

cis-Dioxocyclam

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Received 21 January 2002

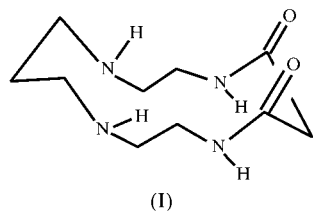
Accepted 18 February 2002

Online 21 March 2002

Molecules of 1,4,8,11-tetraazacyclotetradecane-5,7-dione, or *cis*-dioxocyclam, $C_{10}H_{20}N_4O_2$, lie across mirror planes in space group *Cmca*; the crystal structure reveals interleaved columns of *cis*-dioxocyclam molecules along the 2_1 screw axis parallel to the crystallographic *b* axis. The columns are interconnected in a chain-like arrangement by an amido hydrogen-bonding network ($N\cdots O = 2.816 \text{ \AA}$) and an amino hydrogen-bonding network ($N\cdots N = 3.193 \text{ \AA}$). The intracolumn spacing is 9.02 \AA .

Comment

cis-Dioxocyclam, (I), is a diamido-diamino derivative of the well studied macrocycle 1,4,8,11-tetraazacyclotetradecane, or cyclam. Whereas both cyclam and *cis*-dioxocyclam contain four nitrogen donors for the chelation of transition metal ions, the latter provides the dual features of a macrocyclic polyamine and an oligopeptide (Kimura, 1986). Recently, cyclam was reported as a supramolecular synthon for the encapsulation of superanions (Airey *et al.*, 1999). The crystal structure of cyclam consists of intramolecular hydrogen-bonded tetraamine macrocycles stacked in a columnar array *via* intermolecular hydrogen bonds (Airey *et al.*, 1999). The present study addresses perturbation of the stacking resulting from changes in the hydrogen-bonding network upon substitution of two of the amines by amides. The crystal structure of *trans*-dioxocyclam has been reported previously as the dihydrate (Hubin *et al.*, 2001; Frémond *et al.*, 2000).



Compound (I) exists as a neutral molecule in the endo-tetrate conformation (Subramanian & Zaworotko, 1993). The structure of a single molecule of (I) is shown in Fig. 1. The amino H atom of N1 is disordered, with 50% occupancy at position H1NA, above the N_4 plane of the molecule, and 50%

occupancy at position H1NB, directed toward the centre of the N_4 plane. The resulting $N1\cdots N1'$ distance of $2.967 (1) \text{ \AA}$ and $N1-H1NB'-N1'$ angle of $131.0 (14)^\circ$ are similar to the intramolecular hydrogen bonds reported for cyclam, with average values of 2.941 \AA and 134.4° , respectively.

An extensive intermolecular hydrogen-bonding network links each molecule of (I) to three neighbours (Fig. 2). The amido atoms N2 and N2' serve as hydrogen-bond donors to the amido O atoms of a single neighbouring molecule. This pair of hydrogen bonds yields a 12-membered ring, with $N\cdots O$ distances of $2.815 (1) \text{ \AA}$ and an $N-H-O$ angle of $164.9 (13)^\circ$. In addition, each molecule of (I) acts as a hydrogen-bond acceptor *via* O1 and O1' in an identical interaction with an alternate neighbour. These four intermolecular hydrogen bonds result in an interleaved columnar array along the 2_1 screw axis parallel to *b*.

The centroid-to-centroid distance between stacked molecules of (I) is long (9.02 \AA), as expected. In addition, the amino moiety atoms N1 and N1' are also involved in the intermolecular hydrogen bonding. The disordered positioning of atom H1N is interpreted as alternating the ordering of the H atom and the lone pair of electrons of each N atom, resulting in an eight-membered ring. This ring, comprising atoms N1, N1', H1NA and H1NB' on neighbouring molecules, is held together by covalent $N-H$ bonds, an intramolecular $N1\cdots H1NB'-N1'$ hydrogen bond and an intermolecular $N1-H1NA\cdots N1'$ hydrogen bond. This last has an $N\cdots N$ distance of $3.190 (1) \text{ \AA}$ and an $N1-H1NA\cdots N1'$ angle of $173.9 (15)^\circ$.

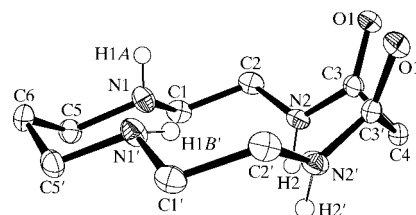


Figure 1

A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

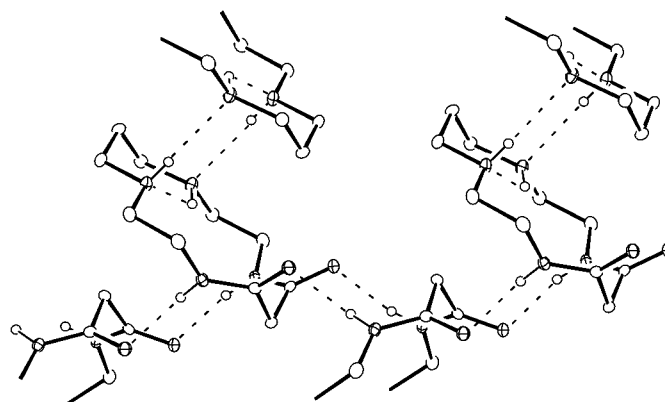


Figure 2

A view of the hydrogen-bonding network in (I).

