

Hexagonal packing of *cis,cis*-cyclohexane-1,3,5-tricarboxamide

Binoy K. Saha

Department of Chemistry, Pondicherry University, Puducherry 605 014, India
Correspondence e-mail: binoypu@yahoo.co.in

Received 19 July 2007

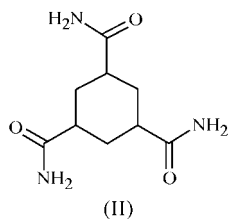
Accepted 12 August 2007

Online 22 September 2007

The title compound, $C_9H_{15}N_3O_3$, which has crystallographically imposed threefold symmetry, crystallizes as a hexagonal columnar structure. The crystal structure is stabilized by a less common amide–amide synthon, where one amide group is hydrogen bonded to four others. The amide groups form cyclic amide–amide hexamers *via* $N-H\cdots O$ hydrogen bonds.

Comment

Acid and primary amide functional groups have been well studied in organic supramolecular chemistry. They generally form a centrosymmetric dimer synthon in the absence of other strong hydrogen-bonding functional groups. The strong and directional nature of the hydrogen bonds formed by these functional groups has made them useful in crystal engineering. Very often, the primary amide dimers form 5.1 Å tapes (Palmore & MacDonald, 2000; Saha *et al.*, 2005) *via* $N-H\cdots O$ hydrogen bonds, which are perpendicular to the amide dimer motif. The trigonal molecule trimesic acid forms the expected acid dimer but crystallizes in the $C2/c$ space group instead of crystallizing with trigonal symmetry (Duchamp & Marsh, 1969). *cis,cis*-Cyclohexane-1,3,5-tricarboxylic acid forms a hydrate and also crystallizes in the $C2/c$ space group (Bhogala *et al.*, 2002). The crystal structure of trimesic carboxamide has not been reported so far. However, *cis,cis*-cyclohexane-1,3,5-tris(α -picolin-6-yl)tricarboxamide, (I), crystallizes in the $R3c$ space group (Fan *et al.*, 1995). The solid-state architecture of *cis,cis*-cyclohexane-1,3,5-tricarboxamide, (II), is described here.



The compound crystallizes in the $R\bar{3}$ space group with the molecule lying about a threefold axis. The molecular geometry and atom numbering of (II) are shown in Fig. 1. Instead of

forming the usual amide dimer tape, the amide group is linked to four other amide groups *via* strong $N-H\cdots O$ hydrogen bonds using two $N-H$ donors and the bifurcated $C=O$ acceptor (Fig. 2). The hydrogen-bond geometry is listed in Table 1. This type of synthon is not very common for amide functional groups. The trigonal molecules are bonded *via* amide–amide hydrogen bonds to form a three-dimensional network, where the two-dimensional layer contains hexagonal arrays surrounded by six amide groups (Fig. 3) and these six amide groups form a cyclic hexamer *via* six $N-H\cdots O$ hydrogen bonds. The remaining six NH groups form $N-H\cdots O$ hydrogen bonds with adjacent layers. The hexagonal arrays are partially occupied by cyclohexyl rings from neigh-

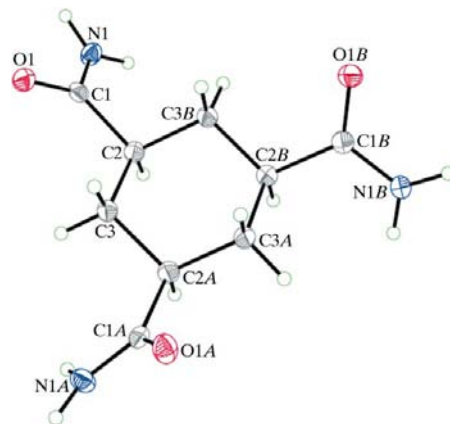


Figure 1
A view of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry codes: (A) $-y + 1, x - y, z$; (B) $-x + y + 1, -x + 1, z$.]

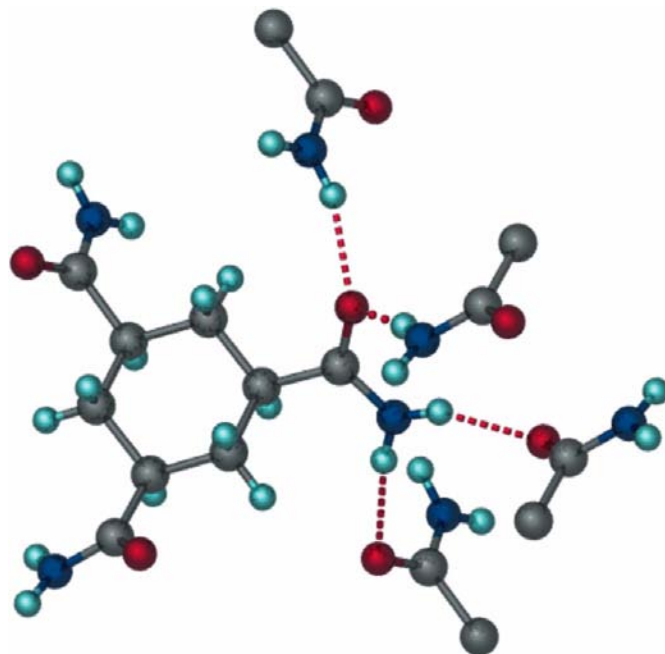


Figure 2
One amide group is bonded to four other amide groups *via* $N-H\cdots O$ hydrogen bonds (dashed lines).

