Inclusion Complexation of 1,4-Dioxan by an Azaparacyclophane; an *X*-Ray Crystallographic Study

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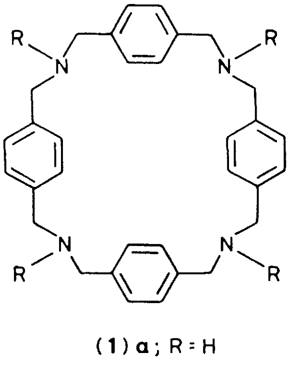
An *X*-ray crystallographic study shows that 1,4-dioxan forms a 1 : 1 complex *via* incorporation within the dish cavity of the host *N,N′,N″,N‴*-tetramethyl-2,11,20,29-tetra-aza[3.3.3.3]paracyclophane.

The design of polyfunctional host molecules for the *specific complexation* of guest species is an area of immense importance. In this context, we have had occasion to examine functionalised derivatives of the paracyclophane (**1**). Several di- and tetra-*N*-alkyl derivatives of this compound[1,2] and related systems[3,4] have been reported elsewhere. Urushigawa *et al.*[2] showed that the tetra-*N*-methyl derivative (**1b**) formed microanalytically pure benzene and 1,4-dioxan solvates. Herein, we report an *X*-ray crystallographic study of the latter, complex (**2**).



(**1**) **a**; R = H
b; R = Me

The host–guest complex (**2**) crystallised from dioxan to form a 1 : 1 solvate. *Crystal data:* Crystals of the complex, $C_{36}H_{44}N_4 \cdot C_4H_8O_2$, $M = 620.9$, are monoclinic, $a = 25.091(4)$, $b = 5.691(1)$, $c = 13.440(3)$ Å, $\beta = 112.06(2)°$, $U = 1779$ Å^3, space group $C2$, $Z = 2$, $D_c = 1.16$ g cm^{-3}. A total of 1340 independent reflections ($\theta \leqslant 58°$) were measured on a diffractometer using Cu-K_α radiation and of these 83 had $|F_o| < 3\sigma(|F_o|)$ and were classed as unobserved. The structure was solved by direct methods and refined anisotropically to $R = 0.056$.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

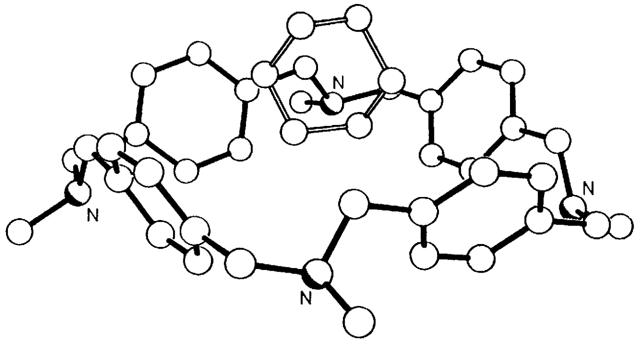

Figure 1. The molecular structure of the 1 : 1 complex of (**1b**) with 1,4-dioxan.

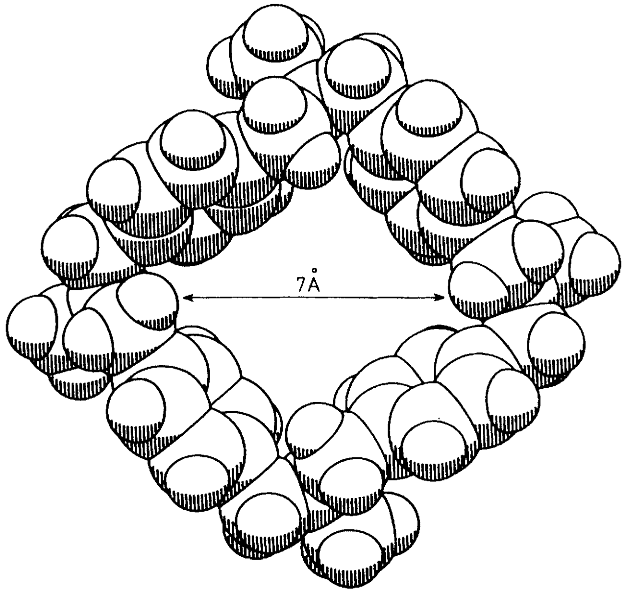

Figure 2. Space-filling drawing of the host in the complex (**2**) viewed down the crystallographic C_2 axis.

The complexed host molecule (Figure 1) adopts a 'dished' conformation with the planes of the aromatic rings nearly equally inclined (27.4 and 28.2°) to the crystallographic C_2 axis which passes through the centre of the macrocycle. Despite this dishing of the molecule, inspection of the space-filling representation of the host (Figure 2) shows there is still a significant free passage through the centre of the macrocycle. The molecules pack one above the other producing a continuous channel along the *b* direction. The maximum and minimum channel clear pathways are 7.0 and 4.4 Å respectively. A consequence of the dished conformation of the molecules and their packing one above another is the production of a 'cone in cone' structure (Figure 3) resulting in a widening of the channel from *ca.* 5 Å to a maximum of *ca.* 7 Å in the region between each layer of molecules and producing secondary cavities within which the guest dioxan molecules are located. These cavities are larger than are necessary to tightly hold the dioxan molecules which, as a consequence, adopt slightly differing orientations within each cavity.

This structural arrangement is similar to that observed for the complexation of durene by 1,6,20,25-tetra-aza[6.1.6.1]-paracyclophane.[4] However, in that instance the planes of the aromatic rings were parallel and the durene molecule inserted completely into the centre of the macrocycle. However in the complex (**2**) the host has appreciable conformational flexibility and hence the potential to adapt to include a wide range of guest species.

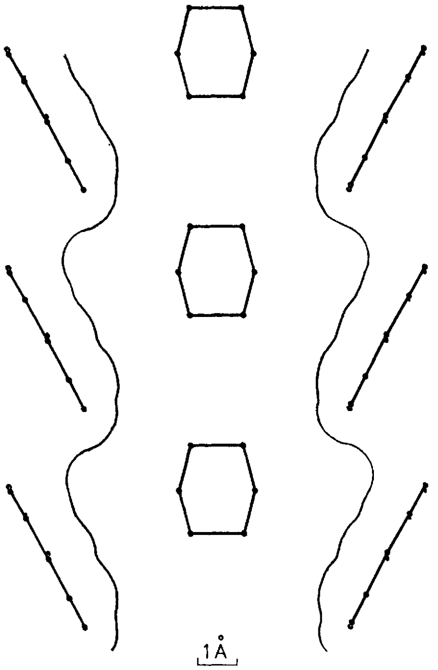

Figure 3. Cross-section of the channel showing the 'cone-in-cone' structure, the environment of the dioxan molecule, and the van der Waals' surface.

Inclusion complexation of this type is in striking contrast to that exhibited by the closely related tricyclic compounds such as tri-*o*-thymotide[5] and differently substituted trianthranilide derivatives.[6] In these, the channels or cavities are created by the packing of the molecules, *i.e.* in the intermolecular regions, whilst in the complex (**2**) they are created either partially or completely within the molecules themselves, *i.e.* intramolecularly.

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