Two-dimensional hydrogen-bonded networks in two novel glycoluril derivatives

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Two new glycoluril derivatives, namely diethyl 6-ethyl-1,4-dioxo-1,2,2a,3,4,6,7,7b-octahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-2a,7b-dicarboxylate, $C_{14}H_{21}N_5O_6$, (I), and 6-ethyl-2a,7b-diphenyl-1,2,2a,3,4,6,7,7b-octahydro-5H-2,3,4a,-6,7a-pentaazacyclopenta[cd]indene-1,4-dione, $C_{20}H_{21}N_5O_2$, (II), both bearing two free syn-urea NH groups and two ureidyl C=O groups, assemble the same one-dimensional chains in the solid state running parallel to the [010] direction via N—H⋯O hydrogen bonds. Furthermore, the chains of (I) are linked together into two-dimensional networks via C—H⋯O hydrogen bonds.

Comment

Glycoluril, a biurea compound known for about 130 years, has established an impressive career as a building block for molecular and supramolecular chemistry during the past two decades. For example, glycoluril derivatives have been used in a variety of applications, including polymer crosslinking (Jacobs *et al.*, 1996), explosives (Yinon *et al.*, 1994), the stabilization of organic compounds against photodegradation (Krause *et al.*, 1997), textile waste stream purification (Karcher *et al.*, 1999) and combinatorial chemistry, and furthermore in the fields of cucurbituril chemistry (Freeman *et al.*, 1981; Kim *et al.*, 2000; Pryor & Rebek, 1999; Lee *et al.*, 2003; Burnett *et al.*, 2003) and anion sensors (Kang *et al.*, 2004; Kang & Kim, 2005). The intriguing structural feature in a number of glycoluril derivatives is the twisting observed about the bridgehead dihedral angle, and the rigid and nonplanar glycoluril skeleton, with well defined geometry, is more favourable for constructing a three-dimensional structure, which suggests that glycoluril derivatives have significant potential as building blocks in crystal engineering studies. Rebek and co-workers have reported that achiral glycolurils form chiral hydrogen-bonded ribbons in the solid state, and subsequently observed four complementary hydrogen bonds

between sulfamides and ureas linking adjacent hydrogen-bonded ribbons (Johnson *et al.*, 2002, 2003). Isaacs and co-workers have reported similar hydrogen-bonded ribbons in a related syn-protected glycoluril derivative (Wu *et al.*, 2002). One of our laboratory interests is to develop a robust supramolecular synthon based on glycoluril for crystal engineering (Wang *et al.*, 2006; Chen *et al.*, 2007). As part of our research programme aimed at the study of hydrogen-bonding interactions involving glycoluril, the present work has been undertaken. We report here the two-dimensional hydrogen-bonded networks formed by two novel glycoluril derivatives, (I) and (II), that adopt an unusual twisted conformation in the solid state (Matta *et al.*, 2000; Li *et al.*, 1994; Duspara *et al.*, 2001).

(I) R=COOEt
(II) R=Ph

Hydrogen-bonded chain
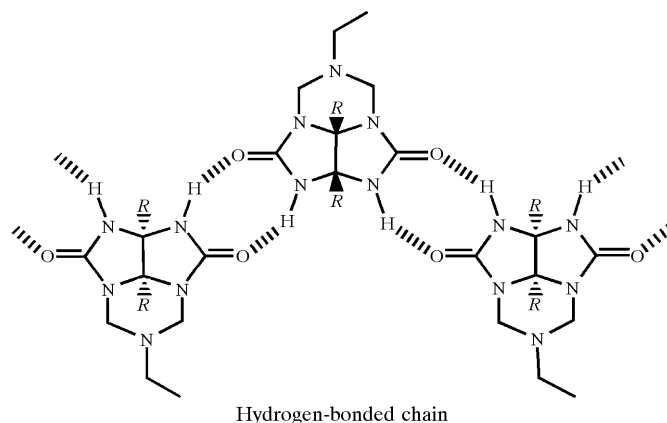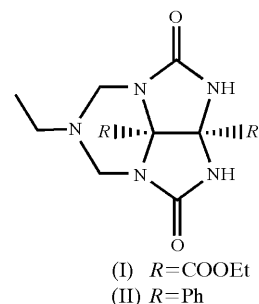
The molecular structures of (I) and (II) (Fig. 1) are built up from three fused rings, namely two nearly planar imidazole five-membered rings that adopt envelope conformations, with the C=O groups at the flap positions, and one six-membered triazacyclohexane ring that adopts a chair conformation. These rings bear two CO_2Et groups in (I) and two Ph groups in (II) on their 'convex' faces. The bond lengths and angles in both compounds are similar to those reported previously (Johnson *et al.*, 2002, 2003; Wu *et al.*, 2002; Wang *et al.*, 2006; Chen *et al.*, 2007). The =O⋯O= distances are 5.657 (2) Å in (I) and 5.691 (2) Å in (II). All Csp^2—N and Csp^3—N distances lie in the ranges 1.349 (4)–1.381 (4) and 1.442 (3)–1.478 (4) Å, respectively. Obviously, the N—C(carbonyl) bond distances are much shorter than the other N—C bond distances in the three fused rings, indicating some electron delocalization within these rings. Again, the cis-fused five-membered rings bearing CO_2Et or Ph groups enforce their cup-shaped geometry. The angle between the mean planes defined by the

