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## Structure of 1,4,7,10-Tetraazacyclododecane Trihydrate

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### Abstract

The neutral 1,4,7,10-tetraazacyclododecane molecules exhibit crystallographic twofold rotation symmetry and have a [3333] quadrangular conformation with C atoms occupying corner positions. The H atoms bound to the N atoms at the 1 and 7 ring positions are directed outward, away from the center of the ring, while the H atoms bound to the N atoms at the 4 and 10 ring positions are pointed inward, toward the center of the ring. Each N atom is hydrogen bonded to one water molecule. The quadrangular conformation is important in the preorganization of 1,4,7,10-tetraazacyclododecane and its derivatives prior to complexation to metal ions [ $(C-C)_{ave} = 1.518(7)$ ,  $(C-N)_{ave} = 1.464(3)$  Å].

### Comment

The structure of the title compound, also known as cyclen, was determined to establish the conformation of the twelve-membered cyclododecane ring. Fig. 1 shows the structure and the numbering scheme used. The ring conformation is important in understanding the effect of preorganization on complex stability and selectivity for metal ions (Hancock & Martell, 1989; Weber & Vogtle, 1981;

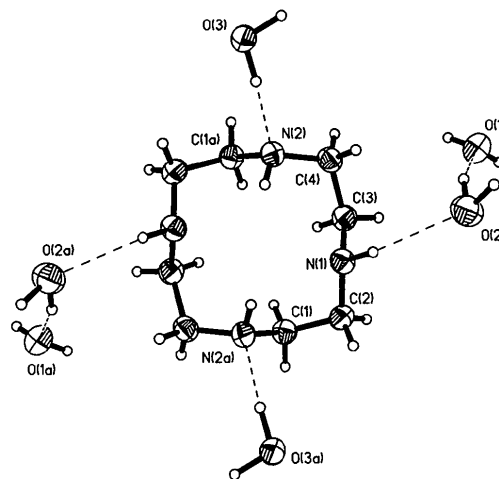


Fig. 1. Thermal ellipsoid plot (50% probability) of cyclen.3H<sub>2</sub>O; H atoms are shown as spheres of arbitrary radius.

Cram & Trueblood, 1981). Previous work (Reibenspies & Anderson, 1990) has shown that the twelve-membered ring of the protonated H<sub>4</sub>cyclen<sup>4+</sup> cation folds to form four repeating units, each containing two adjacent bonds with *gauche* configuration and one bond with *anti* configuration. The resulting combination of configurations is labeled the [3333] quadrangular conformation (Dale, 1980). The present study shows that the neutral cyclen molecule also prefers the [3333] quadrangular conformation in the crystalline state. The two similar structures (H<sub>4</sub>cyclen<sup>4+</sup> and cyclen) differ in the position of the N atoms in the ring with respect to the side and corners of the conformation. For the protonated cyclen cation, the N atoms are located at the corners of the square while for the neutral cyclen molecule the N atoms are located along the sides. As expected, the average C—N distance is significantly shorter for the neutral cyclen molecule [1.464(3) Å] than for the protonated cyclen cation [1.497(3) Å]. The average C—C distances in the cyclen cation and the neutral cyclen molecule [1.527(7) and 1.518(7) Å respectively] do not differ significantly. Three molecules of water are located at special positions. Two water molecules [O(2) and O(3)] are hydrogen bonded to the N atoms of the cyclen molecule [N(1)—O(2) 3.186(3), N(2)—O(3) 2.835(2) Å] and the third water molecule, O(1), is hydrogen bonded to other water molecules [O(1)—O(2) 2.998(3), O(1)—O(3) 2.894(2) Å].

### Experimental

#### Crystal data

C<sub>8</sub>H<sub>20</sub>N<sub>4</sub>.3H<sub>2</sub>O  
 $M_r = 226.3$   
 Orthorhombic  
*Ccca*  
 $a = 16.636(4)$  Å  
 $b = 16.873(3)$  Å  
 $c = 8.881(2)$  Å

Mo K $\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 25 reflections  
 $\theta = 9.19$ – $27.53^\circ$   
 $\mu = 0.086$  mm<sup>-1</sup>  
 $T = 296$  K

$V = 2492.9 (8) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.206 \text{ Mg m}^{-3}$

