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3-Acetamidoadamantane-1-carboxylic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.123
Data-to-parameter ratio = 11.0

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

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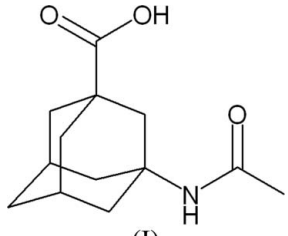
The title compound, $C_{13}H_{19}NO_3$, crystallizes with two molecules, *A* and *B*, in the asymmetric unit. Intermolecular O—H···O hydrogen bonds link symmetry-related molecules into infinite chains parallel to the [101] direction, with short O···O distances of 2.534 (2) and 2.618 (2) Å in the chains of *A* and *B* molecules, respectively. Intermolecular N—H···O hydrogen bonds cross-link these two chains.

Comment

Acetamido derivatives of adamantane have been studied intensively, mainly due to their biological activity (Geigy, 1966). The title compound, (I) (Fig. 1), is a useful intermediate in the preparation of unnatural amino acids, such as 3-amino-1-adamantanecarboxylic acid. This acid has been incorporated into small peptides which showed antitumor activity *in vitro* (Horvat *et al.*, 2006). Here we report the crystal structure of (I).



(I)

The title compound crystallizes in the space group $P2_1/n$, with two independent molecules, *A* and *B*, in the asymmetric unit. Most geometric parameters of *A* and *B* coincide within three standard uncertainties (Fig. 2) and agree with the literature data for the same atom types and hybridizations (Allen *et al.*, 1987). The only significant differences ($\delta \geq 3\ \sigma$) are those involving the torsion angles defining the orientations of the acetamide and carboxyl units (Table 1).

In the early stages of data reduction and structure solution, *E*-statistics revealed a hypercentric structure. Two molecules, *A* and *B*, which are related by a pseudo-inversion centre at *ca* (1/5, 1/4, 1/4) (Fig. 3) generate hypersymmetry. When transformed into a standard setting ($P2_1/c$), the spatial arrangement of the molecules in the unit cell (Fig. 3) and the location of the pseudo-inversion centre agree with those observed for $P2_1/c$ structures with $Z' = 2$ (Zorky, 1996; Pidcock, 2006).

The crystal packing is dominated by double hydrogen-bonded chains running in the [101] direction (Fig. 3) generated by pseudo-inversion centres. There are four symmetry-independent hydrogen bonds (Table 2), grouped into two pairs related by a pseudo-inversion centre. Two O—H···O bonds

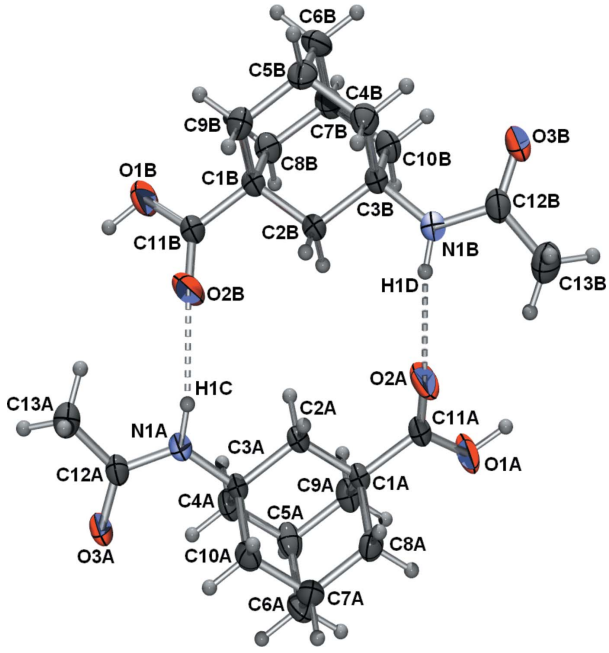


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability and H atoms are depicted as spheres of arbitrary radii. Intermolecular hydrogen bonds between molecules *A* and *B*, related by a pseudo-inversion centre, are shown as dashed lines.