five-membered rings is 115.1 (1)° in (I) and 112.9 (1)° in (II). The glycoluril units are both almost coplanar, which is indicated by the key torsion angles [(I): N1—C3—C7—N3 = 2.9 (3)° and C4—C3—C7—C8 = 9.6 (3)°; (II): N1—C1—C8—N3 = −4.7 (2)° and C2—C1—C8—C9 = −5.1 (3)°]. These slight differences are thought to be due to the different substituents on the 'convex' faces.

In their supramolecular structures formed via N—H···O and C—H···O hydrogen bonds, the molecules of both (I) and (II) are linked into two-dimensional networks. In (I), the crystal packing can be easily analysed in terms of two simple substructures. In the first substructure, amide atoms N1 and N2 in the molecule at (x, y, z) act as hydrogen-bond donors, via atoms H1 and H2, respectively, to carboxyl atom O2 in the
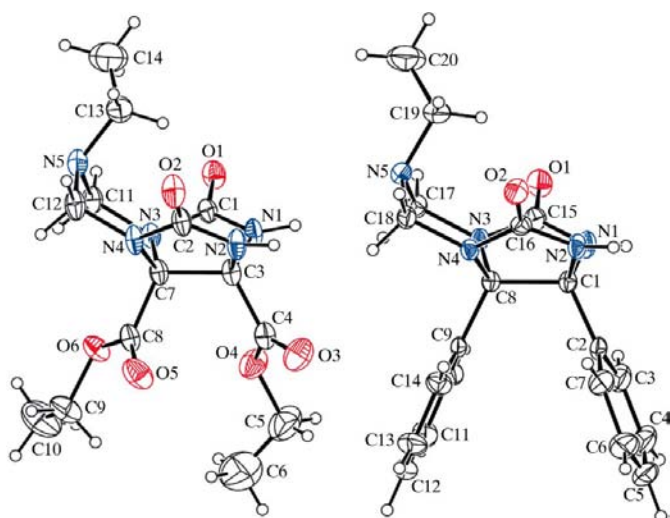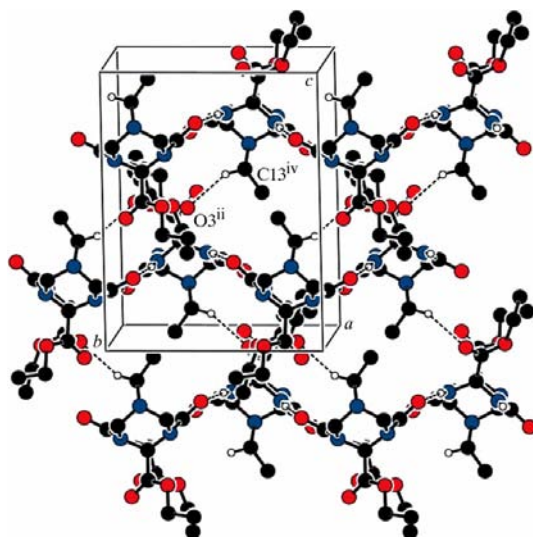