boring layers and form a hexagonal close-packed structure. The cyclohexyl rings are stacked along the *c* axis and form a Piedfort unit of *C3i* symmetry (*C3i*-PU; Thalladi *et al.*, 1998; Saha & Nangia, 2007), as shown in Fig. 4, but they are not packed efficiently along *c* (Fig. 5). The plane of each amide group is tilted by 48.6° with respect to the mean plane of the cyclohexyl ring, and the distances between the mean planes of

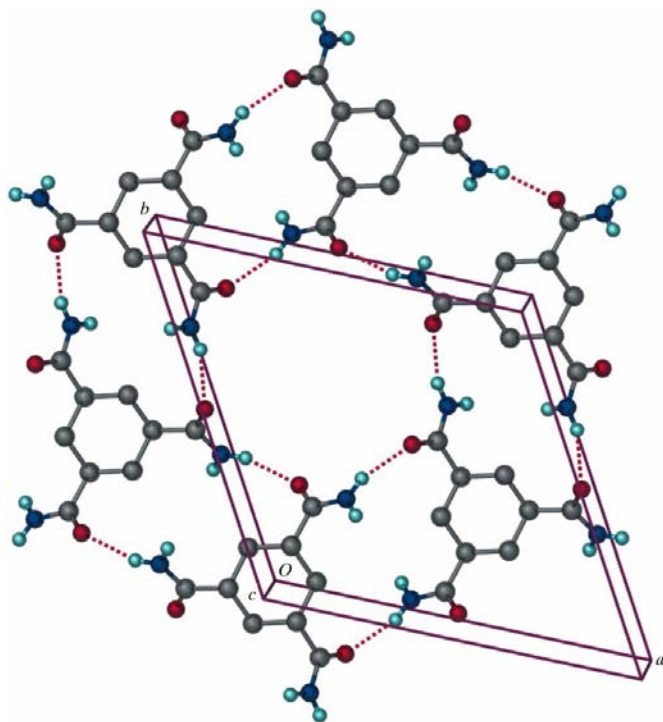


Figure 3
The packing of the two-dimensional layer, showing a hexagonal array surrounded by a cyclic amide hexamer bonded *via* N—H...O hydrogen bonds.

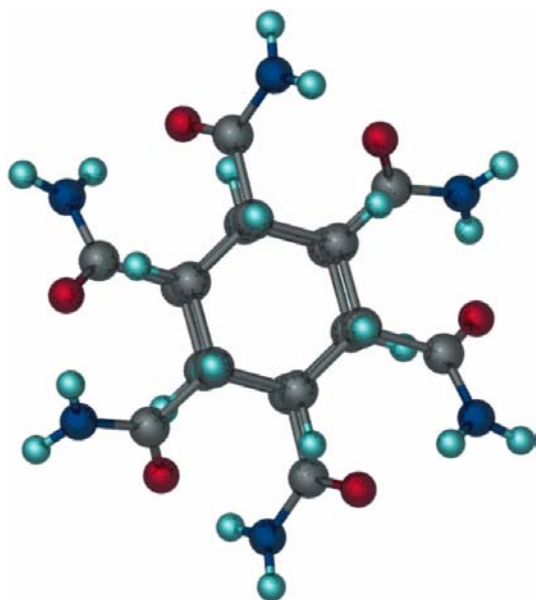


Figure 4
Two molecules are stacked to form a Piedfort unit of *C3i* symmetry (*C3i*-PU).

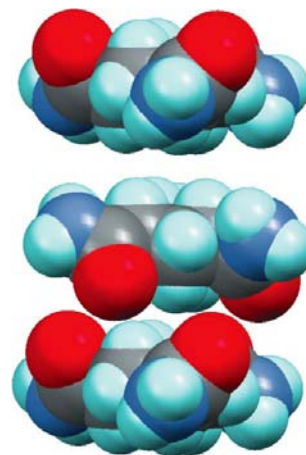


Figure 5
The packing along the *c* axis, shown in a space-fill model. Note that the molecules are not packed efficiently.

two consecutive rings are 5.13 and 5.66 Å (at 100 K). The consecutive two-dimensional layers are linked *via* strong N—H...O hydrogen bonds to form the three-dimensional network. By comparison, the distance between the mean planes of the cyclohexyl rings is only 4.85 Å in the crystal structure of (I).

