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A DMSO-capped dimeric glycoluril derivative

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.123
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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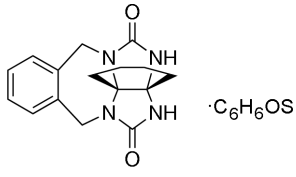
The crystal structure of the title compound, 1,2,3,4,8,13-hexahydro-4a,14-(iminomethano)-4a*H*,14*H*-benzimidazo-[1,7a-*b*][2,4]benzodiazepine-6,15(5*H*)-dione dimethyl sulfoxide solvate, $C_{16}H_{18}N_4O_2\cdot C_2H_6OS$, is reported. Unlike related glycoluril-derived compounds which form hydrogen-bonded tapes when crystallized from solvents of lower polarity, the title compound forms discrete hydrogen-bonded dimers in the crystal. Solvent molecules cap these dimers by accepting hydrogen bonds from their edges and thus prevent further supramolecular assembly.

Comment

The glycoluril skeleton has served as an important building block for the preparation of a wide variety of supramolecular assemblies, including molecular clips (Rowan *et al.*, 1999; Wu, Chakraborty *et al.* 2002), molecular capsules (Hof *et al.*, 2002), xerogels (Kölbel & Menger, 2001), the cucurbit[*n*]uril family (Freeman *et al.*, 1981; Kim *et al.*, 2000; Day *et al.*, 2001; Lagona *et al.*, 2003), and, most recently, anion-binding receptors (Kang *et al.*, 2004). Recently, we and others (Wu, Fettinger *et al.*, 2002; Johnson *et al.*, 2002, 2003; Moon *et al.*, 2003) have demonstrated that dialkylated glycoluril derivatives form hydrogen-bonded tapes in the solid state when crystallized from solvents that do not contain strong hydrogen-bond donor or acceptor groups. In this paper, we report the crystal structure of *o*-xylylene-derived glycoluril, (I), which contains a fused cyclohexane ring on its convex face.



(I)

The molecular structure of (I) is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The most unusual structural feature of (I) is the boat conformation of its cyclohexyl ring imposed by the ring fusion at C2—C4. The remaining structural features of (I) are similar to those reported previously for related benzylated glycolurils (Wu, Fettinger *et al.*, 2002; Johnson *et al.*, 2002).

The three-dimensional packing of (I) in the crystal structure (Fig. 2) is the result of the interaction motifs described below. First, two molecules of (I) undergo dimerization by forming an eight-membered hydrogen-bonded (N3—H3···O3) ring (Table 2). The dimerization of (I) takes place between enantiotopic ureidyl NH groups, resulting in the orientation of their

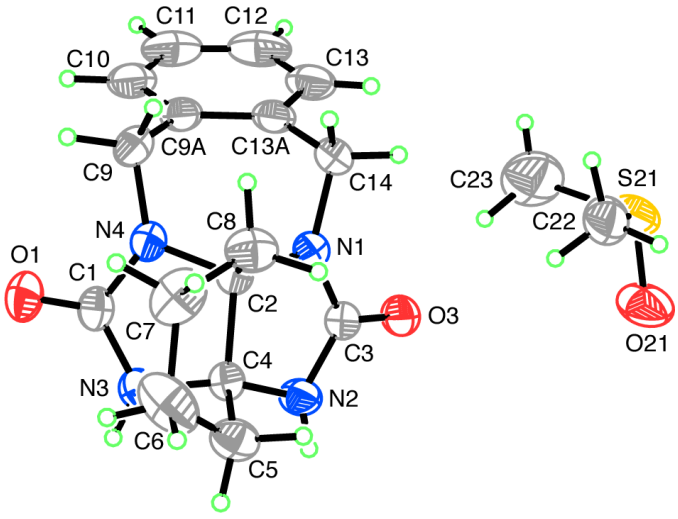


Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

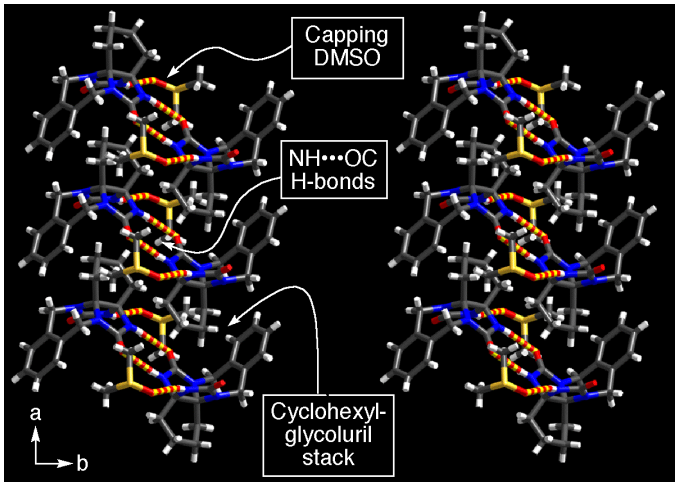


Figure 2
Cross-eyed stereoview of (I) in the crystal structure, viewed down the *c* axis. Color coding: C gray, H white, N blue, O red, S yellow, and hydrogen bonds red and yellow striped.

cyclohexyl groups in opposite directions. Secondly, the remaining ureidyl NH groups hydrogen bond to solvating dimethyl sulfoxide (DMSO) molecules (N2—H2···O21) to create discrete dimeric entities in the crystal. Thirdly, these S-shaped hydrogen-bonded dimers grow along the *a* axis by nesting their cyclohexyl groups into the clefts shaped by neighboring glycoluril dimers. Lastly, these stacks of dimers align with their long axes parallel (Fig. 3).