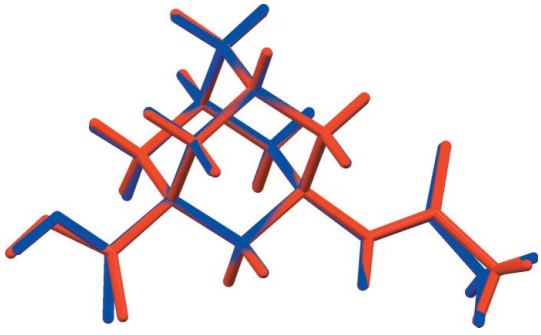


Figure 2
Overlay of molecules *A* (blue) and *B* (red); small conformational differences involve acetamido and carboxyl groups (Table 1).

are relatively short for their type and can be classified as medium-strong to strong according to Jeffrey (1997). The hydrogen bonds between the hydroxyl and amide sp^2 O atoms (O—H···O) link symmetry-equivalent molecules (*A*···*A*; *B*···*B*) while pairs of amide and carboxyl sp^2 O atoms (N—H···O) cross-link *A*···*B* molecules. The hydrogen-bonded units create a hydrophilic core, whereas the adamantyl units are located at the outer parts of the hydrogen-bonded chains. Alternating hydrophilic and hydrophobic regions characterize the molecular assembly in the solid state (Fig. 3).

Experimental

The title compound, (I), was prepared by treating adamantane-1-carboxylic acid with oleum in acetonitrile (Novikov *et al.*, 1980). After work-up, single crystals were obtained from the crude product by slow evaporation of a methanol solution.

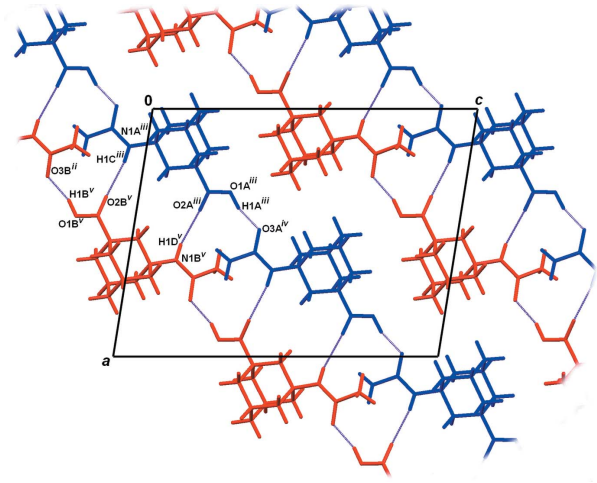


Figure 3
Crystal packing of (I) in the *ac* plane with hydrophilic interiors of hydrogen-bonded chains and hydrophobic adamantyl groups. Molecules *A* are blue, *B* are red, and hydrogen bonds are violet. [Symmetry codes: (ii) $x-\frac{1}{2},\frac{3}{2}-y,z-\frac{1}{2}$; (iii) $x-\frac{1}{2},\frac{3}{2}-y,\frac{1}{2}+z$; (iv) $x,y,1+z$; (v) x,y,z.]

Crystal data

$C_{13}H_{19}NO_3$
M_r = 237.29
Monoclinic, $P2_1/n$
a = 13.3487 (6) Å
b = 10.5295 (5) Å
c = 17.2793 (7) Å
β = 99.073 (3)°
V = 2398.31 (18) Å^3
Z = 8
D_x = 1.314 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 293 (2) K
Prism, colourless
0.3 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (8 reflections; North *et al.*, 1968)
T_{min} = 0.845, T_{max} = 0.892
5262 measured reflections
5043 independent reflections
3856 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 76.5°
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.123
S = 1.03
5043 reflections
460 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 0.8403P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00042 (10)

Table 1
Selected torsion angles (°).

C13*A*—C12*A*—N1*A*—C3*A*	−174.35 (16)	C13*B*—C12*B*—N1*B*—C3*B*	171.35 (16)
O3*A*—C12*A*—N1*A*—C3*A*	3.9 (3)	O3*B*—C12*B*—N1*B*—C3*B*	−6.2 (3)
C2*A*—C1*A*—C11*A*—O1*A*	164.46 (15)	C2*B*—C1*B*—C11*B*—O1*B*	−168.34 (15)
C2*A*—C1*A*—C11*A*—O2*A*	−17.9 (2)	C2*B*—C1*B*—C11*B*—O2*B*	12.7 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A···O3A^{i}	0.95 (3)	1.61 (3)	2.534 (2)	163 (3)
O1B—H1B···O3B^{ii}	0.92 (4)	1.73 (3)	2.618 (2)	163 (3)
N1A—H1C···O2B^{iii}	0.85 (2)	2.17 (2)	2.976 (2)	158 (2)
N1B—H1D···O2A^{iv}	0.85 (2)	2.22 (2)	3.006 (2)	154 (2)

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

H atoms were located in a difference Fourier map and refined freely.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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