[2]Catenane or not [2]Catenane?

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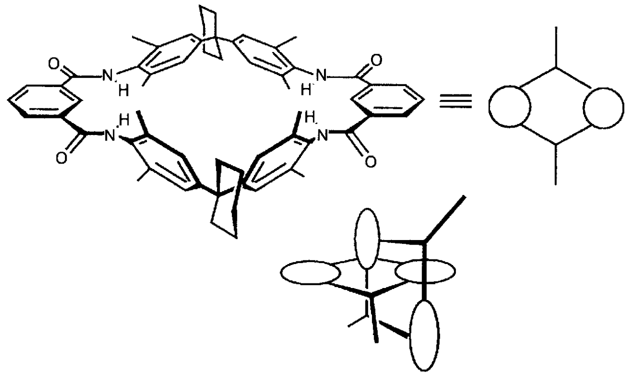
The X-ray crystal structure of a [2]catenane is reported; the two cycles which comprise the link are related by crystallographic symmetry, so only when a packing diagram is generated is the interlocked structure revealed.

A few years ago, we reported the structure determination of a [2]catenane **1** using two-dimensional NMR.[1] The structure revealed a number of hydrogen-bonding interactions between the amide groups of the macrocycles, which are presumably responsible for templating the synthesis of the interlocked ring structure. Although the NMR data was of sufficient quality to demonstrate that **1** is a catenane, there were some ambiguities in its conformation and the number of hydrogen bonds between the two macrocycles which could not be resolved. In addition, molecular mechanics calculations gave a conformation which conflicted with some of the NMR data. Since then a number of other catenanes in this family have been reported, but no X-ray crystal structure of these unusual molecules has yet been published.[2,3]

Compound **1** is a white solid which, on slow evaporation from chloroform solution, yields very large rhombohedral crystals. However, these crystals lose solvent extremely rapidly on removal from the mother liquor, and despite repeated attempts by several groups over four years, we have never obtained a good data set. Low-temperature data collection was not possible as the crystals degraded on cooling. Recently, we found that recrystallisation from CH_2Cl_2–MeOH–MeCOMe gave more stable crystals which, when coated in glue, survived for one week at room temperature. Although decomposition during data collection led to a rather large *R* factor, the X-ray crystal structure which we have determined does unequivocally show that **1** is a [2]catenane.†

When the structure was first solved, we were surprised to find that the lowest symmetry element in the crystal consists of a single macrocycle as shown in Fig. 1. However, on generating a packing diagram of all symmetry-related macrocycles in the unit cell, the interlocked [2]catenane structure was revealed (Fig. 2). The two macrocycles which make up the catenane are identical and are related by crystallographic symmetry. The two rings are locked together by a total of six hydrogen bonds. This structure and conformation are exactly the same as determined by NMR and differ significantly from the molecular mechanics structure we reported previously.[1] In each macrocycle, one isophthaloyl subunit has its amide groups *cis* to another, forming a pocket to hydrogen bond to the carbonyl of the other macrocycle, but the other isophthaloyl subunit adopts a *trans* conformation.



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The solvent molecules in the crystal could not be located. The catenanes are connected in the crystal by a network of hydrogen-bonding interactions. The outwardly-directed amide NH of the 'inside' isophthaloyl group [N(1) in Figs. 1 and 2] forms a hydrogen bond to a carbonyl of the 'outside' isophthaloyl group [O(3) in Figs. 1 and 2] of another catenane. The ground state conformation of the catenane is chiral, but both enantiomeric conformations are present so the crystal is overall achiral.

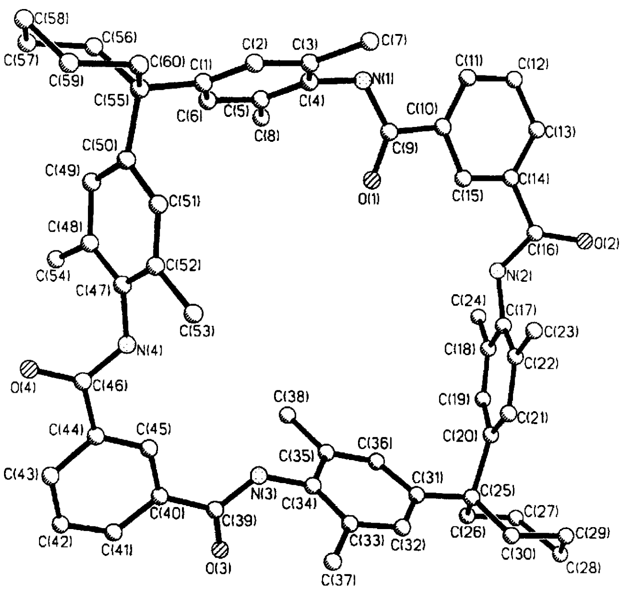

Fig. 1 The molecular structure of the lowest symmetry element in the crystal structure of **1**

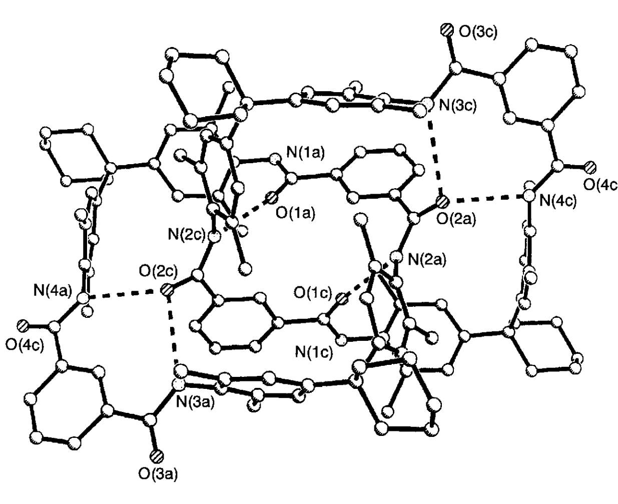

Fig. 2 The molecular structure of **1** revealed by generating two macrocycles related by crystallographic symmetry. The lengths of the hydrogen bonds shown are: O(2c)–N(4a) = O(2a)–N(4c) = 3.132, O(2c)–N(3a) = O(2a)–N(3c) = 3.225, O(1a)–N(2c) = O(1c)–N(2a) = 2.891 Å.

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Footnote

† *Crystal data* for $C_{120}H_{126}N_8O_8$: M = 1808.29, crystallises from dichloromethane–methanol–acetone as colourless blocks; crystal dimensions 0.66 × 0.50 × 0.35 mm, monoclinic, a = 23.607(13), b = 17.176(6), c = 35.85(2) Å, β = 105.96(4)°, U = 13977(11) Å^3, Z = 4, D_c = 0.859 g cm^{-3}, space group $C2/c$, Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-Kα) = 0.054 mm^{-1}, $F(000)$ = 3864. Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 40°$ on a Siemens P4 diffractometer by the omega scan method. The 2978 independent reflections (of 6425 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.1723 ($wR2$ = 0.4553, for all 6425 data, 614 parameters, mean and maximum δ/σ 0.000, 0.140), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.415 and 1.318 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 0.000P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93 as implemented on the Viglen 486dx computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 C. A. Hunter, *J. Am. Chem. Soc.*, 1992, **114**, 5303.

2 F. Vögtle, S. Meier and R. Hoss, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1619; F. Vögtle and R. Hoss, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 375; F. Vögtle, S. Ottens-Hildebrandt, S. Meier and W. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1767.

3 F. J. Carver, C. A. Hunter and R. J. Shannon, *J. Chem. Soc., Chem. Commun.*, 1994, 1277.