rotaxane of this type. Despite the industrial importance of anionic sulfonated naphthalene azo dyes, few crystal structure determinations of these dyes have been reported, which reflects their reluctance to form suitable crystals.[2] The crystal structure of **1** provides valuable insights into the conformational behaviour of both the azo dye and cyclophane components, and shows how these units interact.

Slow diffusion of butanone into a saturated solution of **1** in DMSO and *n*-butanol gave small single crystals suitable for analysis by synchrotron X-ray diffraction at 160 K.† The crystals were highly solvated; six water and five DMSO molecules were located in the asymmetric unit, which contains one rotaxane molecule. **1** crystallises in a centrosymmetric space group P1. The unit cell contains both enantiomeric conformations of the rotaxane. The cyclophane embraces the centre of the dye as shown in Fig. 1. There are no face-to-face stacking π–π interactions between the biphenyl and the cyclophane, but there may be edge-to-face interactions between the four central hydrogens of the biphenyl and the cyclophane aromatic rings (H–centroid distances are 2.87, 3.17, 3.20 and 3.27 Å).[3]

The two ends of the azo dye dumbbell have essentially the same geometry; average bond lengths are shown on Fig. 2. A sodium cation chelates between the β-naphthol oxygen and the sulfonate, yet, like most β-naphthol azo dyes,[2a,b,4] this dye is predominantly the hydrogen-bonded hydrazone, rather than azo, tautomer (Scheme 1). This is evident from the short C–O bond (1.25 Å; *cf.* 1.36 Å in PhOH and 1.21 Å in cyclohexanone),[5] short C_α–N bond (1.33 Å; *cf.* 1.24 Å in *E*-azobenzene[6] and 1.39 Å in 1,2-diphenylhydrazine[7]) and long C_α–C_β bond (1.45 Å; *cf.* 1.37 Å in naphthalene[8] and 1.52 Å in cyclohexane[9]).‡ Each half of the dye is approximately planar, with twists of 8.6 and 6.7° about the N–N linkages; the twist about the biphenyl link is 39.8°. The methyl of the tolidine resides near the β-naphthol oxygen, as observed in solution by NMR spectroscopy.[1]

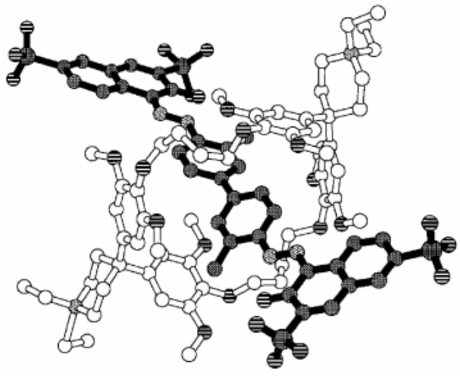


Fig. 1 Molecular structure of rotaxane **1**, not showing solvent molecules, hydrogen atoms and sodium cations.

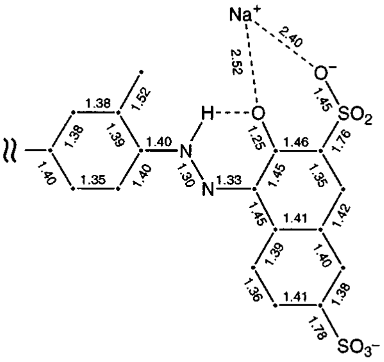
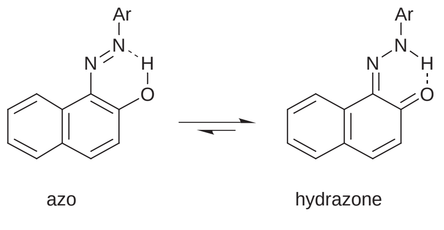


Fig. 2 Average bond lengths (Å) in the azo dye dumbbell componentof **1**.



Scheme 1

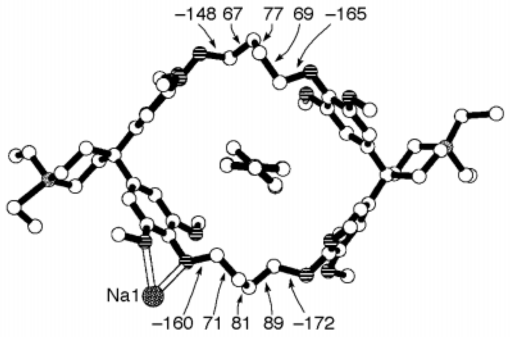


Fig. 3 Structure of the cyclophane component of **1**, showing selected torsion angles (°), viewed down the axis of the biphenyl unit of the dye, which is shown at the centre.

