

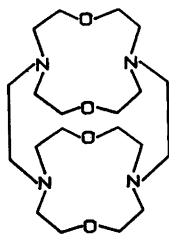
Short Communications

The Crystal Conformation of 1,10-Dimethyl-7,16,21,26-Tetraoxa-1,4,10,13-Tetraazatricyclo-[11.5.5.5.^{4,10}]octacosane Diiodide Hemihydrochloride Hemihydrate at -130°C

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The crystal structures of the free doubly N,N' -bridged bis(1,7-dioxa-4,10-diazacyclododecane) and its dihydrochloride dihydrate have recently



been determined.¹ The free ligand was treated with methyl iodide in order to explore contingent effects on the ring conformation caused by methylation. As no definite conclusion on this point could be reached spectroscopically, an X-ray crystal structure analysis was undertaken. This revealed that the reaction product was contaminated with hydrochloride and had taken up water. The results of the analysis are now reported.

The crystals of $\text{C}_{22}\text{H}_{44}\text{N}_4\text{O}_4^{2+} \cdot 2\text{I}^- \cdot \frac{1}{2}\text{HCl} \cdot \frac{1}{2}\text{H}_2\text{O}$ belong to the monoclinic system with space group Cc , cell dimensions $a=21.656(7)$, $b=8.410(4)$, $c=21.078(7)$ Å, $\beta=128.27(2)^{\circ}$, and $Z=4$ ($D_x=1.56$ g cm^{-3} , $D_m=1.55$ g cm^{-3}). With $2\theta_{\text{max}}=50^{\circ}$ and $\text{MoK}\alpha$ -radiation 3778 independent reflections were measured on an automatic four-circle diffractometer at *ca.* -130°C . Using an observed-unobserved cutoff at $2.5\sigma(I)$, 2261

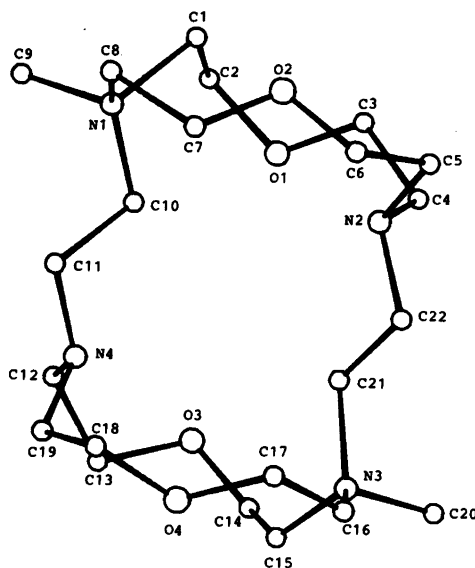
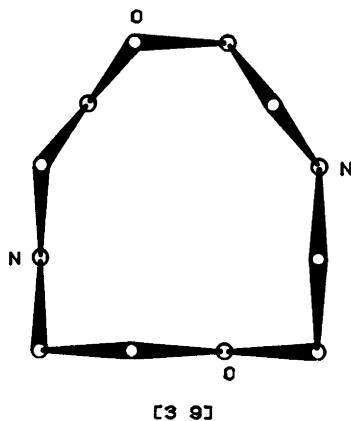


Fig. 1. Schematic drawing showing the numbering of atoms.

reflections were recorded as observed. The intensity data were corrected for absorption [$\mu=2.19$ mm^{-1} , crystal size (0.3×0.2×0.1)mm]. However, for unknown reasons the final R -values were about 1% higher than those arrived at when refining with uncorrected intensities, and therefore the latter were used.

The structure was solved by direct methods² and refined by full-matrix least squares technique.³ All programs used (except those for phase determination) are included in Ref. 3]. Methyl hydrogen atoms were localized in a difference Fourier map. A small peak (about 0.9 Å from N) was taken as the hydrochloride "half-hydrogen". Peaks corresponding to water half-hydrogens did not show up. Other H-atom positions were calculated. These atoms were included in structure factor calculations, but not refined. Anisotropic temperature factors were introduced for iodine and chlorine, while other non-hydrogen atoms were refined isotropically. Weights in least squares were calculated from the

standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I)=[C_T+(0.02 C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N the net count. The final R -value was 3.5% ($R_w=4.3\%$) for 2261 observed reflections. Final fractional coordinates for non-hydrogen atoms are given in Table 1. Within the large estimated limits of error (due to the presence of iodine), the bond distances and angles of Table 2 are normal. Fig. 1 is a schematic drawing, showing the numbering of atoms. The torsional angles of Table 3 show that both 12-membered rings adopt the [3 9] conformation⁴ which is different from the [2 10] conformation of the free ligand,¹ but has been observed earlier.^{1,5,6}



