Glycoluril diamide dihydrate

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The crystal structure of the title compound, *cis-N,N'*-bis(2-hydroxyethyl)-4,8-dioxo-2,6-dioxa-3a,4a,7a,8a-tetraazacyclo-penta[*def*]fluorene-8b,8c-dicarboxamide dihydrate, $C_{14}H_{20}N_6O_8 \cdot 2H_2O$, is reported. The compound forms tape-like structures comprising 14- and 10-membered hydrogen-bonded rings. These hydrogen-bonded tapes form hydrogen-bonded sheets and stacks of sheets by hydrogen-bonding interactions with the solvent water molecules.

Comment

Glycoluril and its derivatives have found widespread use in supramolecular chemistry including the preparation of cucurbiturils (Freeman *et al.*, 1981; Kim *et al.*, 2000; Day *et al.*, 2001), molecular capsules (Hof *et al.*, 2002), molecular clips (Rowan *et al.*, 1999), and xerogels (Kölbel & Menger, 2001). Recent studies even suggest that glycoluril derivatives have significant potential in crystal engineering studies (Wu *et al.*, 2002; Johnson *et al.*, 2002). Our group has prepared a series of glycoluril bis(cyclic ethers) bearing carboxylic acid derived functional groups (acid, ester, amide, and imide) on their convex face as novel monomers for the synthesis of cucurbit[*n*]uril derivatives (Burnett *et al.*, 2003) and analogs (Lagona *et al.*, 2003). This paper describes the first crystal structure of a glycoluril derivative bearing amide functional groups.

(I)
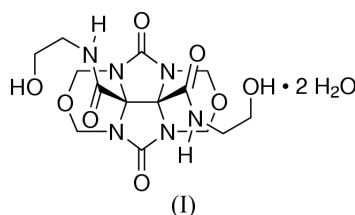
The molecular structure of the title compound, (I), in the crystal structure is shown in Fig. 1. Selected bond distances, angles, and dihedral angles are given in Table 1. The structural features of (I) are similar to those reported previously for related glycoluril bis(cyclic ethers) (Burnett *et al.*, 2003). Of particular interest are the O2···O5 (5.10 Å) and O3···O6)5.02 Å) distances, and the angle between the mean planes of the glycoluril five-membered rings (106.6°), since these parameters define the curvature of the molecule. One of the amide substituents forms an intramolecular ten-membered hydrogen-bond ring with the adjacent amide group (O2*D*—H2*D*···O1*B*).

The three dimensional packing of (I) in the crystal structure (Fig. 2) is a result of the interaction motifs described below.
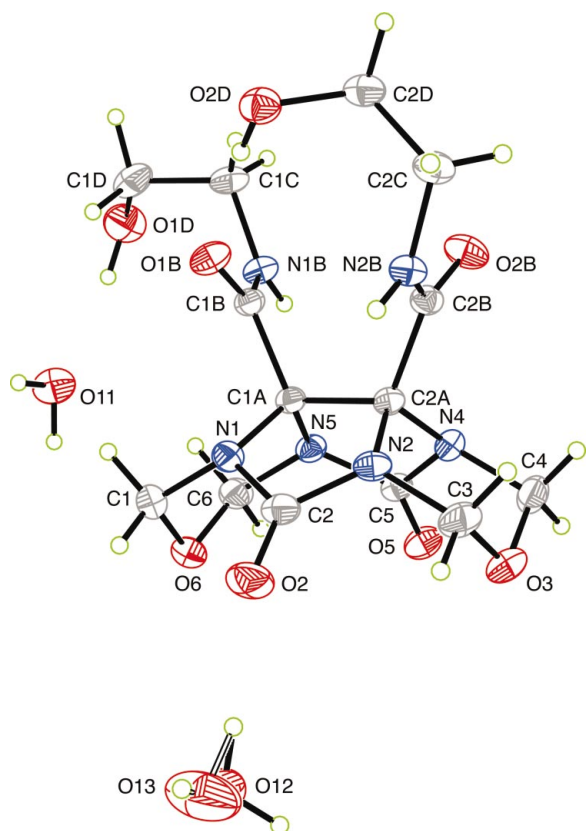
Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Both solvent disorder components are shown.