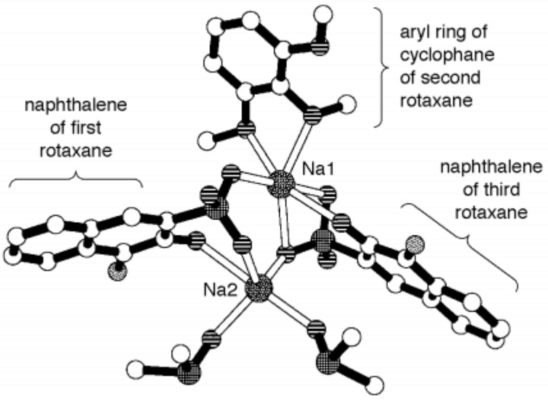


Fig. 4 Two sodium cations coordinate to two anionic dyes; Na1 also binds to the oxygens of the cyclophane of another rotaxane unit, while Na2 binds two DMSO molecules, giving irregular six- and five-coordination geometries.

The conformation of the cyclophane is remarkably convoluted. Both $O(CH_2)_4O$ links are in helical $ag^+g^+g^+a$ conformations, as shown by the torsion angles in Fig. 3. This allows the cyclophane to contract round its guest, which explains how it binds strongly to guests which seem too small to fill the cavity. Three previous crystal structures of cyclophanes of this type have $O(CH_2)_4O$ links with three *anti* and two *gauche* bonds.[10] A sodium cation (Na1) chelates to two *ortho* oxygens on one ring of the cyclophane, twisting it away from the cavity.

Pairs of sodium cations act as a 'glue', binding together the naphthalenes of two separate dyes and a cyclophane of a third rotaxane, as shown in Fig. 4. One sodium cation (Na2) is also coordinated by two DMSO solvent molecules. The Na–O interactions marked in Fig. 4 are in the range 2.24–2.60 Å (mean 2.39 Å); the next shortest Na–O distance is 3.25 Å. Thus the dyes are linked together, generating one-dimensional polymeric strands in the direction of the *a*-axis. Sodium coordination to the cyclophane links these strands together in the *b*-direction, to form double strand ladders. Electrostatic attraction between sulfonates and diethylammonium groups locks these ladders together in the *c*-direction (Fig. 5). Many features of the polyrotaxane network may be unique to this crystal structure, but the conformations of the azo dye and the cyclophane, and the coordination of both components with sodium, are relevant to the behaviour of molecules of this type in solution.

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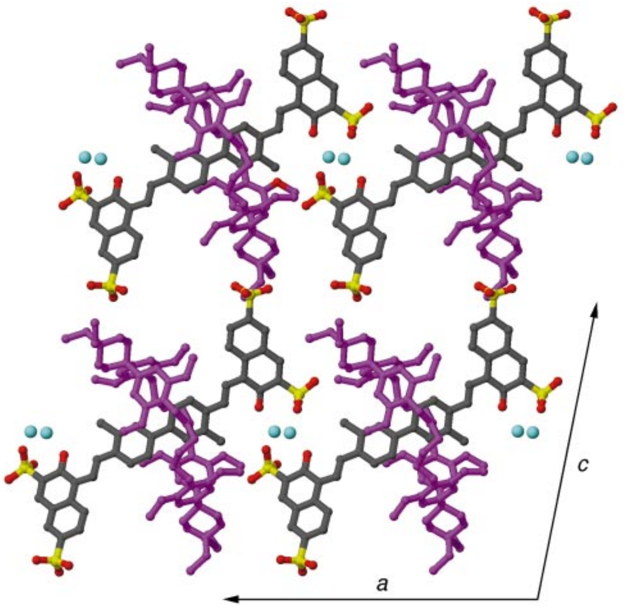

Fig. 5 Packing diagram showing four molecules of **1** in the *ac* plane (Na: blue, O: red, S: yellow and cyclophane: magenta; solvent molecules not shown).

Notes and references

† *Crystal data* for **1**·5DMSO·6H_2O: $C_{102}H_{148}N_6Na_2O_{37}S_9$, $M = 2384.8$, triclinic, space group $P1$, $a = 17.1896(12)$, $b = 12.3108(14)$, $c = 19.7639(14)$ Å, $\alpha = 100.579(2)$, $\beta = 101.242(2)$, $\gamma = 98.719(2)°$, $U = 6204.7(8)$ Å^3, $Z = 2$, $\lambda = 0.6865$ Å, $\mu = 0.25$ mm^{-1}, $T = 160$ K, $R1 = 0.140$ for 12142 'observed reflections' [$F^2 > 2\sigma(F^2)$] and $wR2 = 0.418$ for all 21076 unique reflections ($\theta < 50°$). Disorder in DMSO and water molecules could be only approximately modelled, with the aid of partial occupancies and restraints on geometrical and displacement parameters, and there is residual electron density of up to 1.63 e Å^{-3}. Methods and programs were as described elsewhere (ref. 11). CCDC 182/1039.

‡ Estimated standard deviations in bond lengths and angles involving C, N and O atoms are 0.01–0.02 Å and 0.5–1.0°.

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