It may be pointed out that the torsion angles $N1-C10-C11-N4$ and $N2-C22-C21-N3$ are *anti* in the present compound, while corresponding dihedral angles are *gauche* in the four previously reported structures.^{1,5,6}

Although the H-atoms of the half-water molecule remain undetermined, it may be stated that

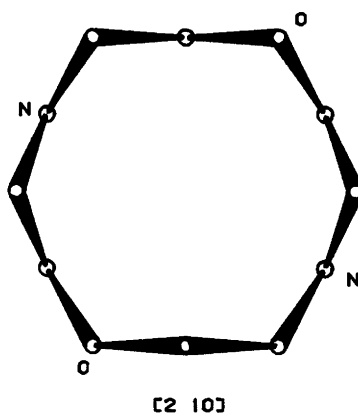


Table 3. Dihedral angles with estimated standard deviations.

DIHEDRAL ANGLE		(°)
C2 - O1 - C5 - C4		149.(2)
C5 - O1 - C2 - C1		-79.(2)
C6 - O2 - C7 - C8		-160.(1)
C7 - O2 - C6 - C5		159.(1)
C15 - O3 - C14 - C15		-72.(2)
C14 - O3 - C15 - C12		151.(1)
C17 - O4 - C18 - C19		140.(1)
C18 - O4 - C17 - C16		-164.(2)
C1 - N1 - C8 - C7		-82.(2)
C8 - N1 - C1 - C2		160.(2)
C9 - N1 - C1 - C2		-88.(2)
C1 - N1 - C10 - C11		-175.(1)
C10 - N1 - C1 - C2		42.(2)
C9 - N1 - C8 - C7		162.(2)
C8 - N1 - C10 - C11		67.(2)
C10 - N1 - C8 - C7		59.(2)
C9 - N1 - C10 - C11		-49.(2)
C4 - N2 - C5 - C6		154.(1)
C5 - N2 - C4 - C3		-87.(2)
C4 - N2 - C22 - C21		-82.(2)
C22 - N2 - C4 - C3		156.(1)
C5 - N2 - C22 - C21		159.(1)
C22 - N2 - C5 - C6		-88.(1)
C15 - N3 - C16 - C17		-76.(2)
C16 - N3 - C15 - C14		172.(1)
C20 - N3 - C15 - C14		-69.(2)
C15 - N3 - C21 - C22		175.(1)
C21 - N3 - C15 - C14		44.(2)
C20 - N3 - C16 - C17		168.(2)
C16 - N3 - C21 - C22		55.(2)
C21 - N3 - C16 - C17		47.(2)
C20 - N3 - C21 - C22		-71.(2)
C11 - N4 - C12 - C13		159.(1)
C12 - N4 - C11 - C10		-80.(2)
C11 - N4 - C19 - C18		-84.(2)
C19 - N4 - C11 - C10		155.(1)
C12 - N4 - C19 - C18		149.(1)
C19 - N4 - C12 - C13		-73.(2)
N1 - C1 - C2 - O1		-77.(2)
O1 - C5 - C4 - N2		-63.(2)
N2 - C5 - C6 - O2		-75.(2)
O2 - C7 - C8 - N1		67.(2)
N1 - C10 - C11 - N4		175.(1)
N4 - C12 - C13 - O3		-73.(2)
O3 - C14 - C15 - N3		-86.(2)
N3 - C16 - C17 - O4		59.(2)
O4 - C18 - C19 - N4		-75.(2)
N3 - C21 - C22 - N2		-175.(1)

it is bonded to O1 and O3. ($OW\cdots O1=2.81 \text{ \AA}$, $OW\cdots O3=2.88 \text{ \AA}$, $O1\cdots OW\cdots O3=104^\circ$). The presence of an intra-molecular hydrogen bond between N2 and O1 is also probable ($N2\cdots O3=2.85 \text{ \AA}$, $N2-HCl=0.93 \text{ \AA}$, $O3\cdots HCl=2.25 \text{ \AA}$, $N2-HCl\cdots O1=120^\circ$).

Lists of thermal parameters, hydrogen atom parameters and observed and calculated structure factors are available from the author.

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