First, two molecules undergo dimerization by the formation of a 14-membered hydrogen-bonded (N1B—H1···O5^{iv}) ring

(symmetry codes are in Table 2). Second, these dimers undergo oligomerization to form tape-like structures by the formation of ten-membered hydrogen-bonded (N2B—H2···O2D^{iii}) rings. Third, these hydrogen-bonded tapes, which run along the ab diagonal, align with their long axes parallel due to the formation of water-bridged inter-tape hydrogen bonds, resulting in the formation of hydrogen-bonded sheets. Fourth, these hydrogen-bonded sheets are connected along the c axis by the formation of water-bridged inter-sheet hydrogen bonds.

Experimental

Compound (I) was prepared according to the literature procedure of Burnett *et al.* (2003). Single crystals suitable for structure determination were obtained from a methanol—water solution.

Crystal data

$C_{14}H_{20}N_6O_8 \cdot 2H_2O$	$D_x = 1.541$ Mg m^{-3}
$M_r = 436.39$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7457
$a = 28.0466\ (14)$ Å	reflections
$b = 9.0833\ (4)$ Å	$\theta = 2.4$–$30.0°$
$c = 14.7948\ (7)$ Å	$\mu = 0.13$ mm^{-1}
$\beta = 93.5870\ (10)°$	$T = 203\ (2)$ K
$V = 3761.7\ (3)$ Å^3	Block, colorless
$Z = 8$	$0.50 \times 0.42 \times 0.36$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	5486 independent reflections
	4948 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.018$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{max} = 30.0°$
	$h = -38 \rightarrow 39$
$T_{min} = 0.938$, $T_{max} = 0.954$	$k = -12 \rightarrow 12$
36186 measured reflections	$l = -20 \rightarrow 20$

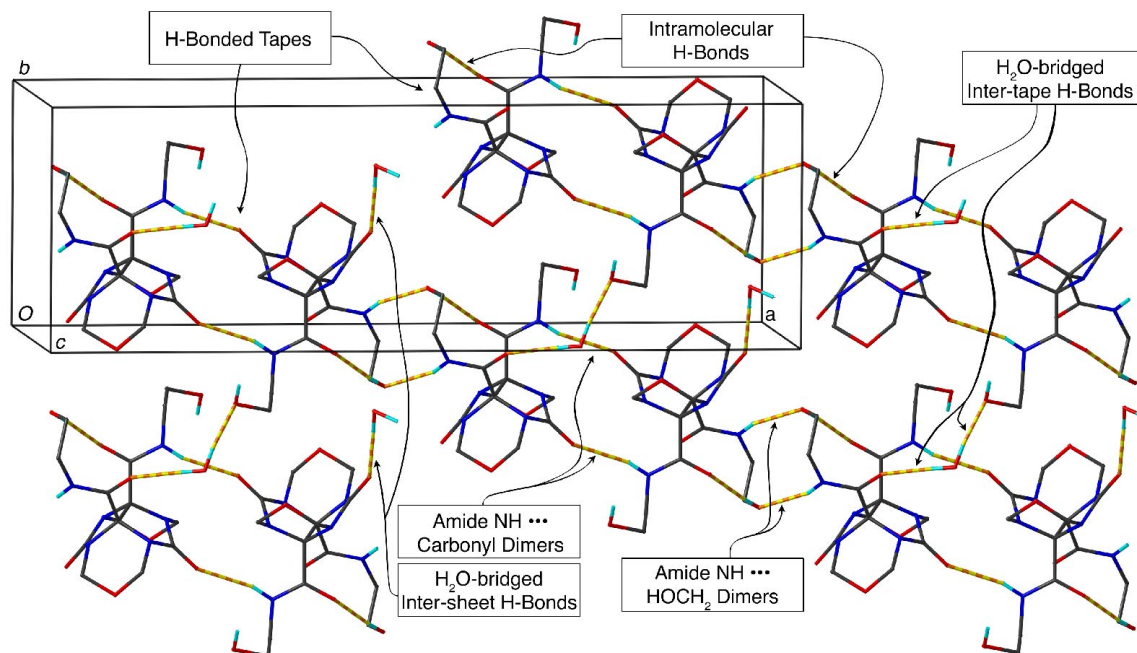**Figure 2**
Packing diagram for (I). Color coding: C grey, H turquoise, N blue, O red, and hydrogen bonds orange–yellow striped.

Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2$	
$R[F^2 > 2\sigma(F^2)] = 0.034$		$+ 1.3549P]$	
$wR(F^2) = 0.099$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.05$		$(\Delta/\sigma)_{max} = 0.001$	
5486 reflections		$\Delta\rho_{max} = 0.37$ e Å^{-3}	
380 parameters		$\Delta\rho_{min} = -0.21$ e Å^{-3}	
All H-atom parameters refined			

Table 1
Selected geometric parameters (Å, °).

C1A—N5	1.4545 (8)	C2A—N2	1.4551 (8)
C1A—N1	1.4555 (8)	C2A—N4	1.4555 (8)
C1A—C2A	1.5736 (8)	N4—C5	1.3900 (8)
N1—C2	1.3889 (9)	C5—O5	1.2156 (8)
C2—O2	1.2164 (9)	C5—N5	1.3860 (8)
C2—N2	1.3787 (9)		
C2—N1—C1	119.69 (6)	C5—N4—C4	119.10 (6)
C2—N1—C1A	110.74 (5)	C5—N4—C2A	110.39 (5)
C1—N1—C1A	114.82 (6)	C4—N4—C2A	114.79 (5)
C2—N2—C2A	111.80 (5)	C5—N5—C6	121.31 (5)
C2—N2—C3	121.90 (6)	C5—N5—C1A	111.24 (5)
C2A—N2—C3	116.10 (5)	C6—N5—C1A	115.99 (5)
C1B—C1A—C2A—C2B	1.86 (7)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O11—H11B$\cdots$O2B^i	0.881 (13)	1.898 (14)	2.7642 (8)	167.4 (13)
O11—H11A$\cdots$O1D^{ii}	0.888 (15)	1.945 (15)	2.8264 (9)	171.3 (13)
N2B—H2$\cdots$O2D^{iii}	0.857 (10)	2.035 (10)	2.8491 (8)	158.4 (9)
O2D—H2D$\cdots$O1B	0.853 (14)	1.951 (14)	2.8011 (8)	174.1 (13)
O1D—H1D$\cdots$O11	0.888 (15)	1.921 (15)	2.8009 (9)	170.8 (14)
N1B—H1$\cdots$O5^{iv}	0.882 (11)	2.176 (11)	3.0264 (8)	162.0 (10)
O12—H12A$\cdots$O2	0.903 (17)	1.948 (17)	2.8127 (18)	159.8 (17)
O12—H12B$\cdots$O1B^v	0.95 (3)	2.04 (3)	2.9712 (17)	168 (3)
O13—H13A$\cdots$O2	1.010 (16)	1.948 (17)	2.912 (2)	158.9 (15)

Symmetry codes: (i) $x, 2 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, 2 - y, -z$; (iv) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (v) $x, y - 1, z$.

All H atoms of the organic molecule were initially placed in calculated positions and then allowed to refine freely, while those attached to the water molecules were located directly from subsequent difference Fourier maps and also refined. One water molecule (O12 and O13) was disordered, and was refined as two overlapping moieties with one H atom common to both.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL*.

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