The amino hydrogen-bonding network further links the columnar array into a 'chain' of interleaved columns, with the cavities of the molecules of (I) aligned as parallel channels through the crystal (see supplementary figure). In total, the extended hydrogen-bonding network consists of one intramolecular and six intermolecular interactions per molecule of (I).

It is noteworthy that in the diprotonated form, as [H₂dioxocyclam][PtCl₄]·H₂O, the amido-O to amido-NH hydrogen-bonding network breaks down (Macíček *et al.*, 1992). In [H₂dioxocyclam][PtCl₄]·H₂O, one amido O atom is hydrogen bonded to an amino-NH₂⁺, while the other is hydrogen bonded to a water solvent molecule.

Experimental

Compound (I) was synthesized from equimolar amounts of 3,7-diaza-1,9-nonanediamine and diethyl malonate under reflux conditions in ethanol (37.5 mM) for 3 d, according to the published method of Tabushi *et al.* (1977). Recrystallization of the white solid from boiling ethanol yielded (I) as colourless blocks upon slow cooling for 15 h at 295 K.

Crystal data

C ₁₀ H ₂₀ N ₄ O ₂	<i>D_m</i> measured by pycnometry
<i>M_r</i> = 228.30	Mo <i>K</i> α radiation
Orthorhombic, <i>Cmca</i>	Cell parameters from 7156 reflections
<i>a</i> = 15.1714 (9) Å	<i>θ</i> = 2.4–28.3°
<i>b</i> = 9.0190 (5) Å	<i>μ</i> = 0.09 mm ⁻¹
<i>c</i> = 17.2111 (10) Å	<i>T</i> = 100 (2) K
<i>V</i> = 2355.0 (2) Å ³	Block, colourless
<i>Z</i> = 8	0.45 × 0.37 × 0.32 mm
<i>D_x</i> = 1.28 Mg m ⁻³	
<i>D_m</i> = 1.23 Mg m ⁻³	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1455 independent reflections
<i>ω</i> scans	1359 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	<i>R</i> _{int} = 0.017
<i>T</i> _{min} = 0.96, <i>T</i> _{max} = 0.97	<i>θ</i> _{max} = 28.3°
9566 measured reflections	<i>h</i> = -20 → 19
	<i>k</i> = -11 → 11
	<i>l</i> = -22 → 21

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 1.24P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + F_c^2)/3$
$wR(F^2) = 0.088$	(Δ/σ) _{max} = 0.013
<i>S</i> = 1.08	$\Delta\rho_{max} = 0.36 \text{ e \AA}^{-3}$
1455 reflections	$\Delta\rho_{min} = -0.14 \text{ e \AA}^{-3}$
98 parameters	
H atoms treated by a mixture of independent and constrained refinement	

All H atoms were located in difference maps. The amine H atom was found to be disordered over two half-occupancy sites; the two half H atoms were refined independently. The coordinates and *U*_{iso} value of the amide H atom were also refined. The displacement

Table 1

Selected geometric parameters (Å, °).

O1—C3	1.236 (1)	N2—C3	1.333 (1)
N1—C1	1.457 (1)	N2—C2	1.456 (1)
N1—C5	1.465 (1)		
C1—N1—C5	112.56 (7)	O1—C3—N2	123.72 (8)
C3—N2—C2	123.12 (7)	O1—C3—C4	121.33 (8)
N1—C1—C2	111.50 (7)	N2—C3—C4	114.86 (8)
N2—C2—C1	110.29 (7)	N1—C5—C6	111.92 (8)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1NA···N1 ⁱ	0.80 (2)	2.40 (2)	3.190 (1)	173.9 (15)
N1—H1NB···N1 ⁱⁱ	0.84 (2)	2.35 (2)	2.967 (1)	131.0 (14)
N2—H2NA···O1 ⁱⁱⁱ	0.87 (1)	1.97 (2)	2.815 (1)	164.9 (13)

Symmetry codes: (i) *x*, 1 - *y*, 1 - *z*; (ii) -*x*, *y*, *z*; (iii) *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*.

parameters for the methylene H atoms were allowed to refine, while their positions were constrained so that C—H = 0.99 Å.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Bruker, 2001).

We thank the Kentucky Research Challenge Trust Fund for the purchase of CCD X-ray equipment and the upgrading of our X-ray facility.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1641). An additional figure is also available. Services for accessing these data are described at the back of the journal.

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