Parallelepiped  
 $0.26 \times 0.24 \times 0.19 \text{ mm}$   
 Colourless

#### Data collection

Siemens R3m/V diffractometer  
 $R_{\text{int}} = 0$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = 0 \rightarrow 19$   
 Absorption correction: none  
 $k = 0 \rightarrow 20$   
 $l = -10 \rightarrow 0$   
 1273 measured reflections  
 1270 independent reflections  
 814 observed reflections  
 $[F > 2.5\sigma(F)]$   
 3 standard reflections  
 frequency: 97 min  
 intensity variation: 5%

#### Refinement

Refinement on  $F$   
 Final  $R = 0.0520$   
 $wR = 0.0586$   
 $S = 1.452$   
 814 reflections  
 71 parameters  
 Calculated weights,  
 $w = 1/[\sigma^2(F) + 0.0005F^2]$   
 $(\Delta/\sigma)_{\text{max}} = 0.0021$   
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$   
 Extinction correction: Larson (1967)  
 Extinction coefficient: 0.0004 (2)  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Siemens P3VAX version 3.4. Data reduction: REFRED (Reibenspies, 1992). Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to refine structure: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

The title compound was obtained from the Aldrich Chemical Co. and recrystallized from water. A suitable crystal was chosen and mounted on a glass fiber with epoxy cement at room temperature. Inspection of axial photographs about each of the three axes confirmed axis length and Laue symmetry.  $\omega$  scans of several intense reflections indicated acceptable crystal quality.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j$$

	x	y	z	$U_{\text{eq}}$
O(1)	0.5000	0.2500	-0.0269 (3)	0.049 (1)
O(2)	0.5000	0.1484 (2)	0.2500	0.058 (1)
O(3)	0.1268 (1)	0.2500	0.2500	0.041 (1)
N(1)	0.3702 (1)	0.0230 (1)	0.1368 (2)	0.036 (1)
N(2)	0.2220 (1)	0.1240 (1)	0.1367 (2)	0.034 (1)
C(1)	0.3335 (2)	-0.1024 (2)	0.0152 (3)	0.036 (1)
C(2)	0.4010 (2)	-0.0513 (2)	0.0753 (3)	0.039 (1)
C(3)	0.3534 (2)	0.0826 (2)	0.0211 (3)	0.038 (1)
C(4)	0.3014 (2)	0.1491 (2)	0.0840 (3)	0.038 (1)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

N(1)—C(2)	1.460 (3)	C(1)—C(2)	1.513 (4)
N(1)—C(3)	1.465 (3)	C(3)—C(4)	1.523 (4)
N(2)—C(4)	1.464 (3)	C(1)—N(2) <sup>i</sup>	1.466 (3)
N(2)—C(1) <sup>i</sup>	1.466 (3)		
C(2)—N(1)—C(3)	113.2 (2)	N(1)—C(2)—C(1)	111.1 (2)
C(4)—N(2)—C(1) <sup>i</sup>	113.9 (2)	N(1)—C(3)—C(4)	110.9 (2)
C(2)—C(1)—N(2) <sup>i</sup>	110.5 (2)	N(2)—C(4)—C(3)	114.7 (2)

Symmetry codes: (i)  $\frac{1}{2} - x, -y, z$ .

The  $2\theta$  scan width was  $2.0^\circ + K\alpha$  separation, with a variable  $\theta$  scan rate of  $1.5\text{--}14.6^\circ \text{ min}^{-1}$ . Background measurements were made by stationary crystal and stationary counter techniques at the beginning and end of each reflection for half the total scan time. Intensities were corrected by a peak-profiling method (Diamond, 1969). Carbon-bound H atoms were placed in idealized positions [ $\text{C—H} = 0.96 \text{ \AA}$ ,  $U(\text{H}) = 0.08 \text{ \AA}^2(\text{fixed})$ ]. Nitrogen-bound and oxygen-bound H atoms were located in a difference Fourier map. The nitrogen-bound H atoms were set to an idealized bond distance [ $\text{N—H} = 0.90 \text{ \AA}$ ,  $U(\text{H}) = 0.08 \text{ \AA}^2(\text{fixed})$ ]; the distances of the oxygen-bound H atoms were not modified [ $U(\text{H}) = 0.08 \text{ \AA}^2(\text{fixed})$ ]. The H-atom parameters were not refined.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55237 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1013]

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### 1-Benzenesulfonyl-3-methyl-2-oxo-2,3-dihydroindol-3-yl Acetate

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#### Abstract

The title compound was synthesized via a novel oxidation employing manganese(III) acetate. All bond distances and angles are similar to those found in previously reported oxindole-ring systems. In the title compound,