The Cambridge Structural Database (CSD, Version 5.28 of November 2006; Allen, 2002) was searched to check the frequency of the amide–amide interaction pattern present in the crystal structure of (II). The criteria used for this search were a 2.0–3.0 Å cutoff for N...O distance, three-dimensional coordinates determined, $R \leq 0.1$, no disorder, no errors, not polymeric, no ions, no powder structures, and only organic compounds. There are 889 hits where primary amide groups are present and 312 hits contain the usual cyclic dimer pattern. There are only 16 crystal structures (excluding multiple hits, see supplementary information for CSD refcodes) where one amide group is linked to four other amide groups *via* N—H...O hydrogen bonds and no cyclic dimer pattern is present. Among these 16 crystal structures, acetamide (refcode ACEMID01; Denne & Small, 1971) and 3,3',3''-nitrotripropionamide (JALHIN01; Hahn *et al.*, 1990) form similar cyclic amide hexamers but the pattern is different from the hexamer pattern (Fig. 3) found in (II). Therefore, the amide hexamer pattern in the crystal structure of (II) is unique.

The cyclohexyl groups in the crystal structure of (II) stack to form columns of cyclohexyl rings similar to the crystal structure (I), but the hydrogen-bonding pattern is completely different. The molecular symmetry and the three amide functional groups play an important role in driving the hexagonal crystal structure and the amide–amide synthon. Currently, the synthesis and crystallization of different types of anilide derivatives of *cis,cis*-cyclohexane-1,3,5-tricarboxylic acid are underway.

Experimental

cis,cis-Cyclohexane-1,3,5-tricarboxylic acid (639 mg, 3 mmol) was refluxed in thionyl chloride (2 ml) for half an hour and then evapo-

rated to dryness under vacuum. Aqueous ammonia (10 ml) was added to the solid mass at 273 K and stirred overnight. The material was precipitated by addition of water (100 ml) and then the solid was washed with methanol. Diffraction quality block-shaped crystals were obtained from dimethyl sulfoxide (DMSO). $^1\text{H NMR}$ (DMSO- d_6): δ 7.21 (s, 3H), 6.72 (s, 3H), 2.13 (t, 12 Hz, 3H), 1.77 (d, 12 Hz, 3H), 1.35 (q, 12 Hz, 3H). IR (KBr): 3342, 3192, 1676, 1622 cm^{-1} .

Crystal data

$\text{C}_9\text{H}_{15}\text{N}_3\text{O}_3$ $Z = 6$
 $M_r = 213.24$ Mo $K\alpha$ radiation
 Hexagonal, $R\bar{3}$ $\mu = 0.11 \text{ mm}^{-1}$
 $a = 12.8094 (8) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $c = 10.7854 (13) \text{ \AA}$ $0.20 \times 0.20 \times 0.16 \text{ mm}$
 $V = 1532.6 (2) \text{ \AA}^3$

Data collection

Bruker SMART CCD area-detector 1881 measured reflections
 diffractometer 672 independent reflections
 Absorption correction: multi-scan 608 reflections with $I > 2\sigma(I)$
 (SADABS; Sheldrick, 2003) $R_{\text{int}} = 0.016$
 $T_{\text{min}} = 0.968$, $T_{\text{max}} = 0.985$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$ 66 parameters
 $wR(F^2) = 0.098$ All H-atom parameters refined
 $S = 1.10$ $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
 672 reflections $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1-H1B}\cdots\text{O1}^i$	0.893 (17)	1.975 (18)	2.8615 (14)	171.2 (14)
$\text{N1-H1A}\cdots\text{O1}^{ii}$	0.897 (18)	2.030 (18)	2.8834 (14)	158.4 (13)

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

H-atom parameters were refined freely, giving C—H distances in the range 0.986 (14)–0.991 (14) \AA .

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

The author thanks Professor Ashwini Nangia, University of Hyderabad, for providing laboratory facilities and for X-ray data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3051). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Bhogala, B. R., Vishweshwar, P. & Nangia, A. (2002). *Cryst. Growth Des.* **2**, 325–328.
 Bruker (1997). SMART (Version 5.054) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2001). SHELXTL. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
 Denne, W. A. & Small, R. W. H. (1971). *Acta Cryst.* **B27**, 1094–1098.
 Duchamp, D. J. & Marsh, R. E. (1969). *Acta Cryst.* **B25**, 5–19.
 Fan, E., Yang, J., Stoner, T. C., Hopkins, M. D. & Hamilton, A. D. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1251–1252.
 Hahn, F. E., Tamm, M., Weimann, R. & Pickardt, J. (1990). *Acta Cryst.* **C46**, 1567–1569.
 Palmore, G. T. R. & MacDonald, J. C. (2000). *The Amide Linkage: Selected Structural Aspects in Chemistry, Biochemistry, and Materials Science*, edited by A. Greenberg, C. M. Breneman & J. F. Liebman, pp. 291–336. Chichester: John Wiley.
 Saha, B. K. & Nangia, A. (2007). *Cryst. Growth Des.* **7**, 393–401.
 Saha, B. K., Nangia, A. & Jaskólski, M. (2005). *CrystEngComm*, **7**, 355–358.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). SADABS. Version 2.10. University of Göttingen, Germany.
 Thalladi, V. R., Brasselet, S., Weiss, H.-C., Bläser, D., Katz, A. K., Carrell, H. L., Boese, R., Zyss, J., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 2563–2577.