Figure 1
The molecular structures of compounds (I) (left) and (II) (right), showing the atom-numbering schemes. In both cases, displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
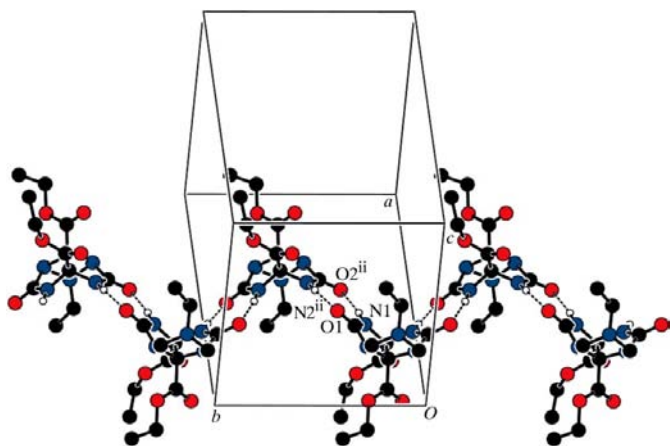
molecule at $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$ and atom O1 at $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$, both producing one-dimensional chains running parallel to the [010] direction generated by the 2_1 screw axis at $(\frac{1}{4}, y, \frac{1}{4})$. These two types of [010] chains are interlinked by an approximately centrosymmetric $R_2^2(8)$ (Bernstein et al. 1995) hydrogen-bonding motif centred at (0.257, 0.295, 0.249), forming a one-dimensional chain structure along the [010] direction (Fig. 2 and Table 1). Four chains of this type pass through each unit cell; two of these, running along the $(\frac{1}{4}, y, \frac{1}{4})$ and $(\frac{3}{4}, y, \frac{3}{4})$ directions, respectively, are antiparallel to the other two, which run along the $(\frac{3}{4}, y, \frac{1}{4})$ and $(\frac{1}{4}, y, \frac{3}{4})$ directions, respectively. As reported by Wu et al. (2002), if all the CO$_2$Et groups were located on one side of the molecule, this would lead to cyclic structures for these analogues. We did not observe these cyclic structures in the solid state of (I), which may be due to the unfavourable entropy associated with the formation of cyclic structures. In the second substructure, ethyl atom C13 in the molecule at (x, y, z) acts as a hydrogen-bond donor, via atom H13B, to carboxyl atom O3 in the molecule at $(x, -y, z + \frac{1}{2})$, forming another one-dimensional chain along the [001] direction generated by a c-glide plane at $y = 0$, which suffices to link the [010] chains into a two-dimensional network (Fig. 3) running parallel to the (100) direction. No direction-specific interactions between adjacent two-dimensional networks are observed.

Similar to compound (I), molecules in compound (II) also form one-dimensional hydrogen-bonded tapes in the solid state along the [010] direction (Fig. 4 and Table 2). Structure (II) can also be easily analysed in terms of two one-dimensional substructures. In the first substructure, two amide atoms, N1 and N2, in the molecule at (x, y, z) act as hydrogen-bond donors, via atoms H1 and H2, respectively, to carboxyl atom O2 in the molecule at $(-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$ and atom O1 at $(-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$, both producing one-dimensional

Figure 2
The packing of (I), showing the formation of a one-dimensional hydrogen-bonded $R_2^2(8)$ chain along the b axis involving syn-NH atoms and C=O groups. Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

Figure 3
Part of the crystal structure of (I), showing the formation of the two-dimensional network linked by C—H···O hydrogen bonds along the [100] direction. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.]
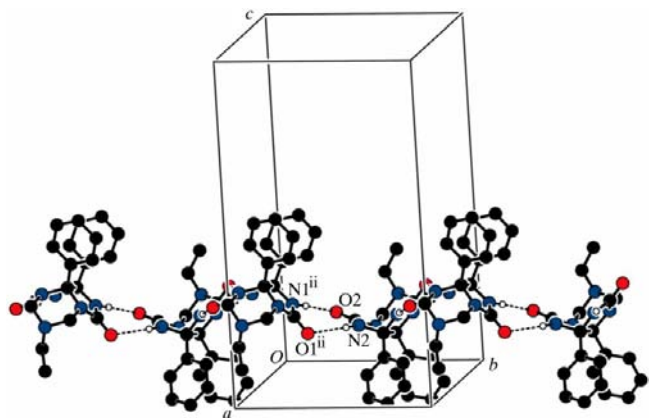
Figure 4
The packing of (II), showing the formation of a one-dimensional hydrogen-bonded $R_2^2(8)$ chain along the b axis involving *syn*-NH atoms and C=O groups. Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

chains running parallel to the [010] direction generated by the 2_1 screw axis at $(\frac{3}{4}, y, \frac{3}{4})$. These two type [010] chains are interlinked by the approximately centrosymmetric $R_2^2(8)$ (Bernstein *et al.* 1995) hydrogen-bonding motif centred at (0.966, 0.400, 0.279), forming a one-dimensional chain structure along the [010] direction. In comparison with the formation of the four chains in each unit cell in compound (I), only two one-dimensional chains pass through each unit cell in (II); these two chains run along the $(\frac{3}{4}, y, \frac{1}{4})$ and $(\frac{1}{4}, y, \frac{3}{4})$ directions, respectively.