Previously, we and others demonstrated that dibenzylated glycolurils form hydrogen-bonded tapes in the crystal structure when crystallized from non-polar solvents. In this paper, we show that crystallization from DMSO affords glycoluril dimers which are capped by hydrogen-bonding interactions with the solvating molecules. This study highlights the importance of solubility in planning crystal-engineering studies based on glycoluril building blocks.

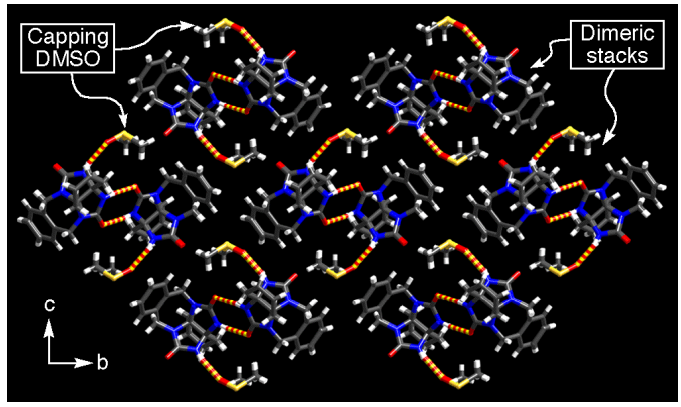


Figure 3
Illustration of the three-dimensional packing of (I) in the crystal structure. Color coding as in Fig. 2.

Experimental

Compound (I) was prepared according to the literature procedure of Wu, Chakraborty *et al.* (2002). Single crystals suitable for structure determination were obtained from a DMSO solution.

Crystal data

$C_{16}H_{18}N_4O_2\cdot C_2H_6OS$
M_r = 376.47
Monoclinic, $P2_1/c$
a = 6.6874 (2) Å
b = 16.5431 (5) Å
c = 16.7931 (5) Å
β = 97.3630 (10)°
V = 1842.51 (10) Å^3
Z = 4
D_x = 1.357 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5047 reflections
θ = 2.5–28.5°
μ = 0.20 mm^{-1}
T = 193 (2) K
Block, colorless
0.41 × 0.26 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 1996)
T_{min} = 0.932, T_{max} = 0.975
19374 measured reflections
4232 independent reflections
3620 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 27.5°
$h = -6 \rightarrow 8$
$k = -21 \rightarrow 21$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.123
S = 1.11
4232 reflections
331 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.4304P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—C8	1.5287 (19)	C7—C8	1.514 (2)
C2—C4	1.5694 (17)	O21—S21	1.4900 (13)
C4—C5	1.5219 (18)	S21—C22	1.776 (2)
C5—C6	1.527 (3)	S21—C23	1.786 (3)
C6—C7	1.521 (3)		
C3—N1—C2	112.90 (10)	C1—N4—C2	112.34 (10)
C3—N1—C14	122.39 (11)	C1—N4—C9	123.57 (11)
C2—N1—C14	122.31 (11)	C2—N4—C9	122.39 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O21^{i}	0.829 (19)	2.062 (19)	2.8484 (18)	158.2 (17)
N3—H3···O1^{i}	0.869 (18)	2.005 (19)	2.8667 (15)	171.2 (17)

Symmetry code: (i) $1-x, -y, 1-z$.

H atoms were located directly in two difference Fourier maps and refined freely.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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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References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2001). *SMART* (Version 5.054) and *SAINT* (Version 6.28A). Bruker AXS Inc., Madison, Wisconsin, USA.
Day, A., Arnold, A. P., Blanch, R. J. & Snushall, B. (2001). *J. Org. Chem.* **66**, 8094–8100.
Freeman, W. A., Mock, W. L. & Shih, N. Y. (1981). *J. Am. Chem. Soc.* **103**, 7367–7368.
Hof, F., Craig, S. L., Nuckolls, C. & Rebek, J. Jr (2002). *Angew. Chem. Int. Ed.* **41**, 1488–1508.
Johnson, D. W., Hof, F., Palmer, L. C., Martin, T., Obst, U. & Rebek, J. Jr (2003). *Chem. Commun.* pp. 1638–1639.
Johnson, D. W., Palmer, L. C., Hof, F., Iovine, P. M. & Rebek, J. Jr (2002). *Chem. Commun.* pp. 2228–2229.
Kim. J., Jung, I.-S., Kim, S.-Y., Lee, E., Kang, J.-K., Sakamoto, S., Yamaguchi, K. & Kim, K. (2000). *J. Am. Chem. Soc.* **122**, 540–541.
Kölbel, M. & Menger, F. M. (2001). *Chem. Commun.* pp. 275–276.
Kang, J., Jo, J.-H. & In, S. (2004). *Tetrahedron Lett.* **45**, 5225–5228.
Lagona, J., Fettinger, J. C. & Isaacs, L. (2003). *Org. Lett.* **5**, 3745–3747.
Moon, K., Chen, W.-Z., Ren, T. & Kaifer, A. E. (2003). *CrystEngComm*, **5**, 451–453.
Rowan, A. E., Elemans, J. A. A. W. & Nolte, R. J. M. (1999). *Acc. Chem. Res.* **32**, 995–1006.
Sheldrick, G. M. (1994). *SHELXTL.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS.* University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Wu, A., Chakraborty, A., Witt, D., Lagona, J., Damkaci, F., Ofori, M. A., Chiles, J. K., Fettinger, J. C. & Isaacs, L. (2002). *J. Org. Chem.* **67**, 5817–5830.
Wu, A., Fettinger, J. C. & Isaacs, L. (2002). *Tetrahedron*, **58**, 9769–9777.