As noted above, the same one-dimensional hydrogen-bonded chains along the [010] direction are found here for (I) and (II). This may be ascribed to the same motifs of these two novel glycoluril derivatives, which both bear two free *syn*-urea NH groups and two ureidyl C=O groups. The C—H···O hydrogen bonds [along the [001] direction in (I) and along the [100] direction in (II)] link these one-dimensional helical chains into two-dimensional networks.

Experimental

The preparation of the glycoluril monomers (I) and (II) followed a well established methodology (Yin *et al.*, 2006; Li *et al.*, 2006), but ethanol was used as a solvent. When diethoxycarbonyl- or diphenylglycoluril are combined with equivalent ethylamines in the presence of anhydrous formaldehyde in ethanol under reflux, the expected compounds, the new glycolurils, were obtained in good yields. EtOH and the ethylamines were freshly distilled. A suspension of diethoxycarbonylglycoluril (1.43 g, 5 mmol) or diphenylglycoluril (1.47 g, 5 mmol) in anhydrous formaldehyde (0.3 g, 10 mmol) and EtOH (50 ml) was brought to reflux under magnetic stirring. A solution of ethylamine (5 mmol) in EtOH (10 ml) was added dropwise (over 1 h) to the mixture. Refluxing was continued for 10–12 h and the reactions were monitored by thin-layer chromatography. The solvent was removed under reduced pressure and the products were separated by column chromatography (silica gel) in 80 and 50% isolated yields, respectively. Crystals of (I) and (II) suitable for X-ray data collection were obtained by slow evaporation of dichloroethane–methanol solutions (4:1 *v*/*v*) at 293 K.

Compound (I)

Crystal data

$C_{14}H_{21}N_5O_6$
$M_r = 355.36$
Monoclinic, $C2/c$
$a = 23.898 (2)$ Å
$b = 10.4791 (9)$ Å
$c = 15.9302 (13)$ Å
$\beta = 119.4120 (10)°$

$V = 3475.2 (5)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 296 (2)$ K
$0.20 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.979$, $T_{max} = 0.989$

10973 measured reflections
3061 independent reflections
2206 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.172$
$S = 1.07$
3061 reflections
236 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^i	0.93 (3)	1.98 (4)	2.886 (3)	166 (3)
N1—H1···O2^{ii}	0.91 (3)	1.89 (4)	2.786 (3)	170 (3)
C13—H13B···O3^{iii}	0.97	2.45	3.342 (4)	153

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

Compound (II)

Crystal data

$C_{20}H_{21}N_5O_2$
$M_r = 363.42$
Monoclinic, $P2_1/n$
$a = 8.0724 (5)$ Å
$b = 11.6462 (7)$ Å
$c = 19.2338 (12)$ Å
$\beta = 100.462 (1)°$

$V = 1778.16 (19)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 295 (2)$ K
$0.20 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.982$, $T_{max} = 0.991$

16184 measured reflections
3860 independent reflections
2581 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.159$
$S = 1.03$
3860 reflections
251 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^i	0.89 (3)	2.20 (3)	3.043 (3)	158 (2)
N1—H1···O2^{ii}	0.93 (3)	1.96 (3)	2.873 (3)	168 (2)

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

organic compounds

For both (I) and (II), all H atoms bonded to C atoms were initially located in difference Fourier maps and then constrained to their ideal geometry positions, with C—H = 0.96 (methyl) or 0.97 Å (methylene), and with $U_{iso}(H) = 1.5U_{eq}$(methyl C) or $1.2U_{eq}$(methylene C). H atoms bonded to N atoms were found in difference maps; the N—H distances were refined freely [0.89 (3)–0.93 (3) Å] and $U_{iso}(H)$ values were set at $1.2U_{eq}(N)$.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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